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Poly (8-Hydroxyquinoline) Properties, Different Methods for Characterization, and New Applications for Different Uses: Review Article

Mohamed M. Shahata
Environmental Affairs Department, Assiut University Hospitals,
mohamedshahata67@hotmail.com.

ABSTRACT

Poly (8–Hydroxyquinoline) (PHQ) has been synthesized by oxidation of the 8–hydroxyquinolate. In addition, Polymeric metal has a great significance in various areas of chemistry. It has several different methods that, used for characterization as FTIR spectroscopy, ^{1}HNMR Spectroscopic, Differential Scanning Calorimetry (DSC), Thermal Gravimetric (TG), Differential Thermal Gravimetric (DTG) have been used. The cathodic stripping voltammetric of the PHQ at the hanging mercury dropping electrode (HMDE) shows a very weak signal at negatively charged electrode potential. Spectro analytical Sensitivity for PHQ coordination polymers with different metal ions have been calculated. Potentiometric Studies of a Polymeric and Coordination Polymeric Form of 8- Hydroxyquinoline. Cation exchange properties have been researched by spectrophotometric technique. Immobilization of Monomeric, Polymeric and Polymeric Chelates Forms of (8-Hydroxyquinoline) Matrix incorporated in Aluminum Oxide used to be studied. Also, Immobilization of Monomeric, Polymeric and Polymeric Chelates Forms of (8-Hydroxyquinoline) Matrix into Silica Gel has been carried out. Various applications for previous studies in different areas can be used as: Analytical Application, Preconcentration of some metal Ions, and get a patent about Poly(8-Hydroxyquinoline) immobilized on some substance as risen for removal of metal ion.

Keywords: Poly(8-Hydroxyquinoline), Voltammetry, spectra, Immobilization, Aluminum Oxide, Silica gel.

1 Preparation and Characterization

Lately, the electroactive polymers have attracted has received much attention, possibly, this could be due to potentialities to their application to different fields such as chemical sensor, lightweight batteries, and printing circuit boards in a micro-circuit technology [1–10]. Numerous useful reviews have previously been published in this field. For instances, the review by Murray [11-12] which provides a good summary of early work in this field, and reviews by Hillman et. al. [13–14] are also taken into consideration the importance of the electroactive polymer. The Greater recent reviews [15–20] survey the experimental technique used to quantitative transport in electroactive polymer. Moreover, electroactive polymers have attracted considerable interest in the electrochemical community in recent years owing to the wide range of applications of these materials in electrocatalysis, molecular electronics, biosensor technologies, energy conversion and storage, and as a media for controlled drug release [21]. Surveys of structural, chemical, and synthetic aspects of 8-hydroxyquinoline (8-HQ) and its derivatives are examined. A special attention is paid to the

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applications of recently developed 8-HQ derivatives in different areas such as OLEDs, chemo sensors, medicinal drugs, and insecticidal agents [22]. Different polymers bearing 8–quinolinol have multiple applications, for example, as antifouling paints, as antimicrobial surgical materials, as disinfectants in solutions, gels, and ointment for therapeutic uses [23–25].

1.1 Preparation of poly (8 – hydroxyquinoline) (PHQ).

Poly (8–Hydroxyquinoline) (PHQ) was synthesized by oxidation of the 8–hydroxyquinolate anion produces a radical cation which can react further with a phenol form of 8–HQ to give a predominately *para*–linked dimeric radical [26]. Subsequent reaction, then produces oligomers and, finally, a polymeric material (polyphenylene oxide). FTIR spectrum of PHQ illustrates the presence of peaks at ~1055, 1160, and 1285 cm^{-1}, that the presence of ether (C-O-C) [27] linkage. The absence of the signal of the hydroxyl group of 8–HQ in the ^{1}HNMR spectra of PHQ (Figure 1 a, b) verified the polymerization of 8–HQ. The vanishing of the absorption band at 3158 cm^{-1}, *v* (O–H) in the FTIR spectra of PHQ indicates the absence of a free hydroxyl group. Molecular modeling calculations (MM+) to verify this polymerization; they demonstrated that the geometrical energy of the PHQ dimer (the minimum polymer unit) to be 1.460, 397 $kcal.mol^{-1}$, with a gradient of 0.097, 576. This indicates that the geometric configuration of this polymer is highly stable. The purity of this compound was examined by FTIR and ^{1}H NMR spectroscopy Figure 1.

1.2 Preparation of solid coordination of Some Polymeric Materials with Some Metal Ions

Metal containing polymers are essential science, these systems offer an edge over non-polymeric metal salts in a wide range of chemical reactions [28–31]. Polymeric metal, even greater over, are of great significance in various areas of chemistry, e.g. catalytic reactions, mining separations, biochemistry, medicine, environmental chemistry, etc. [32–35]. For instance, molecular chelates with Rh(III) were found to be good hydrogenation catalysts for olefins and some acid derivatives [36]. Polymers that includes Triethylenetetramine side chains and/or thio-groups complexed with metals revealed an antibacterial activity against Escherichia coli or staphylococcus aurous [37]. Instead, many complexes may be created on the solid surface electrodes by reactions of metal ions with immobilized organic polymer [38–39]. Though, some limitations are imposed on the complexes formed at the solid-solution interface, since the attached ligands have reduced mobility.

Thomsen et. al. [40] have discovered a promising method to enhance the chelating ability of 8–quinolinol compounds for the formation of coordination polymers by utilizing a bidentate 8–quinolinol in which two 8–hydroxyquinolines end groups are joined by a linear aliphatic bridge. Light scattering is well specified in the way for determination both M_w and the dimensions of polymer coils [41]. The polymer chelates supplying a unique structural environment for complexation and functionalized by multidentate ligands, are frequently used for this purpose. The complexation of such a ligand is determined by different factors as the nature of the polymer backbone, and the nature of the complexing media.

The preparation of solid coordination polymers was carried out in accordance with the following procedure[42]. The elemental analysis of the PHQ–Cu (II) matrix is given in table1 in combination with proposed formulas that is given different stoichiometries the amounts of water. These data are

compatible with the empirical formula of the polymer complex that is, PHQ coordinates with one central metal ion at four coordination sites with two water molecules per Cu (II).

1.3 FTIR Spectroscopic Characterization of PHQ-Cu(II) Matrix

The IR spectra of PHQ, and PHQ – coordinated with copper ion are shown in the Figure 2. The broadband is remarked at about 3300 – 3400 cm^{-1} is due to the adsorbed water (Figure 2, a). This band is sharper and stronger in the coordination polymer which were in (Figure 2, b), and suggests that the chelated polymer, [PHQ–Cu(II)], may have a higher hydrophilicity than unchelated PHQ matrix. The absorption bands at 1430, 1500, 1550, and 1600 cm^{-1} characteristic of the 8–HQ portion of the PHQ polymer chain. Various of the bands in the polymer are shifted to higher wave numbers (viz., To 1460, 1510, and 1570 cm^{-1}, respectively) in conformity with the complexation with the Cu (II) ion [43]. This red shift is in a manner consistent with metal coordination. Furthermore, the FTIR spectrum of the PHQ–Cu (II) ion complex, when in comparison to the PHQ alone, indicates that the absorption peak at ~1640 cm^{-1}) (i.e., quinolinic azomethine band) is shifted to reduce the frequency (1600 cm^{-1}). The band at ~1430 cm^{-1} in PHQ is allocated to in-plane –O–deformation. This band is similarly shifted to a higher frequency (1460 cm^{-1}) in the coordination polymer [PHQ–Cu (II)] owing to the formation of metal–oxygen bond. This shift is in line with a polymer matrix that is bonded to the metal ion through the nitrogen atom of the azomethine group [44]. To Conclude, the presence of metal coordination is confirmed by a strong band at 1105 cm^{-1}, which corresponds to a C–O – Cu is stretching vibration [45].

1.4 ^{1}HNMR Spectroscopic Characterization of PHQ-Cu(II) Matrix

The 1HNMR spectra of the 8–HQ, PHQ, and PHQ–Cu (II) matrix are displayed in (Figure 3 a, b and c). There is no shift in the quinolinic azomethine proton signal (δ = 8.8342 ppm) from the monomer to the corresponding polymer (Figure 3, a and b). After chelation with Cu(II), an up field shift to 8.55 ppm is observed (Figure 3 c). This shift means that the PHQ matrix is coordinated with Cu (II) ion, probably through the nitrogen atom of the azomethine group. That the integrated intensity of the signal decreases to half on metal complexation is in accordance with the formula given in Scheme 1.

1.5 Differential Scanning Calorimetry (DSC) of PHQ – Cu(II) Matrix

The thermal performance of copper acetate mono-hydrated, PHQ, and PHQ-coordinated with Cu (II) is extracted from the DSC Figure 4. The DSC thermogram of Cu $(CH_3COO)_2 .H_2O$ (Figure 4 a) is referring to the characteristic endothermic band at 141^{o}C that relates to the evolution of water [46]. This change is in compliance with the first observed weight–loss (I) in the TGA of the salt (Figure 5 a).

The DSC thermogram of PHQ matrix (Figure 4 b) implies a strong endothermic peak at 71.5 ^{o}C, which is ascribed to the release of water, probably H–bonded to the polymer. The existence of water is also adsorbed in the mass spectrogram of PHQ (Figure 6 a), which shows a major ion at m/z: 17.9. The DSC thermogram of PHQ–Cu (II) complex (Figure 4 c) is comparable to that of Cu $(CH_3COO)_2.H_2O$ and PHQ. And also, There are many broad DSC endothermic peaks in the temperature range of 150–180 ^{o}C, which may be due to melting and/or decomposition of PHQ. The metal–complexes polymer displays a originally sharp endothermic change at 87 each, that is equivalent to the release of water. The comparable weight loss is viewed in the TGA and DTG thermogram at 72.4 ^{o}C (Figure 5). The DSC thermogram presents a small endothermic change near 150 – 180 ^{o}C, which is similar to that noted for PHQ and probably includes release of organic fragments from the PHQ matrix. This is also in line with the mass spectrum (Figure 6 b). The DSC endothermic peak at 333 ^{o}C, arises ~50 ^{o}C higher than for the copper acetate. This peak is being ascribed to the thermal degradation of the complexed

polymer and demonstrates that the copper coordination increases the thermal stability of the polymer matrix.

1.6 Thermal Performance of the PHQ-Cu (II) Matrix

The TGA of PHQ–Cu(II) displays the weight loss below ~ 200 ^{o}C, and that is owing to the loss of matrix water molecules which are weakly bound to the polymer chain. The number of moles of water (n) can be calculated from the TGA peak use up Eq. (1) [47], where W is the mass and M is the molecular mass.

$$n = [W_{water} / M_{water}] / [W_{polymer} / M_{repeat\ unit}] \quad (1)$$

The value of n for the copper salt and its chelates with PHQ matrix has been computed and are summarized in Table 2.

It is interesting to note that n for PHQ–Cu (II) matrix is about twice that of the copper salt (Figure 5 a and 5 c). Furthermore, it has been reported that the conductivity of some polymers is very dependent on the redox state, doping level and moisture content of the polymer matrix [48].

The thermal degradation of PHQ displays only a one-step decomposed at the 152 ^{O}C (Figure 5 b). The mass spectrogram (Figure 6 a) displays a base peak due to the 8–HQ molecule at m/z: 144. The TGA of the PHQ–Cu(II) complex indicates that the matrix continue to remain stable to 300 ^{o}C following the loss of water and that the complexed polymer is more thermaly stable than the copper salt. The TGA weight loss and the DTG peak heights are the same for the second (II) and third (III) stages of heating. The DTG thermogram of the PHQ–Cu(II) matrix displays a third decomposition step (III) at ~ 450 ^{o}C, which is about 100 degrees higher (ca.350 ^{o}C) than the next (II) step.

2 Various techniques of research on the behavior of PHQ Matrix

2.1 Differential Pulse Polarographic (DPP) behavior of PHQ Matrix

Differential pulse polarography was quite suitable in sensitivity for the analysis of electroactive drugs for example the adenosine, cytidine, and thio nucleotides have been conducted by Temerk et al., [49-54]. Polarographic studies have been carried out on 8–hydroxyquinoline (oxine) and 8-hydroxyquinoline –5-sulfonic acid (OSA) [55–57]. Derivatives of quinoline containing polarographically active or inactive substituents have similarly been the subject of several investigations [58–61]. Many Different extractions–polarographic methods have been applied to determination of metal ions as complexes, with 8-quinolinol (oxine) as the complexing agent [62–64]. It has been previously investigated the complexation of 8–hydroxyquinoline–5– sulfonyl hydrazide with metal ions [65–69]. Lately, found that electrical conductivity, electroactivity and spectro-electroactivity could be stimulated in poly (O–Toluidine) and/or polypyrole emeraldine base form after doping [70–75]. The electrochemical methods are made up of a complexometric titration combined with differential pulse Polarography (DPP) has been used extensively to estimate both the concentration of organic macromolecules and/or the stability constants of the corresponding metal complexes [76–78].

Quantification of heavy metal ions is extremely important since heavy metals pose a significant risk to health. For instance, Lead build up in the body over several years and may be causing damage to the brain, red cells and kidneys and can slow down the normal mental and physical growth of children [79–86]. The actual content of some metal ions [87] in mental finishing waste solutions per monthly average should not excised the following boundaries: (ppb); Cd(II) : 260; Cu(II) : 2070; Pb(II) : 430 ppb. In complexes with poly electrolytes have been used as a medical material (bio– compatibilizer and microcapsule) and are of considerable interest because of potential application in gene and drug

delivery systems [88–89]. Rajeshwar and co – workers [90], applied conductive poly pyrrole for the removal of toxic Cr(VI) from aqueous solutions .

2.2 Differential Pulse Polarographic (DPP) behavior of the complexed Cu(II) with PHQ

DP- polarograms of Copper ion in the absence of PHQ matrix were recorded [46] in the universal buffer solutions containing 10 % DMF solution (pH 3.25–11.25) The reduction behavior of PHQ is heavily dependent on the pH of the solution, Figure 7a. While, Figure 7 b, displays the single reduction peak of Cu (II) ion with a peak potential (E_p) sited at the potential range of – 0.04 to -0.12 V. The peak half–width of this reduction is nearly 130 mV, showing a highly irreversible Cu(II) ion reduction process in universal buffer solutions containing DMF. In the presence of PHQ matrix a new cathodic reduction peak has been observed in the range –0.1 to –0.45 V (pH-dependent) over the pH rang examined. The shift in the reduction peak potential of complexed Cu(II) (~350 mV), relative to the free Cu(II) ion, implies the strong interaction between Cu(II) and the PHQ matrix *via* the complexation mechanism. The maximum response of the reduction peak of Cu(II) chelates has been identified at pH 9.25, (Figure 7 b). The peak was at least three orders of magnitude greater than the reduction peak corresponding to PHQ alone under the same conditions. A medium pH of 9.25 was therefore selected for the determination of PHQ matrix as a Cu(II) chelate, while the peak height is highly sensitive towards the PHQ concentration

2.3 Electroactivity motivated in PVA by the incorporation of the PHQ – Cu(II) matrix

Disagreements have been observed between the DP-polarograms for mixtures and pure PHQ–Cu(II), because of an increase in the resistivity of the conducting polymers and changes in their ionic permeability. The electroactive (0.685 %) PHQ–Cu(II) could, instead, induce electroactivity of nearly 240 nA in the insulating PVA matrix, as displayed in the Figure 8. The decrease in the ip of PHQ – Cu(II) complex in the presence of insulating PVA may be because of a PHQ – Cu(II) – PVA composite. This might work as insulating layer interference with the electron transfer. The high linear dependency (r = 0.997) of ip on the weight percentage of PHQ – Cu(II) in the PVA matrix is useful for the preparation of the PHQ – Cu(II) – PVA electroactive synthesis .

2.4 Cathodic Stripping Differential Pulse Voltammetry (CSDPV) of Poly (8 – Hydroxyquinoline) Matrix at HMDE

The electrochemical characteristics of 8–hydroxyquinoline (8–HQ) and its derivatives at the dropping mercury electrode (DME) screen a cathodic reduction peak, which is the equivalent to the reduction of the quinolic azomethine group [66-68]. The (CSDPV) behavior of PHQ at the hanging mercury dropping electrode (HMDE) at different pH media have been investigated [91]. Under the conditions that, in acidic and neutral media (pH < 7.10) and /or in alkaline media (pH > 7.1), the DPCSV peak of PHQ may not be used as a sensitive signal for its analytical determination using such technique.

2.5 CSDPV of PHQ in the presence of Cu(II)

Cathodic stripping voltammetry (CSV) techniques also involve complexation of the metal ions of concern, and the use of a hanging mercury drop electrode (HMDE) [92–93]. Several CSV methods for directly analyzing aqueous metal have also been established previously. These methods all utilize the technique of first accumulating metal from solution by electro depositing ($M_2^{n+}O_n$) on anodically on the working electrode and later stripping of reduced M^{n+} ions by sweeping the potential cathodically [94]. Cathodic stripping voltammetry has demonstrated suitable for several organic compounds

including drugs at hanging mercury dropping electrode were examined [95–96] in solutions of differing pH.

The CSDPV performance of PHQ in the presence of Cu(II) illustrates a very well-defined and intense cathodic reduction peak (i_p = 1.8 μA, E_p = – 4.5 V) at the midpoint of the potential scale [91]. This peak is corresponding to the reduction of the chelated Cu (II) of the PHQ – Cu (II) system, which is heavily accumulated and adsorbed at the HMDE surface. It was observed that the more sensitive CSDPV signal for the reduction of the PHQ–Cu (II) matrix detected at pH 7.10 and the peak height decreases with increasing or decreasing the pH. Therefore, pH 7.10 is selected as the optimum pH medium for the trace determination of Cu (II) and/or PHQ matrix. This signal is profoundly Cu (II) and/or PHQ concentration dependent.

2.6 Determination of PHQ as PHQ–Cu(II) matrix

The cathodic stripping differential pulse voltammetric (CSDPV) behavior of PHQ chelates with copper ion [PHQ–Cu(II) matrix] have been documented [91] over a wide pH range (1.4–11.25) as displayed in Figure 9. The cathodic reduction peak at potential –0.45 V corresponds to the reduction of the chelated Cu(II) ion of the strongly adsorbed and accumulated PHQ–Cu(II) matrix at the dropping mercury electrode surface. The sensitivity of the CSDPV signal of the PHQ–Cu(II) matrix are fully researched by variation of concentration of PHQ on Cu(II) ion solution, displayed in the Figure 9. In the case of determination of Cu(II) as PHQ–Cu(II), the linearity range for determination of Cu (II) in the presence of PHQ is the range (0 – 4 $\mu molL^{-1}$), and the detection limit was $1x10^{-7}$ $molL^{-1}$. While At The Same Time, the variation of the peak height of CSDPV a reply with the concentration of PHQ is linear, and the linearity range for determination of PHQ in the range (0.01–0.2 $\mu molL^{-1}$). It should be noted that, the detection limit was $1x10^{-8}$ $molL^{-1}$.

2.7 Impact of interfering ions on the PHQ–Cu (II) chelates

The recovery percentage (%) of the peak height on relative to the peak height of Cu (II) and PHQ was documented [91], calculated as an ideal condition. It was discovered that, In the presence of mixtures of K(I), Na(I), Ca(II), Ba(II), Mg(II), Mn(II), Pb(II), Cd(II), Co(II), Ni(II), and Zn(II), the peak height reductions by 6.25% and 9.37% respectively. The results indicated that the degree of the recovery of PHQ in 0.1 μM of the PHQ–Cu (II) system is in the range of 90.63 and 93.75%. The extent to which of recovery of 0.1 $\mu molL^{-1}$ PHQ–Cu(II) system in the presence mixture of $CHCOO^-$, BO_4^{2-}, PO_4^{3-}, SO_4^{2-}, NO_3^-, and CO_3^{2-} is about 98.65%. This result indicates that all these anions are not in competition against the adsorb ability of the examined varieties at the mercury electrode surface. It is interesting to note that the addition of Triton X-100 does not highly affected at the cathodic reduction peak height (i_p) of the chelated Cu(II) ion, while the degree of the recovery about 97.25 %. Although the addition of 10 and 100 $\mu molL^{-1}$ of glutaric acid, as an example for amino acids, to 0.1 $\mu molL^{-1}$ of the PHQ–Cu (II) system the response current due to the reduction of Cu (II) chelated has decreased about 2.13 %. Nevertheless, in the presence of EDTA the i_p of the chelated Cu(II) signal is almost reduced and the degree of the recovery of PHQ is ~ 24.14 %. This dramatic effect is owing to the very strong chelating efficiency of EDTA on the way to Cu(II) than PHQ matrix.

2.8 Effect of insulating matrix

In front of insulating matrix such as poly (vinyl alcohol) (PVA), the extent to which the recovery of the PHQ–Cu (II) system (0.10 : 0.05 $\mu molL^{-1}$) was found to be closed down 93 %. This observation indicates that the PVA do not screen the Cu(II) towards reaction with PHQ chain. Additionally, the above matrixes do not compete with the adsorb ability of the examined system at the mercury electrode surface. Furthermore, the peak height and the peak potential of the CSDPV peak of the chelated Cu(II) are almost a constant in the presence of PVA matrix. At The Same Time, in the presence of poly (vinyl pyrrolidine) (PVP), the reduction peak height (i_p) of chelated Cu(II) with PHQ was greater than the reduction peak height (i_p) of the PHQ–Cu(II) system only. This implies that the PVP matrix enhanced the absorbability at the mercury electrode surface which caused increased in the peak high of chelated Cu(II), as demonstrated in Figure 10. The calibration plot of reduction peak height (i_p / μA) was increased with increasing the PHQ concentration.

2.9 Spectro analytical Sensitivity of the Co- ordination Polymers Based on PHQ Matrix

Quantitative spectrophotometry has been significantly improved using a variety of multivariate statistical methods. Exceptionally principal component regression (PCR) and partial least squares regression (PLS) analysis. The common use of these methods is due to the proliferation of commercial software for laboratory computers and to the advancement of photodiode array detectors capable of reading full spectra very rapidly. The theory and application of PCR and PLS in spectrometry have been discussed by multiple researchers [97-99]. Additionally, several multi component determinations of organic macromolecular (polymer) matrix and/or organometallic polymers (coordinated polymers) substances based on the application of these techniques to spectrophotometric data have been documented [100–101].

Zero-order derivatives (normal spectra) of the absorption spectra for PHQ matrix and PHQ coordinated with Cu(II) ion were documented [42] against the reagent blank is shown in the Figure11a. The maximum possible absorption spectrum of PHQ in an ethanol (60%)-water mixture (pH, 7.03) was discovered at ~ 305 nm; the color was pale-yellow. After the addition of Cu(II) ion solution to PHQ, the maximum possible shifts to higher wavelength (~ 380 nm) and the color changed to greenish-yellow. A red shift indicates that the copper ion is incorporated in the PHQ matrix. Moreover, the spectral curves, absorption maximum for the PHQ – Cu(II) matrix has been observed (Figure 11 a and b). These findings suggest that the first-order derivatives are at least 1.5-times the magnitude of the zero-order derivative. when the spectra under the same conditions. The amazing changes in the color [i.e., from pale-yellow to greenish-yellow] can be attributed to the *intra*-molecular charge-transfer. In this particular case, the delocalization of electrons is promoted by an elongation (unfolding) of the compact structure a coil-like polymer chain. At Exactly The Same Time, chain expansion results in a reduction in-defects that are caused by a twisted of the metal as the Cu(II) ion content is increased. The visual appearance of a new absorption band at 380 nm should be useful for analytical purposes and the spectral properties of these complexes may lead to new materials that are appropriate for electrochromic devices [102–104].

2.10 UV-visible Absorption Spectra of the Coordination Polymer Based upon PHQ

Absorption spectra are helpful in the determination of stability constants (log β) and the structure of the coordination complexes as for instance the PHQ–Cu (II). The molar ratio and the continuous

variation method may be used by planning the absorbance (A) against the mole fraction of added metal ion [105].

the stability constant is

$$\beta_{1:2} = [\ PHQ : (M^{n+})_2\ ] / [\ PHQ\ ][\ M^{n+}\ ]^2$$

$$= [\ A / A_{max}\ ] / [\ 4C^2(1 - A/A_{max})^3\ ] \quad (2)$$

Table 3 represent the stability constants (log β) and other analytical data. The computations indicate that the largest stability constant and free energy change correspond the most relevant to the 2:1 stoichiometry, (2PHQ : 1Mn+). Such complexes normally have the metal ions coordinated through oxygen and nitrogen as in the poly chelates of poly (8-acryloyloxy quinoline) [44] and the dimeric form of 8–HQ moiety [106]. A small increases in the formation constants in case of the coordination polymers of 2PHQ : 1Cu(II) in the presence of anions and/or PVA (100-folding excesses), in comparison with the 2PHQ : 1Cu(II) individually, was observed table 3. This behavior may be due to an increase in the ionic strength of the medium. These views are compliant with the elemental analysis results and the calculated values of the lowest potential energy and dipole moment for the suggested optimum structure (Scheme 2) as previously discussed.

2.11 Potentiometric Studies of a Polymeric and Coordination Polymeric Form of 8- Hydroxyquinoline

Monitoring the titration progress by means of potentiometric measurements with a pH glass electrode allows the accomplishment of tasks of various complexity, from the simple quantitation of a single solute to the determination of the composition of multi-component mixtures together with the acidity constants of poly functional acids, computer programs [107–108] at various levels of sophistication have been proposed, and are being continuously developed, in order to allow systems of increasing complexity to be dealt with in agreement with the principles of statistical analysis of data.

Potentiometric titration technique can be used to determine the hydrogen ion concentration in solutions at constant ionic medium which contains an excess of, for example, sodium ions. Furthermore, complex formation M^{n+} (metal ion) and coordinated compound (ligand) in the presence of H^+ can be examined using the glass electrode. The pH values of the mixed solvent-water media were remedied by the method given by Douheret [109].

Determination of the Stability Constant

When an increasing volume (V) of a solution containing the weak acid HA at concentration (C) is added the gradual to a volume (V^o) of solution containing the same acid at concentration $C^o > 0$, the amount (moles) of acid in the solution is given by:

$$C^oV^o + CV \quad (3)$$

Increases in proportion to the added volume (V) (note that the same is not true for the concentration, unless $V << V^o$). By conveying this amount in terms of its functional the relationship between experimental variable, V and $[H^+]$, equation (4) is obtained [21]:

$$F = (V^\circ + V)([H^+] - \frac{K_w}{[H^+]})(1 + \frac{[H^+]}{K_a})$$

$$= C^{O}V^{O} + CV \quad (4)$$

Where $[H^+]$ is quantified variable of hydronium ion concentration measured as a pH, pK_a, is the acidity constant of the weak acid. This equation identifies an auxiliary variable F, which is necessarily a linear function of V, in analogy with the "Rigorous Gran function " [21] for weak acid titration. The case is currently in the process of interest, not previously considered, is multiple addition of a sample containing the weak acid or highly conjugated matrix (such as PHQ) at concentration C to a known volume of water or of an aqueous solution of an inert electrolyte. By placing the initial concentration of weak acid in the measured solution, (C^{O}), equal to zero, the equation (4) shall be reduced to the equation:

$$F = (V^{\circ} + V)([H^+] - \frac{K_w}{[H^+]})(1 + \frac{[H^+]}{K_a})$$

$$= C\,V \quad (5)$$

Otherwise, by defining other suitable auxiliary variables X and Y that can be calculated for each pair of experimental data V and $[H^+]$, it is possible to rearrange equation (5) to obtain different Linear equation of the form:

$$Y = a + b\,X \quad (6)$$

Consequently, C and K_a can be obtained by numerical or graphical linear fit of the values of X and Y, computed from the experimental data as:

$$(V^{\circ} + V)[H^+]^2 = K_a\{CV - (V^{\circ} + V)[H^+]\} \quad (7)$$

2.11.1 Potentiometric Titration Studies of PHQ

From the potentiometric titration curves, the parameter, (n_A) average number of protons associated with the ligand (the polymer under investigation, PHQ) was computed at different pH values provided by [22]:

$$n_A = Y + \frac{(V_1 - V_2)(N^{\circ} + E^{\circ})}{(V_o + V_1)(T_{cL^{\circ}})} \quad (8)$$

Where, Y : is the number of dissociable protons in the repeating unit of the PHQ,

V_o : is the initial volume,

V_1 and V_2 : are the volume of alkali required to reach the identical pH in the presence of mineral acid (HNO_3) and (HNO_3 + PHQ) solutions, respectively.

$T_{cL}{}^{o}$: is the total concentration of the PHQ,

N^{O} : is the normality of the standard alkali and,

E^{O}, is the initial concentration of the free mineral acid (HNO_3).

The proton–PHQ (repeating unit) formation curves obtained by plotting n_A vs. pH has been represented in the Figure12. The value of log K_1^{H}, the first proton–polymer association constant is determined by interplotation at the half (n_A) values from n_A vs. pH. Average for the value of Acidity constant (pK_a) was found to be 7.75 .

The plotting of the differential of the average number of protons associated with the repeating unit of the polymer Δn_A vs. pH give benefit than the findings of n_A vs. pH, illustrated in the Figure 13.

2.11.2 Potentiometric Titration Studies of PHQ–Coordinated with Some Metal Ions

The potentiometric titration technique was also utilized for the determination of the formation constant (log β) of PHQ–metal complexes was comprised of the pH–metric titration curves of PHQ in the absence and presence of metal ion (M^{n+}) under investigation. Thus, the formation constant of binary metal ion – polymer (M–PHQ) complex was studied [110] by the titration carried out using different molar ratios of the concentration of metal ions and/or repeating unit of the polymer matrix. wherever, in each one the total volume was remained constant (50 ml) aqueous solution. Examination of the different titration curves of the different metal ions (Mn^{+}) and PHQ (PHQ : Mn^{+}) systems at various molar ratios (1 : 2, 1 : 1 and 2 : 1) indicate that the higher shift in the volume of alkali added for metal – polymer complex than the polymer individually. The partition coefficient of each metal between the two phases is a complex function of various equilibrium constants involved ionization of polymer (PHQ) and formation of the complex (PHQ – Mn^{+}). The pH range (3 – 10) was selected because it facilitated the complex extraction of the reagent and huge number of metal ions and/or transition metal ions. The titration curve of PHQ–Cu(II) system is displayed in the Figure14.

Titration curves for certain metal ions system, PHQ-M^{n+} , for example in: Al(III) ,Ca(II) , Cd(II) , Cu(II) , Co(II) , Fe(III) , Mg(II) , Ni(II) , Pb(II) and Zn(II) ions are studied. Thus, the replacement of hydrogen ion is owing to the complexation mechanism.

From these titration curves, it is clear that the potentiometric titration of free mineral acid curves (as curve a in Figure14) are well separated from the polymer titration curves (curves b). The different molar ratio curve is curve c which represent PHQ - M^{n+} with molar ratio (1 M^{n+} : 2 PHQ), curve d for (1M^{n+} : 1 PHQ) and curve e for (2 M^{n+} : 1 PHQ).

2.11.3 Determination of the Association Constant (pK_a) of PHQ– Coordinated with Some Metal Ions

From the relation between $\bar{n}$ vs pH as shown in the (Figure 15 a), the half of raising portions which equivalent to the pH value, give the pK_a value for PHQ.

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V_o + V_2) n_A T^\circ_{CM}} \tag{9}$$

and P_L is the free polymer exponent of at several pH values and can be calculated like this: -

$$P_L = \frac{1 + \beta_1[H^+] + \beta_2[H^+]^2 + \beta_j[H^+]^j}{T^\circ_{CL} - \bar{n}T^\circ_{CM}} \cdot \frac{V_o + V_3}{V_o} \tag{10}$$

Where V_1, V_2 and V_3 are the volumes of alkali required to reach the same pH in the free mineral acid (HNO_3), Polymer + mineral acid and the mineral acid + Polymer + metal in potentiometric titration, respectively.

The more precise method for that is, the value of pH can accurately determine from First–derivatives treatment of $\bar{n}$ ($\Delta\bar{n}$), (Figure 15 b) by the relation of signal vs pH, the peak give the specified point of pH value equivalent to the pK_a.

The values of $\bar{n}$ and P_L for the metal ions under investigation were computed at different pH values. The plots of $\bar{n}$ values against P_L were drown out for some metal ions as for example: Al(III), Ca(II), Cd(II), Cu(II), Co(II), Fe(III), Mg(II), Ni(II), Pb(II) and Zn(II) ions.

The values of $\bar{n}$ and P_L for the metal ions in compliance with the investigation were calculated at different pH values.

2.11.4 Determination of the Formation Constants (log β) of PHQ– Coordinated with Some Metal Ions Based on ($\Delta\bar{n}$) vs. P_L System.

The analysis of potentiometric curves of $\Delta\bar{n}$ vs P_L for metal – PHQ , give formation constant (log β) and partial formation constant (log $\beta_{p\,q}$) is a reference to the equation as:

$$ {}_pM^{j+} + L^{z-} + {}_qH^{+} = M_pLH_q^{(j+p-z)} \qquad (11) $$

Research findings presented that [117], some metals (for the molar ratio 1 metal : 2 polymer) give one species (one value of the formation constant, log β_1) such as: Cu(II) , Zn(II) , Ni(II) and Al(III) as illustrated in the (Figure 16 a and b).

Other metal ions provide two species such as: Fe(III) , Pb(II) , Co(II) and Mg(II) ions. These species suggest that there are two partial formation constant (log β_1) and (log β_2), for example as illustrated in the (Figure 17 a and b).

Both Ca(II) and Cd(II) give three species then have three values of partial formation constant (log β_1), (log β_2) and (log β_3) respectively, for example as demonstrated in the (Figure 18 a and b).

The values of the formation and partial formation constants for PHQ – M^{n+} matrix were mentioned in the table 4

At the study [111] protonation constants and complex formation equilibria between poly(8-Hydroxyquinoline) with some transition and heavy metal ions such as: Al(III), Ca(II), Cd(II), Cu(II), Co(II), Fe(III), Mg(II), Ni(II), Pb(II) and Zn(II) ions have been examined in aqueous solution at 25.0±0.1 ◦C, by use glass electrode potentiometrically. The protonation constants of the ligands and formation constants of the subsequent complexes have been calculated from titration data.

The overall protonation constants of ligands and the stability of their metal complexes were computed. The findings presented that, some metals such as: Cu(II) , Zn(II) , Ni(II) and Al(III) (for the molar ratio 1 metal : 2 polymer) possess the one value of the formation constant (log β1). Other metal ions as for example: Fe(III) , Pb(II) , Co(II) and Mg(II) ions provide the two partial formation constant (log β1) and (log β2). Both Ca(II) and Cd(II) have three values of partial formation constant (log β1), (log β2) and (log β3).

3 Cation-Exchange Mechanism on Poly (8-Hydroxyquinoline) Matrix

A great deal of interest has grown-up in the last decades in synthetic inorganic ion-exchangers [112] because of their higher resistance to high radiation and high temperature. Inorganic ion exchangers have been widely used for the removal of heavy toxic metals from wastewater, which are created as untreated or partially treated by-product of different industries.

Inorganic ion-exchangers also have applications in the advancement of ion selective electrodes [113], construction of ion-exchange membranes and their uses to electro-dialysis for metal ion separations. The synthesis, description, and ion-exchange behavior of a high thermally and chemically stable new inorganic cation-exchanger was labeled [114]. The material was used effectively for quantitative

column separations of some binary mixtures of metal ions. Improvement in inorganic ion exchangers is not only owed to their high thermal stability and resistivity but also for their unfamiliar selectivity for ionic species and versatility in separation sciences, ion-selective exchangers have attracted attention for their applications in waste water treatment [97]. The synthesis and structure of a novel inorganic solid electrolyte which contains a huge number of Na+ cations with high-level mobility in the inter lamellar space and the cavities of its layered crystal structure. Its cation-exchange properties demonstrate that it is an excellent ion exchanger and a hopeful extracting for lead and lithium. Zeolites are microporous aluminosilicates, which is made up of an anionic structure with tetrahedral SiO_4 and AlO_4, mobile cations (usually alkali and alkaline earth cations) for charge balance, and water molecules in the cavities [98]. Zeolite beta (BEA) is a high-pitched silica zeolite with larger pores. Generally, it is an intergrowth of polymorph A (tetragonal) and polymorph B (monoclinic) in a 50:50 proportion [99]. Therefore, it has a high concentration of lattice defects, from slight structural disorder because of the random stacking of these two phases. High temperature oxide melts solution calorimetry decided the dehydration enthalpy and the formation enthalpy from the constituent oxides [100].

The inclusion of Al(III) cation into a poly(8-Hydroxyquinoline) (PHQ) as an alternative of some metal ions like for instance: Co(II), Ni(II), Zn(II), Fe(III), Cu(II), Mg(II), Cr(III), Mn(II) and Mo(VI) ions via cation-exchange mechanism has been studied by various techniques. The presence of Al(III) and the absence of Co(II) ions been demonstrated by elemental analysis of the polymer chelates product verified that the inclusion of Al(III) ion instead of Co(II) ion via cation-exchange mechanism.

Molecular Mechanics (MM+) calculations including MM2 and MMP2 force field [115- 118] have been conducted assuming the investigated molecule in the gas phase. Also, The energy of a molecule is affected by the atomic coordinates and could be calculated. The search for a minimum energy of the molecule geometry caused in a 3D structure. MM+ calculations on an iterative change the position of atoms towards the structure described by lower energy until the molecule internal energy has been minimized.

A sequence of PHQ–metal ion complexes were ready. Cation exchange properties have been researched by spectrophotometric technique. The reduction of the absorbance of each PHQ-Co(II), PHQ-Ni(II) or PHQ-Mn(II) associated with increasing concentration of Al(III) revealed the substitution of those metal ions by Al(III) into PHQ chain. At The Same Time, The increase of the absorbance of PHQ-Fe(III), PHQ-Cu(II), PHQ-Cr(III), PHQ-Zn(II), PHQ-Mg(II) and PHQ-Mo(VI) with increasing concentration of Al(III) revealed the improvement of these metal ions by Al(III) into PHQ chain. The cation exchange constant (*Kex*) from PHQ-M(n) by the supplements of Al(III) according to the following sequence [119]:

$$Ni(II) > Co(II) > Mn(II).$$

3.1 Preparation of cation-exchange material

The Preparedness of spectro analytical solutions of the cation-exchange material (PHQ-Al(III) matrix). The baseline correction spectrogram of the solution was documented [119]. Prepared a of polymer (PHQ, 0.5 $mmolL^{-1}$) (1 : 0.5 mmol ratio of PHQ: Co(II)) chelating has been conducted. The absorption spectra have been documented against the reagent blank (all solutions without the analyte). All spectral measurements were being conducted at laboratory temperature (24±1 ºC). Preparation of the polymer chelates [PHQ-M(II)], which use metal nitrate and is based on the PHQ in the solid state, was carried out as follows: A clear warm solution of PHQ and Aluminum or Cobalt nitrates in an

ethanol-water mixture containing 30% ethanol were mixed with constant stirring. The polymer chelates detached from the solution in the form of a solid suspension and were processed on a water bath for one hour. The solid polymer chelates were gathered by filtration, washed with bi-distilled water until the washings were colorless, and then dried in air at room temperature. The yields of the polymer chelate were almost measurable. The elemental composition for the formulas of the polymer chelates that differ only in water content has been calculated and compared to the analysis of the polymer product resulting.

3.2 Molecular Mechanics Calculations

Molecular Mechanics (MM+) calculations of the proposed formula was done to evaluate the potential energy (PE, KJ mol^{-1}) and dipole moment (μ, D) of the molecular geometric (MG) and optimum molecular geometric (OMG) energies of the PHQ−Al(III) and PHQ-Co(II) matrixes. These calculations demonstrated that the potential energy (PE) of the optimum molecular geometric structure (OMG) of the PHQ-Al(III) matrix, Table 5, is approximately seventy six (76.185) more than the PE of the PHQ-Co(II) complex. So, the insertion of Al(III) ions as opposed to Co(II) ions is good. Also, the PE of the OMG is more stable around seven orders (5.82×10^7) than the MG structure of the PHQ-Al(III) matrix. So, optimize the geometry of the molecular structure (OMG) is very important in order to understand the stability of this matrix (Scheme 4.1). The negative value of PE of the OMG and PE and the lowest dipole moment of the repeating unit suggest that the proposed geometric configuration structure of PHQ-Al(III) matrix is considered to be the most stable[119].

3.3 Proposed Formula

The elemental analysis of the PHQ-Al(III) matrix is provided in Table 6, along with proposed formulas that contain different stoichiometric in amounts of water. These information can be found are consistent with an empirical formula of the polymer chelates that is the best characterized by $[(PHQ)_3\text{-Al.}\ 0H_2O]^n$, and that is, three PHQ coordinate with one metal ion at six coordination sites as displayed in the Scheme 4.

3.4 FTIR Spectra of PHQ-Al (III) and PHQ–Co(II) Matrixes

The IR spectra of PHQ-Co(II) and PHQ-Al(III) matrixes are displayed in the Figure19. The broad bands in the 3100 – 3400 cm^{-1} region for the PHQ-Co(II) or PHQ-Al(III) matrix are because of the adsorbed water. This band is more powerful in the PHQ-Al(III) complex than PHQ-Co(II) complex. This observation suggests that the PHQ-Al(III) more hydrophilic nature than the PHQ-Co(II) complex. Additionally, this result suggests that the PHQ-Al(III) complex is expanded coil-like than the PHQ-Co(II) complex. The absorption bands at approximately 1430, 1500, 1550 and 1600 cm^{-1} are characteristic of PHQ polymer chain. Numerous of the bands in the PHQ alone [42] shifted to greater wave numbers (viz, to 1460, 1510, and 1570 cm^{-1}, respectively) upon complexation with Co(II) or Al(III) ions. This red shift is in accordance with metal coordination. Moreover, the spectra of the PHQ- Al(III) or PHQ-Co(II) complexes when in comparison to the PHQ alone showed that the absorption peak at about 1570 cm^{-1} was shifted to lower frequency (1600 cm^{-1}). This shift is in accordance with a polymer matrix that is bonded to metal ion through the nitrogen atom of the azomethine group. The band at about 1430 cm^{-1} in the PHQ is allocated to the in-plane-O-deformation mode [42]. The band is shifted to a higher frequency (1460 cm^{-1}) in the coordination polymer caused by the formation of metal-oxygen bond. After All, the presence of metal coordination has been confirmed by a strong band at 1105 cm^{-1} which corresponds to a C–O–M stretching vibration.

3.5 Thermal Behavior of PHQ-Al(III) and PHQ- Co(II) Matrix

The thermal behavior of PHQ-Al(III) and PHQ-Co(II) matrixes have been obtained [119] from thermal gravimetric analysis (TGA) and differential thermal analysis (DTA). The TGA thermograms, Figure 20, demonstrate that the PHQ-Al(III) matrix is thermally unstable than the PHQ-Co(II) matrix under the same circumstances. These observations suggest that the PHQ-Al(III) is the expanded coil-like form. So, the thermal decomposition is easy than the compacted coil-likes form of PHQ-Co(II) complex. The initial signals in the thermograms of DTA curves, Figure21, are owing to the removal of the adsorbed water and or solvent. This peak at a higher temperature (82.71 ºC) in the DTA curve of PHQ-Al(III) matrix than the PHQ-Co(II) matrix (53.33 ºC). These interpretations could be attributed to the chelated PHQ with Al(III) is heavily adsorbed water than the chelated that with Co(II). This is confirming again that the PHQ-Al(III) matrix is expanded coil-like, at the same time that the PHQ-Co(II) matrix is in a compact form .

3.6 UV-Visible Studies on PHQ-Al(III)

3.6.1 Uv-Visible Absorption Spectra of Coordination Polymer PHQ–Al(III)

Absorption spectra of PHQ at universal buffer solution (pH 7.20 ± 0.1), 30 % ethanol, have been recorded at 305 nm as illustrated in the Figure (22 a). Various concentration of Al(III) ion solution are added to PHQ sample solution and complete to the optimal volume by doubly distilled water in absence of universal buffer solution and without ethanol. The absorbance were reduction in the same position of PHQ peak (305 nm), Figure(22 b-e), until this peak disappeared completely and appear new peak at 370 nm as displayed in the Figure(22 e-h), after addition of Al(III) ion was recorded. These opinion could attributed to the formation of PHQ-Al(II) complex. The coordination polymer PHQ–Al(III) is readily precipitated. The highest possible concentration of Al(III) solution can be added is 1 $mmolL^{-1}$.

At The Same Time That, in universal buffer solution (pH 7.2 ± 0.1) and 30 % ethanol, the absorption peak of coordinated polymer PHQ-Al(III) has been increased. The formation of the coordinated polymer is enhanced. This mean the amount of Al(III) can be added and reacted with PHQ is increased has been achieved to 3 $mmolL^{-1}$. This increase the capacity of polymer to react with metal and is becoming more and more useful for applications.

3.6.2 Uv-Visible Absorption Spectra of Cation-Exchanged Al(III) on PHQ-Co(II)

Spectra of PHQ, Figure (23 a), reacted with Co(II) at universal buffer solution (pH 7.2 ± 0.1), 30 % ethanol, was documented. Anew peak at 370 nm was looked, Figure (23 b), due to coordination of PHQ polymer with Co(II) metal ion to form PHQ-Co(II) complex. The formation of this complex can be written as follow:

$$PHQ + Co\ (II) \longrightarrow [\ PHQ - Co(II)\ ] \quad (12)$$

Addition of specific different concentration of Al(III) ion to PHQ-Co(II) solutions, The absorbance of PHQ-Co(II) peak at 370 nm decrease, Figure(23 c-g). These remark may be attributed to the inclusion of Al(III) into PHQ matrix instead of Co(II) ion, in accordance with the following equation :

$$PHQ\text{-}Co(II) + Al(III) \longrightarrow [\ PHQ\text{–}Al(III)\ ] + Co(II) \quad (13)$$

The highest amount of Al(III) solutions can be added to PHQ-Co(II) solution is 4 $mmolL^{-1}$ which that necessary to disappeared the peak at about 370 nm as viewed in the Figure(23 g).

3.6.3 Cation–Exchange constant (k_{ex}) of Al(III) with PHQ-Co(II), PHQ-Ni(II) or PHQ-Mn(II)

If the equation of the insert of Al(III) as a substitute of each metal ion, [M(II): Co(II), Ni(II) or Mn(II)] according to the equations (33), and (34) which may be written as:

$$PHQ\text{-}M(II) + Al(III) \longrightarrow [\,PHQ\text{–}Al(III)\,] + M(II) \quad (14)$$

If the highest possible absorbance (A_{max}) is the absorbance of PHQ-M(II) matrix at full color development, The absorbance (A) is the absorbance of the polymer chelates existing at equilibrium and (C) is the initial concentration of the cation Al(III) added as an alternative of M(II) ion then :

$$[\,PHQ - Al(III)\,] = C \; A / A_{max} \quad (15)$$

$$and \quad [\,Al(III)\,] = C - [\,PHQ - Al(III)\,]$$

$$= C - C \; A / A_{max} \quad (16)$$

The data were evaluated using linear regression program [120] according to the following formula:

$$A = a + b \; C \quad (17)$$

Where A, and C are the absorbance and concentration of the analyte [Al(III)], at the same time, *a* and *b* are the intercept and slope of the straight line, respectively. Statistical data, regression coefficient and relative standard deviation are presented in the table 7. The slope of this straight line, as illustrated in the figure 24, corresponding to the cation–exchange constant (K_{ex}) [in these cases the value of (K_{ex}) will have negative sign for the reason that the absorbance reduction in the same series, the slope have negative value. The intercept of the straight line (*a*) is ascribed to the initial concentration of the PHQ-M(II) matrix individually (without addition of Al(III)). These values are comprising the well with the appropriate experimental value. The cation exchange constant (K_{ex}) of inclusion Al(III) instead of each metal ion of Co(II), Ni(II) or Mn(II) in PHQ–M(II) polymer chain are: -0.3148, -0.2865 and -0.2724 $mmolL^{-1}$, respectively .

These value signifies that Al(III) ion have ability to substitute the of Co(II) ion in PHQ-Co(II) chain more than the replacement of each Ni(II) and Mn(II) according to data from the series :

$$Co(II) > Ni(II) > Mn(II)$$

The clarification of this arrangement suggested that resulting from the many parameter differences between these metal ions. First-ever reason may be the stability constant of these metal ions with PHQ polymer. Al(III) ion have capability for replacement a metal ion have more stability constant with PHQ polymer. The values of stability constant of PHQ-Al(III), PHQ-Co(II) and PHQ-Ni(II) are: 10.71, 10.7, and 10.65, respectively [42]. The other reason suggested an explanation for this arrangement could be due to ionic radii that could be cause steric hindrance. The ionic radii for Al^{3+}, Co^{2+}, Ni^{2+} and Mn^{2+} are 0.051, .063, 0.069 and 0.08 nm, respectively.

3.7 Coordination of PHQ Polymer with Some Metal Ion in Existence of Al(III) Ion

As noted previously that, Cation exchange capability of Al(III) for replacement as opposed to some metal ion as Co(II), Ni(II) and Mn(II). Coordination of other some metal ions were increase in presence of Al(III). This signifies that, The absorbance of PHQ-M(n) was increased by addition of Al(III) ion solution.

3.7.1 Uv-Visible Spectra of PHQ-Cu(II) in Presence of Al(III) Ion

Spectra of PHQ Figure (25 a), reacted with Cu(II) at universal buffer solution (pH 7.2 ± 0.1), 30 % ethanol, was documented. Anew peak at 370 nm was appeared, Figure (25 b), due to coordination of PHQ polymer with Cu(II) metal ion to form PHQ-Cu(II) complex. The formation of this complex may be written as follow:

$$PHQ \;+\; Cu\,(II) \longrightarrow [\,PHQ - Cu(II)\,] \qquad (18)$$

Addition of individual different concentration of Al(III) ion to PHQ-Cu(II) solutions, The absorbance of PHQ-Cu(II) peak at 370 nm increase, Figure(25 c-h). These surveillance could be attributed to the enhancement induced by Al(III) ion to form metal–metal interchelation which is leading to increase the coordination of (Cu-Al) metals by PHQ polymer. This has been proposed to be written according to the following equation:

$$PHQ\text{-}Cu(II) \;+\; Al(III) \longrightarrow PHQ - [Al\text{-}Cu] \qquad (19)$$

Consequently, the absorbance at 370 nm has been increased. The highest possible amount of Al(III) solutions can be added to PHQ-Cu(II) solution is 6 $mmolL^{-1}$, higher than it, the solution become unclear and begin to precipitation.

3.7.2 Uv-Visible Spectra of PHQ-M(n)[M : Cr(III), Mg(II), or Zn(II)] in presence of Al(III) Ion

Spectra of PHQ at universal buffer solution (pH 7.2 ± 0.1), 30 % ethanol, was documented as illustrated in the Figure (26 a). A 0.25 $mmolL^{-1}$ of metal ion, Cr(III), was added and a recording spectra. A peak at the exact same position of PHQ absorbance peak, at 305, was appeared as demonstrated in the Figure (26 b). These peak owing to the coordination of PHQ polymer with metal ion to form PHQ-M(n) complex. The formation of these complex may be written as follow:

$$PHQ \;+\; M(n) \longrightarrow [\,PHQ - M(n)\,] \qquad (20)$$

Where M : Cr(III), Mg(II), or Zn(II)

Addition of individual separate concentration of Al(III) ion to PHQ-M(n) solutions, The absorbance of PHQ-M(n) peak at 370 nm increase, as displayed in the Figure(26 c-f). These adherence can be attributed to the enhancement caused by Al(III) ion to form metal–metal interchelation which leads to increase the coordination of (M-Al) metals by PHQ polymer. This has been proposed to be written according to the following equation:

$$PHQ\text{-}M(n) \;+\; Al(III) \longrightarrow PHQ - [Al\text{-}M] \qquad (21)$$

Where M : Cr(III), Mg(II), or Zn(II)

Then Again, the absorbance at 305 nm was increased. The highest possible amount of Al(III) solutions can be added to PHQ-M(n) solution was 2 $mmolL^{-1}$, more than it, the solution become unclear and begin to precipitation.

3.7.3 Cation–Exchange Constant (K_{ex}) of Al(III) With Some Metal Ion

In accordance with the equation (17): $\boldsymbol{A = a + b\,C}$

As soon as the concentration of Al(III) ion added ($mmolL^{-1}$) plotted against of the absorbance, as demonstrated in the Figure27, the slope of the straight line (b) equivalent to the cation exchange constant (K_{ex}). At The Same Time That the intercept (a) is attributed to the initial concentration of

PHQ-M(n) matrix individually [without addition of Al(III)], Table 7. The cation exchange constant (K_{ex}) of insertion M(n) ion somewhere [M : Fe(III), Cu(II), Cr(III), Zn(II), Mg(II), or Mo(VI)] instead of Al(III) in PHQ-Al(III) chain, or at least Al(III) ion no longer be able to replace the metal ion in PHQ-M(n) polymer chain. Though, it is causing the enhancement for metal ion (by form metal–metal interchelation) to coordinate with PHQ polymer. The value of (K_{ex}) of these metal are: Fe(III): 0.1496, Mg(II): 0.1616, Zn(II): 0.2148, Cu(II): 0.2313, Cr(III): 0.2512, and Mo(VI): 0.5662 $mmolL^{-1}$. These values are comprising the well with the corresponding experimental value. This signifies that, these metal ions have the power to replacement of Al(III) ion into PHQ polymer chain in accordance with the following series:

Fe(III) > Mg(II) > Zn(II) > Cu(II) > Cr(III) > Mo(VI)

To explain the agreement of this series, has suggested that as previously, many parameters differences between these metal ions. The earliest reason is the stability constant of these metal ions with PHQ. Subsequently, These metals can replacement Al(III) ion (stability constant for PHQ-Al(III) is 10.71) from polymer chain or caused metal interchelation of Al(III) with PHQ-M(n) complex.

The stability constant for PHQ–Fe(III), PHQ-Mg(II), PHQ-Zn(II) and PHQ-Cu(II) are: 10.82, 10.61, 10.43 and 10.13, respectively[42]. The second reason for these metal can replace or interchelation of Al(III) is the ionic radii of these metal ion that cause steric hindrance. The ionic radius for Al^{3+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Mg^{2+}, Cr^{3+}, and Mo^{6+} are: 0.051, 0.074, 0.074, 0.72, 0.066, 0.063, and 0.062 nm. Next To the previous suggests, several cases have specific interaction and strong affinity between metal-metal interchelation corroborated by the corresponding kinetic study.

4 Immobilization of Monomeric, Polymeric and Polymeric Chelates Forms of (8-Hydroxyquinoline) Matrix incorporated in Aluminum Oxide

Nanometer-sized material has got greater focus in recent years because of its special properties. One of its most exciting properties is that most of the atoms are on the surface of the nano particle. The unsaturated surface atoms can bind with other atoms that have strong chemical activity and generate high adsorption capacity [121]. It has been reported that TiO_2, ZrO_2, CeO_2 and ZnO materials have high adsorption capacity [122] and give encouraging results when used for trace metal analyses in biological and environmental samples [123]. The adsorption activities of trace metal ions on nanometer TiO_2 [124], Al_2O_3 [125] and SiO_2 [126] has been reported and the authors came to the conclusion that the nano material is a promising solid phase material for preconcentration and separation of residue metal ions.

Nanometer-sized alumina is resistant to pH changes and has a powerful resistance to swelling when positioned in organic solvents. Because nanometer-sized alumina has a high surface area, high-level adsorption capacity and high-level chemical activity it could be successfully applied for the separation and determination of trace metal ions in environmental samples. Chemical activation of the nanometer-sized alumina with functional groups that contain the N, S, O, and P atoms is highly efficient for the sorption of multiple metal ions. Chromotropic acid is a phenolic compound with the capability to act as a bidentate ligand and has the tendency to make complexes with many metals [127]. Moreover, the chromotropic acid reagent has multiple benefits, including: (i) very high selectivity; (ii) great affinity for immobilization on an alumina nano particle; (iii) improved stability in acid solutions. The coating of chromotropic acid on the nanometer-sized alumina raises the number of binding sites have the ability to interact with metal ions, increases the density of binding sites and modifications to the binding sites in order to enhance the uptake of metal ions.

Tiwari and Singh [128] also are reporting that the high capacity of solid supports may be constructed by loading the support with small molecular size ligands, so that the functionalization is increased and

the steric effects on sorption are reduced. Chromotropic acid coated nanometer sized alumina was used as the micro-column packing material. It is being used for the preconcentration of trace metal ions, Cd^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from environmental samples [129].

4.1 8-Hydroxyquinoline Coordinated with Aluminum

Tris (8-hydroxyquinoline) Aluminum is currently considered as one of the most reliable emitting materials because of its exceptional stability and luminescent properties. In the molecules, the quinolines function as bidentate ligands and bind to aluminum atom through both nitrogen and oxygen atom, and the coordination numbers are 6. The luminescent property of Alq_3 type Mq_3 (M = Al, Ga, In) is linked to the metal–nitrogen bond. As the covalent nature of the metal–nitrogen bond is reduced, the emission shifts to shorter wavelength [130]. A complex without the metal–nitrogen bond has been produced. In the lithium tetra (2-methyl-8-hydroxy-quinolinato) boron (LiBq*m*)$_4$, just oxygen atoms coordinated to the Al atom [131]. The blue-shift of a bis-(2-methyl-8-quinolinolato) aluminum (III) hydroxide complex ($AlMq_2OH$) is ascribed to the steric hindrance provided by the 2-methyl groups on the 8-hydroxyquinoline ligand, which weakened or banned the formation of Al–N bonding [132].

In the past few years, the flat-panel display industry has increased enormously due mostly to the success of liquid-crystal displays (LCD). Though, during this period, the technology of organic light-emitting diodes (OLED's) has improved so that it now can compete directly with LCD for high-information content display applications [133].

The increasingly important complex used in OLED has been tris-(8-hydroxyquinoline) aluminum (III), called Alq_3 [134]. This is an organo metallic complex with one aluminum cation in +3 formal oxidation state, and encircled by three quinolate ligands, resulting in a pseudo-octahedral configuration [135]. Alq_3 can belong to two isomeric forms, which are object of debate about film composition. An assessment of the electronic structure of the Alq_3 was conducted by Curioni et al.[136] on the basis of *ab initio* calculations indicating the coexistence of the two isomers, called mer-Alq_3 and fac-Alq_3. Though, experimental studies have not demonstrated the evidence of the facial isomer [137]. Nevertheless, this disagreement about the film composition, the most of both theoretical and experimental treatments relate to almost exclusively to mer-Alq_3 [138]. Research has been carried out to prepare new compounds with improved performances and stability and/or emitting in a spectral range. Studying these aspects, several complexes of metals such as Be, Zn and Cd with substituted 8-hydroxyquinoline ligand there have been reports [139]. The geometry, electronic structure and reactivity sites of a set of HQ–M (M = Be, Zn, Cd) with application in OLED's have been calculated and compared through computational calculations of both electronic and chemical reactivity for the descriptor. All the geometries were warped tetrahedral, where both angles and bond length the rise in the order $Be^{+2} < Zn^{+2} < Cd^{+2}$. The more reactive sites were found atoms that belonged to the lowest vacant molecular orbital, which are in para-position to the quinoline nitrogen [140].

Tris (8-hydroxyquinoline) aluminum (Alq_3) based transistors applications were extremely limited by relatively low currents and high operational voltages [141]. But recently, hybrid Alq_3-based devices allowing higher operational current densities at low voltages have been reported by Yi et al. [142]. These Al/n-Si/Au/Alq3/Al permeable base transistors (PBTs) demonstrated the high-level common-base current gain. These devices were constructed in vertical architecture because this structure suggests short channel lengths [143], a condition which is relevant because of lower charge carrier mobility in organic semiconductors. In the vertical architecture, the charge transport paths across the organic semiconductors are decided by the layers thickness. Ivo A. Hu¨mmelgen [144] the electrical

characterization transistors with tris(8-hydroxyquinoline) aluminum were constructed. They examine the influence of the V_2O_5 layer thickness and prove that these devices present high common-base and can be operated at very low driving voltages, lower than, common-base and common-emitter modes.

Chang-Hee Hong [145], presented an investigation of amorphous tris(8-hydroxyquinoline) aluminum (Alq_3) molecules transferred into α-phase crystalline nanomaterials by incorporating some weight percentage of crystalline zinc oxide (ZnO) nanoparticles. They ascribed the achievement of higher PL intensity of Alq_3–ZnO hybrids to the inclusion of crystalline ZnO nanoparticles. A blue shift in the PL emission of the hybrid nanomaterials caused, with respect to ZnO content, owing to the quantum confinement effect of the ZnO nanoparticles.

AlQ_3 derivatives for example the $Al(Et)_2Q$ [146], $Al(Et)Q_2$ [147] and $Al(Q)_2(OH)$ [132] can be incorporated into polymers containing OH side groups by condensation reactions. High-level reactivity of the former and low solubility of the latter referred to compounds can be carried away by replacing the ethyl or hydroxide group with long alkoxy groups. Moreover, it has recently been suggested that the aluminum–nitrogen bond strength can be used as a parameter for tuning the complex emission wavelength [130]. otherwise, it may be possible to alter the emission wavelength to some extent using several alkoxy groups. As a contribution to the most recent development of this interesting field. Mostafa M. Amini et.al. [148], report the synthesis and characterization of the first examples of two highly soluble and stable alkoxy derivatives of AlQ_3, $[Al(Q_2)(OCH_2CH_2OR)]$, [R = CH_3 (1) and C_2H_5 (2)]. In supplement to the, their photoluminescence behavior was examined and the molecular structure of complex 2 was determined by X-ray analysis.

Meso porous Alumina has attracted significant attention because of their high surface area. Moreover, the surface of alumina can be modified with organic function groups as (8-Hydroxyquinoline) or its polymer and provide access stability. As an application for a cation exchange of Al(III) in solution, immobilization of 8-Hydroxyquinoline (HQ) or its polymer (PHQ) on the surface of Alumina [Al_2O_3, in this study signed by AlO], can planned. Resulting In, can intended for extraction of some heavy metal ion as: Fe(III), Cu(II), Co(II) and Ni(II) from its solutions.

4.2 Uv-Visible Spectroscopic Studies of HQ Immobilized on AlO [AlO-HQ]

4.2.1 Uv-Visible Absorption Spectra of Cu(II) ion on AlO-HQ

Spectra of AlO-HQ after various addition of Cu(II) ion added at universal buffer solution (pH 7.2) was documented [149] as demonstrated in the Figure28. The solution of Cu(II) ion was added to the solution contain AlO-HQ, record the spectra of that solution. At the initial addition of Cu(II), a peak was appeared at 305 nm which is equivalent to the peak of HQ-Al(III), that produced from HQ immobilized on AlO, the very low concentration of Cu(II) ion yet has no effect. At The Same Time, after addition even greater concentration of Cu(II) ion, a new peak at 380 nm was appeared equivalent to the peak of HQ–Cu(II) complex. The formation of this coordination complex suggest that the solid of HQ immobilized incorporated in AlO can extract the metal of Cu(II) ion from the solution to form AlO-HQ–Cu(II). Increases the concentration of Cu(II) ion with increasing the formation of AlO-HQ–Cu(II) coordinated complex was noticed, that could be confirmed with the increases of the absorbance peak at 380 nm. While, the peak at 305 nm decrease due to the HQ-Al(III) complex was decreased. This inspection imply that the Cu(II) ion has the capability to replacement of Al(III) ion into AlO-HQ chain by cation exchange mechanism .

The highest possible absorbance of this peak as illustrated in the figure (28 f) which corresponding to the added Cu(II) concentration of 2 $mmolL^{-1}$, while the peak at 305 nm was completely vanished. This

Cu(II) ion concentration signify the capacity of AlO-HQ solid for extraction of Cu(II) ion from the solution by stripping HQ from AlO-HQ. This capacity was 100 mmol /g .

4.2.2 Uv-Visible Absorption Spectra of HQ on AlO-Cu(II)

Immobilization of Cu(II) metal ion itself on Alumina (AlO-Cu) was examined and compute the capacity of it, then compared with the capacity of AlO-HQ. Spectra of 20 mg of AlO-Cu at universal buffer solution (pH 7.2) has been recorded as illustrated in the Figure29. A series of various concentration of HQ added to the solution contain AlO-Cu, later contact time, filtrate the content, dissolve the solid precipitate in 5 ml pure ethanol and recording the spectra of each addition. A peak was shown at 380 nm represented to the formation of HQ–Cu coordinated complex. The formation of this complex suggested that the solid of Cu(II) ion immobilized on AlO can extract HQ from the solution to form AlO-HQ–Cu(II).

Ethanol can dissolve the coordination complex HQ–Cu(II) and provide the appeared absorbance peak at 380 nm. Increasing the concentration of HQ added, increase the absorbance peak of formation of HQ–Cu(II), till the Cu(II) ion from AlO-Cu consumed, as demonstrated in the Figure(29 f). This absorbance represent the greatest amount of HQ can be extracted from the solution that expressed in the capacity of AlO-Cu solid, it was 75 mmol / g .

Make A Comparison between capacity of AlO-HQ for extraction of Cu(II) ion and the capacity of AlO-Cu for extraction of HQ, it is noticed that the AlO-HQ has capability more than AlO-Cu. This implies that, the immobilization of HQ on AlO is a positive than immobilization of Cu(II) ion on it .

4.2.3 Linearity Range of Addition of Cu(II) or Fe(III) on AlO-HQ

Scheming of the concentration of Cu(II) or Fe(III) ion added (mmolL-1) against absorbance, as illustrated in the Figure30, the linearity of this curves correspond to the detection limit range. Spectrum within the range (0.0 – 1.0 mmolL-1) was the linear range (r = 0.9914) of addition of Cu(II) ion on AlO-HQ. Additionally, The range during the period (0.0 – 1.0 mmolL^{-1}) was the linear range (r = 0.988) of addition of Fe(III) ion on AlO-HQ. This will be the range that can be used for applications; greater than this concentration give logarithmic curve until attained to 2 mmol L^{-1}.

4.2.4 Uv-Visible Absorption Spectra of Ni(II) ion on AlO-HQ

Spectra of 20 mg of AlO-HQ after separate addition of Ni(II) ion added at universal buffer solution (pH 7.2) was logged [149] as displayed in the Figure31. A peak at 305 nm is equivalent to the formation of HQ-Al(III) coordinated complex was appeared, as can be seen in the Figure(31 a). The solution of Ni(II) ion has been added to the solution contain AlO-HQ, later contact time, filtrate the content, dissolve the solid precipitate in 5 ml pure ethanol and track record the spectra of that solution. Addition of individual distinct concentration of Ni(II) ion, the absorption peak at 305 nm was decreased, as illustrated in the Figure(31 b–h). These surveillance may be attributed to the cation exchange mechanism which demonstrate that Al(III) ion have the power to replacement of Ni(II) ion into HQ-Ni(II) chain when Al(III) was added to the solution of HQ-Ni(II). But Ni(II) ion no longer be able to stripping HQ which immobilized on AlO and forming HQ-Al(III) coordinated complex. Then the decrease of the absorbance peak owing to the formation of metal-metal interchelation among [Al-Ni], Then coordination complex HQ-Al(III) was decreased. The solid of HQ immobilized into AlO may be able to extract the metal of Ni(II) ion from the solution to form Ni-AlO-HQ interchelated complex.

The maximum quantity of Ni(II) can be added to the solution contain 20 mg of AlO-HQ was 1.25 mmol L^{-1}, which the reason for the peak at 305 nm nearly vanished. This concentration correspond to the capacity of AlO-HQ solid for extraction of Ni(II) ion, it was 62.5 mmol /g .

4.2.5 Linearity Range of Addition of Co(II) or Ni(II) on AlO-HQ

Plotting of the concentration of Co(II) or Ni(II) ion added (mmolL^{-1}) versus the absorbance, as displayed in the Figure32, the linearity of this curves correspond to the detection limit range. The variety during the period (0.0 – 1.25 mmolL^{-1}) was the linear range (r = 0.9861) of addition of Ni(II) ion on AlO-HQ. And At The Same Time, The range during the period (0.0 – 2 mmolL^{-1}) was the linear range (r = 0.9767) of addition of Co(III) ion on AlO-HQ.

This is the range which can be used for applications; higher than this concentration give logarithmic curve until have a stable value of low absorbance.

4.3 Uv-Visible Absorption Spectra of AlO-PHQ

Poly(8-Hydroxyquinoline) immobilized on Alumina to form coordinated complex AlO-PHQ. Spectra of various weights of AlO-PHQ at universal buffer solution (pH 7.2) were documented as illustrated in the Figure (33 a and b). The various weights: 10, and 20 mg of AlO-PHQ, have been used. Filtrate the content, dissolve the solid precipitate in 5 ml pure ethanol, and track record the spectra of that solution. The peaks that are displayed at 305 nm corresponding to PHQ absorbance, which has been produced from, dissolved of PHQ immobilized on AlO. Additionally, this peak can be correspond to the formation of PHQ-Al(III) complex. This peak increase by increased the weight of AlO-PHQ till attained to 20 mg which used in this research.

4.3.1 Uv-Visible Absorption Spectra of AlO-PHQ on Cu(II) ion

Spectra of various weight of AlO-PHQ at universal buffer solution (pH 7.2) added in presence of certain concentration of Cu(II) ion (1 mmolL^{-1}) was documented as displayed in the Figure(33 c, d and e). Following contact time (1 min.), filtrate the content, dissolve the solid precipitate in 5 ml pure ethanol and track record the spectra of that solution. Two peaks were looked at 380 nm and 305 nm. The peak at 305 nm is equivalent to the PHQ absorbance, which produced from, dissolved of PHQ immobilized on AlO and also, this peak may be produced from the formation of PHQ-Al(III) complex .

At The Same Time, the peak at 380 nm was corresponding to PHQ–Cu(II) complex. Ever-increasing the weight of AlO-PHQ in the solution, increase the two peaks due to increase the presence of PHQ immobilized on AlO-PHQ.

4.3.2 Uv-Visible Absorption Spectra of Cu(II) ion on AlO-PHQ

Spectra of 20 mg of AlO-PHQ after various addition of Cu(II) ion added at universal buffer solution (pH 7.2) was documented as demonstrated in the Figure34. The solution of Cu(II) ion had been added, after contact time (1 min.), filtrate the content, dissolve the solid precipitate in 5 ml pure ethanol and log the spectra of that solution. A peak at 305 nm was appeared equivalent to the peak of PHQ-Al(III) produced from PHQ immobilized on AlO. A new peak at 380 nm was shown corresponding to the peak of PHQ–Cu(II) complex. The formation of this coordinated complex suggest that the solid AlO-PHQ can extract the metal of Cu(II) ion from the solution to form AlO-PHQ–Cu(II).

Increases the concentration of Cu(II) ion with rising the formation of AlO-PHQ–Cu(II) coordinated complex was detected, that could be confirmed with the increases of the absorbance peak at 380 nm. And At The Same Time the peak at 305 nm decrease until completely vanished owing to the PHQ-Al(III)

complex was reduced. This observation suggest that the Cu(II) ion possesses the ability to replacement of Al(III) ion into AlO-PHQ chain by cation exchange mechanism .

The highest possible absorbance of this peak as displayed in the Figure(34 f) which corresponding to the added Cu(II) concentration of 10 $mmolL^{-1}$. Here's the capacity of AlO-PHQ solid for extraction of Cu(II) ion from the solution by stripping PHQ from AlO-PHQ was 500 mmol /g .

Make the comparison between the capacity of AlO-PHQ for extraction of Cu(II) ion and the capacity of AlO-HQ, it was noticed that the AlO-PHQ have capability about five times greater than AlO-HQ, as demonstrated in Table 8. This signifies that, PHQ have ability to immobilized on AlO and coordinated with Cu(II) ion greater number by five times than the ability of HQ to accomplish that.

4.3.3 Uv-Visible Absorption Spectra of PHQ on AlO-Cu(II)

Immobilization of Cu(II) metal ion the event on Alumina (AlO-Cu) was examined and calculate the capacity of it, then contrasted with the capacity of AlO-PHQ. Spectra of 20 mg of AlO-Cu at universal buffer solution (pH 7.2) was recorded as demonstrated in the Figure35. A series of various concentration of PHQ added to the solution includes the AlO-Cu, after contact time, filtrate the content, dissolve the solid precipitate in 5 ml pure ethanol and recording the spectra of every single addition. A peak was appeared at 380 nm characterized to the formation of PHQ–Cu coordinated complex. The formation of this complex revealed that the solid of Cu(II) ion immobilized on AlO will be able to extract PHQ from the solution to form AlO-PHQ–Cu(II).

Ethanol has the ability to dissolve the coordinated complex PHQ–Cu(II) and provide the appeared absorbance peak at 380 nm. Ever-increasing the concentration of PHQ added, enhance the absorbance peak of formation of PHQ–Cu(II), till the Cu(II) ion from AlO-Cu consumed, as illustrated in the Figure(35 i). This absorbance represent the highest possible amount of PHQ can be extracted from the solution that stated as the capacity of AlO-Cu solid, it was 200 mmol / g .

The comparison between the capacity of AlO-PHQ for extraction of Cu(II) ion and the capacity of AlO-Cu for extraction of PHQ, it is noted that the AlO-PHQ has capability about 2.5 times greater than AlO-Cu, as illustrated in the Table 8. This implies that, the immobilization of PHQ on AlO is more desirable than immobilization of Cu(II) metal ion on it.

Additionally, In the Comparison between capacity of AlO-Cu for extraction of HQ and PHQ, it was noticed that this capacity is higher by two times in the brief case of PHQ than HQ. This signifies that, the PHQ have capability for coordination more than HQ to do that.

4.3.4 Linearity Range of Addition of Cu(II) or Fe(III) on AlO-PHQ

Scheming of the concentration of Cu(II) or Fe(III) ion added ($mmolL^{-1}$) versus absorbance (a.u.), as displayed in the Figure37, the linearity of this curves correspond to the detection limit range. The variety during the period (0 – 2 $mmolL^{-1}$) proved to be the linear range (r = 0.993) of addition of Cu(II) ion on AlO-PHQ.

Additionally, The variety during the period (0 – 2 $mmolL^{-1}$) proved to be the linear range (r = 0.974) of addition of Fe(III) ion on AlO-PHQ.

This is the range which can be used for an application; higher than this concentration provide the logarithmic curve until reached to 10 $mmolL^{-1}$.

4.3.5 Uv-Visible Absorption Spectra of Ni(II) ion on AlO-PHQ

Spectra of 20 mg of AlO-PHQ after various addition of Ni(II) ion added at universal buffer solution (pH 7.2) was documented as displayed in the Figure36. A peak at 305 nm is equivalent to the formation of PHQ-Al(III) complex. The solution of Ni(II) ion has been added to the solution to include the AlO-PHQ, after contact time, filtrate the content, dissolve the solid precipitate in 5 ml pure ethanol and log the spectra of that solution. Addition of specific various concentration of Ni(II) ion, the peak at 305 nm has been reduced, as illustrated in the Figure(36 b–g). These surveillance can be attributed to a cation exchange mechanism which demonstrate that Al(III) ion have the capacity to replacement of Ni(II) ion into PHQ-Ni(II) chain when Al(III) have been added to the solution of PHQ-Ni(II). But Ni(II) ion can no longer be able to stripping PHQ which immobilized on AlO and forming PHQ-Al(III) coordinated complex. But Then, the decrease of the absorbance peak owing to the formation of metal-metal interchelation among [Al-Ni], Then coordination complex PHQ-Al(III) was reduced. So, The solid of AlO-PHQ can extract the metal of Ni(II) ion from the solution to form Ni-AlO-PHQ interchelated complex.

The maximum quantity of Ni(II) can be extracted from the solution to include the 20 mg of AlO-PHQ proved to be 1.5 $mmolL^{-1}$, which is causing the peak at 305 nm nearly vanished. This concentration correspond to the capacity of AlO-PHQ solid for extraction of Ni(II) ion, it was 75 mmol /g .

4.3.6 Linearity Range of Addition of Ni(II) or Co(II) on AlO-PHQ

Plotting of the concentration of Co(II) or Ni(II) ion added ($mmolL^{-1}$) versus the absorbance (a.u.), as illustrated in the Figure38, the linearity of this curves correspond to the detection limit range. The range during the period (0 – 1.25 $mmolL^{-1}$) proved to be the linear range (r = 0.988) of addition of Ni(II) ion on AlO-PHQ. At The Same Time, The variety during the period (0 – 2 $mmolL^{-1}$) was the linear range (r = 0.992) of addition of Co(III) ion on AlO-PHQ

This is the range that could be used for applications; higher than this concentration give logarithmic curve until be fixed value of low absorbance.

5 Immobilization of Monomeric, Polymeric and Polymeric Chelates Forms of (8-Hydroxyquinoline) Matrix into Silica Gel

5.1 Organo functionalized Silica gel in Preconcentration of metal ions

Several example of immobilization of organic reagent / organic chelating groups on silica surface for preconcentration of metal ions has been reported [150].

Modification of silica gel with eriochrome black T (ECB-T) was described by stirring a mixture of ethanolic solution of ECB-T and silica gel for 30 min [151]. Boric acid infused on silica gel has been reported for chromatographic separation of substances that contain the vicinal *cis*-hydroxyl groups [152]. Substituted benzaldehydes immobilized on silica surface have been discovered to produce more alkylated product by using Grignard reagent when it is compared to alkylation in homogeneous medium [153]. Mono and diethanolamine were infused on silica gel for sorption research of gaseous compounds such as the hydrogen sulfide (H_2S), carbon disulfide (CS_2), methanethiol (CH_3SH) and sulfur dioxide (SO_2) [154]. Formaldehyde in air has been detected and assessed at 365 nm as a hydrazone complex on adsorption to the 2,4-dinitriphenylhydrazine infused silica gel surface [155]. A chelating molecule *N*-propyl-*p*-benzoylbenzamide had been prepared from reaction of *p*-benzoic acid and thionyl chloride in dry toluene and then condensation with *n*-propylamine [156-157]. Lucigenin (bis-*N*-methylacridinium nitrate), a chemi luminescent reagent was immobilized on the silica surface from its aqueous solution for the determination of Fe(II) and V(IV) with a detection limit of 0.8 and 0.7 mg L^{-1}, respectively [158].

Mahmoud [159] used metal chelating agent 1-aminoanthraquinone for the surface modification of silica gel by covalent grafting in addition to physical sorption. Hydrophobic attractions between the methyl groups of the dichlorodimethyl silane, $SiCl_2(CH_3)_2$ or chlorotripropyl silane, $SiCl(C_3H_7)_3$ immobilized silica and the carbon chain of Alamine336 or (2-hydroxy-5-nonylacetophenoneoxime) or Cyanex 272 (di-2,4,4-trimethylpentyl phosphonic acid) developed three modified silica [160-161]. Numerous authors [162-163] has proposed that such hydrophobic attraction or Vander Waals interaction.

Phenol derivatives, 4-(2-pyridylazo) resorcinol (PAR), 1-(2-pyridylazo)-2-naphthol (PAN) and 8-hydroxyquinoline were covalently attached to the silica surface through single-stage Mannich reaction, [164]. Silica gel immobilized with 2-mercaptobenzothiazole (MBT) was produced by the Mannich reaction between MBT and aminopropyltriethoxysilane modified silica gel [165]. Soliman et al. [166] synthesized mono and bis-naphthaldehyde and salicylaldehyde Schiff base ligands immobilized on silica surface in two paths. They treated diethylenetriamine (DETA) with silica gel functionalized with 3-chloropropyltrimethoxysilane.

Silica gel surface was chemically modified with 3-aminopropyltriethoxysilane [167]. Preheated silica gel when treated with the silylating agent, 3-(trimethoxysilyl) propylamine (APTS), in an inert medium produced equivalent organo functionalized silica, that had been further treated with 2,4-dichlorophenoxyacetic acid (2,4-D) to yield modified silica with acidic surface [168, 169]. Silica nanoparticles fixed with dye, tris(2,2-bipyridyl) dichlororuthenium(II) hexahydrate (Rubpy) have been modified with membrane binding reagent, lauroyl chloride and has been used as a biomarker for staining of PTK2 cells and leukemia cells [170]. Synthesis of hydride silica is described [171] wherever dimethylethoxysilane [$(CH_3)_2$ $Si(H)OC_2H_5$] was produced by refluxing a mixture of dry ethanol, dimethylaniline and dimethylchlorosilane.

Among the different methods of covalent bonding of polymeric chain to silica substrate, free radical surface graft polymerization is one with high-level surface coverage [172]. Grafting of vinyl acetate [173] and vinyl pyrrolidone [174] to silica substrate, modified with silane reagent vinyl triethoxysilane, by free radical surface graft polymerization is described. In a different method, a modified silica powder having organophilic properties with a polymerizable ethylenic monomer was described [175]. Block-co-polymers of norborn-2-ene and 7-oxanorborn-2-ene-5,6-dicarboxylate and other derivatives have been prepared by ring-opening metathesis polymerization. It is being used for the preparation of poly(norborn-2-ene)-block-(7-oxanorborn-2-ene-5,6-dicarboxylate)-coated solid materials having good pH stability [176-178]. Octadecyl (C_{18}) bonded silica gel has been reported for separation and preconcentration of platinum group metals (Ru, Rh, Pd, Os, Ir and Pt) as ion associates of their chlorocomplexes with cation of onium salt *N*-(1–carbaethoxypentadecyl)-trimethyl ammonium bromide [179]. Likewise, Cr(VI) separation and preconcentration was developed using C_{18} bonded silica gel as an ion associate of Cr(VI) anion with quaternary onium salts [180]. Selective preconcentration of gold in the form of ion associates of Au(III) chloro complex or Au(I) cyano complex was examined [181]. Extraction of Pd(II) from extremely dilute solution has been described using silica gel impregnated with 2-mercapto-*N*-2-naphthylacetamide [182] or *p*-(dimethylamino) benzylidene rhodanine [183]. Covalent bonding of 5-methylene-2-(2-thiozolyazo)anisole [184] to silica gel is also described to preconcentrate Pd(II) from dilute solution. 2-[(2-(Triethoxysilyl)ethyl)thio]aniline [185] immobilized silica has been reported as an exceptional phase for separation and preconcentration of Pd(II) from a matrix the wealthy in Rh(III) and Ir(III).

5.2 Immobilization of Hydroxyquinoline Derivatives on Silica gel

Basically, all silica –based 8-quinolinol (HQ_x) materials have been prepared employing one of two similar procedures that are described by Hill [186], and Sugawara et. al. [187]. These immobilization procedures require a rather lengthy synthesis. Silylation of the silica surface with an aliphatic amino silane, aromatic nitro group introduction , reduction of immobilized $ArNO_2$ to immobilized $ArNH_2$ diazonium salt formation, and after all diazo coupling to (HQ_x).

Everything the above steps, with the possible exception of diazo coupling to HQ_x, have been implemented from the procedure that is described by Weetall [188] for enzyme immobilization. Though, unlike enzyme immobilization that often involves a spacer between the support and the enzyme, immobilization of relatively small molecules for example the HQ_x should not have the ability to expected to require such a spacer. Consequently, although some effort has been made to optimize the above production [189], little effort has been made to provide a more direct route to silica immobilized HQ_x. A new path to silica immobilized HQ_x was explained [190], which retains the desirable features of diazo coupling reaction at the same time reducing the preparation time and producing products that have exchange capacities. The low capacity of silica- bound ligands has been one of the major problems that are encountered in their use. Moreover, capacities greater than 70 µmol/g have not been observed for silica immobilized HQ_x. Immobilization of 8-Hydroxyquinoline on the inner wall of silicone tubing and assess its use as a support for the concentration of residue metals from seawater [191].

Due To The Fact That the derivatized silica has a high specific binding capacity, the mass of silica to equilibrate with solution desires to be small for studies of reaction with trace-level [µM] metal ions, in a different way, the solution volume required to reach equilibrium becomes excessive [192]. The silica gel modified with (3-aminopropyl-triethoxysilane) may be used for the preconcentration of Cu(II), Pb(II), Ni(II), Fe(III), Cd(II), Zn(II) and Co(II) prior to their determination by flame atomic absorption spectrometry[193]. The simultaneous enrichment and the determination of all the metals are possible if the total load of the metal ions is not more than sorption capacity. A fewer complicated route to silica-immobilized 8-HQ was described [194], during which the 8-HQ are anchored to the surface of previously aminated silica by a one-step Mannich reaction. The SHQ synthesized was used successfully in the determination of trace lead in seawater using on-line flow injection-inductively coupled plasma mass spectrometry (FIA-ICP-MS) method. Immobilization with physical interaction among the modifier solid and solid support by either inclusion in the pores of support material or adhesion method electrostatic interaction. 8-Hydroxyquinoline (HQ) or poly (8-Hydroxyquinoline) (PHQ) was immobilized on silica gel for extractive absorption of metal ions by the activated silica gel.

5.3 FTIR Spectroscopic Studies

FTIR was used to provide information about the total or partial loss of silanol groups bonds of silica and to demonstrate the result resulting from the immobilization of PHQ on the surface of functionalized silica, as displayed in the Figure39:

a) The main characteristic peaks where been allocated as: 1100- 1000, 950-900 and 800-700 cm^{-1} could be attributed to υ(Si–O–Si), υ(Si–OH) and δ(Si–O–Si), respectively. The peak at 3430 cm^{-1} was assigned to υ(C=C).
b) The absorption bands at 1430, 1500, 1550 and 1600 cm^{-1} are characteristic of the HQ the active ingredient in PHQ polymer chain.
c) By comparison with the spectrum of original silica, (a), and spectrum of PHQ, (b), the C=C has been presented and the amplitudes of silanol groups bonds of silica were decrease.

Additionally, the amplitudes of (Si–O–Si) among 800 and 700 cm^{-1} were increased than the original silica due to the fact that PHQ had coupled with silica. These features confirmed that the original silica had reacted with PHQ.

d) Spectrum of Cu(II) have main characteristic peak at 1100 cm^{-1}.

e) The peak was occurring at about 1460 cm^{-1} due to the formation of a metal oxygen bond. A strong band at 1100 cm^{-1}, which is equivalent to the C–O–Cu stretching vibration, validates the presence of metal coordination [46]. Additionally, the band at 1650 cm^{-1} was shown. This must be the characteristic peak of υ(O=C). In the frequency band from 3000 cm^{-1} to 3500cm^{-1} related to hydroxyl groups, a broad band was noted for Si-PHQ–Cu(II) spectrum because silica attached at side chain hampered the formation of hydrogen bond between PHQ chain. This has demonstrated that silica had successfully copolymerized with PHQ–Cu(II).

5.4 Thermal Behavior of Si-PHQ and Si-PHQ- Cu(II) Matrix

Thermal behavior of Si-PHQ and Si-PHQ-Cu(II) were derived from the Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). The TGA thermogram, Figure40, displays a one-step decomposition at about 150 °C exposes that the thermal degradation of PHQ while Si will continue to be stable until 400 °C. The TGA demonstrate that the Si-PHQ in presence of Cu(II) ion as Si-PHQ-Cu is an even greater thermally stable higher than Si-PHQ. The thermal degradation of Si-PHQ-Cu shows many steps for its decomposition. The initial step in Si-PHQ-Cu thermogram is the weight loss below 100 °C, owing to the loss of water molecules. The second phase is more than 100 °C signifies that the Si-PHQ-Cu(II) matrix will continue to be stable to 250 °C after the loss of water and that the complexed polymer is the greater thermally stable than the polymer itself. The last stage at ~ 370 °C equivalent to the decomposition of Si. Throughout the Figure41, it is displayed that the DTA of Si-PHQ, a peak at about 70 °C which is assigned to the release of the water bonded to Si-PHQ. At The Same Time, in the DTA of Si-PHQ-Cu the release of water shown as a peak at 90 °C indicating strongly adsorbed water than Si-PHQ. The other peaks represent of decomposition of each Si-PHQ and Si-PHQ-Cu(II) as discussed previously.

5.5 Uv-Visible Spectra Study of HQ Immobilized on Silica gel

5.5.1 Contact Time

Time that is required for extraction of maximum amount of metal ion from the solution by Si-HQ, called contact time, was examined. Spectra of Si-HQ at universal buffer solution (pH 7.2±0.1), 0.5 $mmolL^{-1}$ of Cu(II) ion solution has been added. Record the spectra of this solution at different time (min.). The contact time of the experimental computed from the addition of metal ion to do filtrate the solution. The best contact time was about 1 min., This means that the time higher than 1 min. has no effect for extraction of metal ions from the solution. The contact time was plotted versus the absorbances which give straight horizontal line for higher than 1 min. also, a long time reached to 24 hours has been recorded which give the same absorbance peak and straight horizontal line for time higher than 1 min., dissolved of HQ immobilized on silica gel. This peak increase by increased the weight of Si-HQ until reached to 100 mg which used in this research.

5.5.2 Uv-Visible Absorption Spectra of Cu(II) ion on Si-HQ

Spectra of Si-HQ after various addition of Cu(II) ion added at universal buffer solution (pH 7.2) was documented [195] as displayed in the Figure42. In every one experiment, solution of Cu(II) ion was added to the solution include the Si-HQ. A peak at 380 nm was appeared equivalent to the peak of

HQ–Cu(II) complex. The formation of this coordination complex suggest that the solid of HQ immobilized incorporated in silica gel may be able to extract the metal of Cu(II) ion from the solution to form Si-HQ–Cu(II). Although, ethanol has the ability to dissolve the coordination complex HQ–Cu(II) and provide the peak at 380 nm. The highest possible absorbance of this peak as demonstrated in the Figure (42 h) which is equivalent to the added Cu(II) concentration of 1 $mmolL^{-1}$. Here's The Cu(II) ion concentration correspond to the capacity of Si-HQ solid for extraction of Cu(II) ion from the solution. Capacity in this area calculated as (concentration of metal ion by mmol / weight of substrate Si-HQ by g). Therefore, the capacity of Si-HQ for extraction of Cu(II) ion from solution is 10 mmol /g , in comparison with the capacity in older surveys which was 70 µ mol /g [190].

Planning of concentration of Cu(II) ion added ($mmolL^{-1}$) versus the absorbance, the linear characteristic variety of this curve represent the detection limit range. The variety during the period (0.0- 0.5 $mmolL^{-1}$) was the linear range of addition of Cu(II) ion on SiHQ. Greater than this concentration provide constant absorbance seems as nearly horizontal line.

5.5.3 Uv-Visible Absorption Spectra of HQ on Si-Cu(II)

Immobilization of Cu(II) metal ion that one on silica gel (Si-Cu) has been studied and compute the capacity of it, then in comparison to the capacity of Si-HQ [195]. Spectra of Si-Cu at universal buffer solution (pH 7.2) was recorded as illustrated in the Figure43. After the first addition of HQ to the solution include the Si-Cu, a peak was shown at 380 nm signified to the formation of HQ–Cu coordinated complex. The formation of this complex revealed that the solid of Cu(II) ion immobilized on silica gel may be able to extract HQ from the solution to form Si-HQ–Cu(II).

Additionally, ethanol can dissolve the coordination complex HQ–Cu(II) and provide the appeared absorbance peak at 380 nm. Ever-increasing the concentration of HQ added, increase the absorbance peak of formation of HQ–Cu(II), till the Cu(II) ion from Si-Cu consumed, then the peak of HQ–Cu complex was vanished and the peak that corresponds to the HQ itself at 305 nm, was appeared, as illustrated in the Figure(43 f).

This absorbance represents the greatest amount of HQ can be extracted from the solution that expressed as the capacity of Si-Cu solid was 7 mmol / g.

The comparison between the capacity of Si-HQ for extraction of Cu(II) ion and the capacity of Si-Cu for extraction of HQ, it is noticed that Si-HQ have capability about 1.5 times more than Si-Cu. Therefore, the immobilization of HQ on silica gel is better than immobilization of Cu(II) ion only.

5.5.4 Behavior of Fe(III) ion with HQ

Spectra of HQ and HQ-Fe(III) has been studied as illustrated in the Figure44. Addition of 1 $mmolL^{-1}$ of Fe(III) ion to 1 $mmolL^{-1}$ of HQ at universal buffer solution (pH 7.2), 30 % ethanol. Another new two peaks were showed, the first peak at 580 nm and the second at 455 nm owing to the formation of HQ–Fe(III) complex .

5.5.5 Uv-Visible Absorption Spectra of Fe(III) ion on Si-HQ

Spectra of various concentration of Fe(III) ion on Si-HQ at universal buffer solution (pH 7.2) was documented as displayed in the Figure 45. Solution of Fe(III) ion has been added to the solution contain Si-HQ. A new two peaks were looked at 580 nm and 455 nm that is equivalent to the formation of HQ–Fe(III) complex. The formation of this coordination complex suggest that the solid of HQ immobilized on silica gel may be able to extract the metal of Fe(III) ion from the solution to form Si-

HQ–Fe(III). Ethanol can dissolve the coordination complex HQ–Fe(III) and provide the two appeared absorbance peaks at 580 nm and 455 nm.

If the spectra of the filtrate, generate from addition of Fe(III) ion at universal buffer (pH 7.2), have been recorded. The excess of HQ free which not coordinated with added Fe(III) displayed as a peak at 305 nm. There Is An Increase of the concentration of Fe(III) ion with increasing the formation of Si-HQ–Fe(III) coordinated complex was detected, then increase the absorbance peaks. Though, in the filtration the peaks at 305 nm decrease due to the fact that the non-coordinated HQ decrease.

The highest possible absorbance peak which is equivalent to the added Fe(III) concentration of 2 $mmolL^{-1}$.

This Fe(III) ion concentration are representing the capacity of Si-HQ solid for extraction of Fe(III) ion from the solution that was 20 mmol / g . In the filtration spectra at maximum concentration the peak of HQ at 305 nm was vanished. Then there is absolutely no free HQ because all HQ coordinate with Fe(III) ion to form Si-HQ–Fe(III) coordinated complex .

5.6 Uv-Visible Absorption Spectra of PHQ

5.6.1 Uv-Visible Absorption Spectra of Cu(II) ion on Si-PHQ

Spectra of various concentration of Cu(II) ion on Si-PHQ at universal buffer solution (pH 7.2) was recorded as illustrated in the Figure 46. In Accordance With Cu(II) ion was added to the solution contain Si-PHQ. Another new peak was appeared at 380 nm that is equivalent to the peak of PHQ–Cu(II) coordinated complex. The formation of this coordinated complex suggest that the solid of PHQ immobilized on silica gel may be able to extract the metal of Cu(II) ion from the solution to form Si-PHQ–Cu(II). Additionally, ethanol can dissolve the coordinated complex PHQ–Cu(II) and provide the appeared absorbance peak at 380 nm.

The highest possible absorbance peak as displayed in the Figure (46 i) which corresponding to the addition of 4 $mmolL^{-1}$ of Cu(II) ion. Here's The Cu(II) ion concentration correspond to the capacity of Si-PHQ solid for extraction of Cu(II) ion from the solution that was 40 mmol / g .

If the spectra of the filtrate, produce from addition of Cu(II) ion at universal buffer (pH 7.2), has been recorded, The excess of PHQ free which not coordinated with added Cu(II) show up as peak at 305 nm. Enhances the concentration of Cu(II) ion with the increase in the formation of Si-PHQ–Cu(II) coordinated complex was detected, that could be confirmed with the increases of the absorbance peak at 380 nm.

Although, in the filtration the peak at 305 nm decrease because the non-coordinated PHQ decrease, up until the peak which is equivalent to the highest possible concentration was disappeared. Then, there is absolutely no free PHQ due to the fact all PHQ coordinate with Cu(II) ion to form Si-PHQ–Cu(II) coordinated complex .

5.6.2 Uv-Visible Absorption Spectra of PHQ on Si-Cu

The capacity of Si-PHQ has been compared with the immobilized Cu(II) metal ion on silica gel (Si-Cu). Spectra of Si-Cu at universal buffer solution (pH 7.2) was documented as displayed in the Figure 47. A sequence of various concentration of PHQ added to the solution contain Si-Cu. Following the first addition of PHQ to the solution contains Si-Cu, a peak was looked at 380 nm which is equivalent to the

formation of PHQ–Cu coordinated complex. The formation of this complex revealed that the solid of Cu(II) ion immobilized on silica gel may be able to extract PHQ from the solution to form Si-Cu–PHQ.

Ethanol can dissolve the coordination complex PHQ–Cu(II) and provide the appeared absorbance peak at 380 nm. Ever-increasing the concentration of PHQ added, increase the absorbance peak of formation of PHQ–Cu(II), till the Cu(II) ion from Si-Cu consumed, as illustrated in the Figure (47 h). The absorbance represent the highest amount of PHQ can extracted from the solution that voiced, as the capacity of SiCu solid was 20 mmol / g .

A comparison between the capacity of Si-PHQ for extraction of Cu(II) ion and the capacity of Si-Cu for extraction of PHQ, it has been observed that, Si-PHQ have capability about two times more than Si-Cu. So the immobilization of PHQ on silica gel is better than immobilization of Cu(II) ion sitting on it. Similarly, the comparison between capacity of Si-PHQ for extraction of Cu(II) ion and the capacity of Si-HQ, it was noticed that the Si-PHQ have capability about four times more than Si-HQ. The capability of Si-Cu to coordinate with PHQ was approximately three times higher than HQ, Table 9. From the preceding comparison, it has been observed that, PHQ have the potential to immobilized on silica gel and coordinated with metal Cu(II) ion greater number by four times than the capability of HQ to do that.

5.6.3 Uv-Visible Absorption Spectra of Fe(III) ion on Si-PHQ

Spectra of various concentration of Fe(III) ion on Si-PHQ at universal buffer solution (pH 7.2) has been recorded as displayed in the Figure 48. Fe(III) ion was added to the solution includes the Si-PHQ. A brand new two peaks were appeared at 580 nm and 455 nm which is equivalent to the formation of PHQ–Fe(III) complex. The formation of this coordination complex suggest that the solid of PHQ immobilized on silica gel may be able to extract the metal of Fe(III) ion from the solution to form Si-PHQ–Fe(III). Ethanol has the ability to dissolve the coordinated complex PHQ–Fe(III) and give the two appeared absorbance peaks at 580 nm and 455 nm. Ever-increasing the concentration of Fe(III) ion, increase the absorbance peaks owing to increase the formation of Si-PHQ–Fe(III) coordinated complex.

The highest possible absorbance peaks as shown in Figure (48 i) which is equivalent to the addition of 4 $mmolL^{-1}$ of Fe(III) ion. This Fe(III) ion concentration signify the capacity of Si-PHQ solid for extraction of Fe(III) ion from the solution which was 40 mmol / g . Comparison among the capacity of Si-PHQ and Si-HQ for extraction of Fe(III) ion from the solution noted that the Si-PHQ have capacity for extraction of Fe(III) approximately two times more than Si-HQ, as shown in Table 9.

Scheming of the concentration of Fe(III) ion added ($mmolL^{-1}$) versus the absorbance. For Si-HQ curve, a range among (0.0 – 1.0 $mmolL^{-1}$) was the linear variety (r = 0.9738) of addition of Fe(III) ion on Si-HQ. Ever-increasing of Si-PHQ , the linear range of this curve signify the detection limit range between (1.0 – 4.0 $mmolL^{-1}$) that had been the linear range (r = 0.9273) of addition of Fe(III) ion on Si-PHQ.

6 Applications

6.1 Analytical Application

Coordination polymers based on the poly(8-hydroxyquinoline) (PHQ) matrix preparations have been made and characterized. Under the best possible conditions, a direct, precise, inexpensive spectrophotometric determination of trace quantities of Cu(II) ion by chelation with the PHQ matrix can be accomplished.

6.1.1 Determination of Cu(II) ion in Haemoton capsules sample

The suggested analytical method for quantitative detection of Cu(II) ion is straightforward and involves no initial separation. For instance, UV-visible Absorption Spectra of the Coordination Polymer Based on PHQ have been successfully applied to the direct determination of Cu(II) ion in a Haemoton capsule (HC) samples. The determination had been carried out on standard copper acetate solution. The spectra of PHQ-HC mixture are provided. A linear relationship (R = 0.987) of the absorbance on the concentration (µmol / L) of added Cu(II) ion was detected. Table 10 demonstrated that the determination of Cu(II) ion (mg / g) by the suggested method is a very good agreement (95.97 %) with the (AAS) analysis of the similar element [Cu(II) ion]. Moreover, determination of Cu(II) ion in HC samples by atomic absorption spectrometric (AAS) measurements have been verified our determination and comparisons to be made by the certified data from an original industrial company (104.97 %).

6.1.2 Determination of Cu(II) ion in Geochemical Sample

In order to verify the accuracy of the UV-visible absorption spectra of the coordination polymer based on PHQ method, a study has been carried out on the different addition of standard Cu(II) ion. The comparative difference between the absorbance obtained with and without Cu(II) does not exceed the $\pm$ 2 %, and the recovery varied from 95.46 % to 100 % as presented in table 11.

To verify the precision of the proposed method, they have also determined the Cu(II) content in identical to the solution by atomic absorption spectrometric (AAS) technique. The study's findings indicates that the determination of Cu(II) ion (mg/kg) by the proposed method has been agreed upon well (95.46 %) with the determination of the same element by (AAS) with the relation coefficient closed agreement.

6.2 Preconcentration of some metal Ions

The surface of Silica gel may be modified with organic function groups as 8-Hydroxyquinoline (HQ) or its polymer, Poly(8-Hydroxyquinoline) (PHQ), and provide access stability. Immobilization of 8-Hydroxyquinoline (HQ) or its polymer (PHQ) on the surface of silica gel, was ready by an easier way than the previous methods. The capacity for extraction of heavy metal ions from solutions also more than the other methods. It was designed for extraction of some heavy metal ion as: Fe(III) and Cu(II) from its solutions in various areas.

Additionally, as an application of cation exchange of Al(III) in solution, immobilization of 8-Hydroxyquinoline (HQ) or its polymer (PHQ) on the surface of Alumina [Al_2O_3], enhancing the capacity for extraction of heavy metal ions from solutions. It was designed for extraction of some heavy metal ion as: Fe(III), Cu(II), Co(II) and Ni(II) from its solutions in various fields.

6.2.1 Preconcentration and Determination of Ferric ion From Sytron Syrup Sample

Immobilized PHQ on silica gel (Si-PHQ) is helpful for many applications like removal of metal ions from solution in various areas. For instance, of these samples, Sytron syrup used for anti–anemic that contain iron as sodium iron edetate. One a supplement of real sample added to solution contain Si-PHQ at universal buffer solution (pH 7.2), after contact time, filtrate the content, the solid dissolved in pure ethanol, the spectra was documented as displayed in the Figure (49 a). Order to guarantee the peak for extraction of Fe(III) and which a variety of amount was extracted, add 0.3 and 1.0 mmol L^{-1} of synthetic Fe(III) ion solution as illustrated in the Figure (49 b and c) respectively. Atomic Absorption