Ion Imprinted Polymer Based Electrochemical Sensor for Environmental Monitoring of Copper(II)

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Plasticized membranes using copper-carboxybenzotriazole have been prepared and explored as Cu^{2+}-selective electrochemical sensors. Effects of three different plasticizers: bis(2-ethylhexyl)sebacate (BEHS), dibutylphthalate (DBP) and Dioctylphthalate (DOP) were studied, optimized and evaluated. Optimum performance was observed with membrane having the following composition: PVC (61%): DBP (35%): IIP (4%). The optimized membrane was used for construction of liquid electrochemical sensor. The sensor was found to work satisfactorily in the concentration range between 1.0×10^{-1}-1.0×10^{-5}M with a Nerstian slope value of about 28.1mV/decade. Wide pH range (3-8), fast response time (22s) and long lifetime (~ 2 months) indicate the potential of the proposed sensors in the determination of copper II ions in synthetic and wastewater samples with excellent recoveries (94%-109%). Potentiometric selectivity coefficient values were determined by separate solution method (SSM), and good selectivity for Cu^{2+} over most interfering ions was achieved.

1. INTRODUCTION

Determination of trace metals at low concentration levels has been a major concern for both health and environmental reasons. Copper is an essential trace element and it is required in minute quantity for proper growth of plants and animals. However, its accumulation in the body system results in a number of diseases such as gastrointestinal disorder, Wilson disease and inhibition of Cortisol production resulting in hypoglycemia [1, 2, 3]. In addition, free copper produces reactive oxygen species which damage proteins, lipids and DNA in the body system [4].

Conventional instrumental methods for monitoring copper such as atomic absorption spectrometry (AAS), anodic stripping voltammetry, HPLC [5, 6, 7] and gravimetric detection [8]

provide accurate methods for detection of copper. However, these methods are time and sample consuming, expensive, destructive and require operational expertise as well as sample pretreatment.

Electrochemical sensors are inexpensive and possess high selectivity, low detection limit, hence employ as alternatives to sophisticated instrumental techniques.

Ion and molecularly imprinting technology have been receiving serious attention in recent years especially in catalysis [9, 10], drug analysis and delivery [11, 12], chemical and biosensors [13, 14]. Ion imprinted polymers (IIP) are designed to have greater selectivity for a particular ion over other metallic ions. The imprinted polymer is prepared based on the formation of a complex between the target analyte (template) and an ionophore in the presence of functional monomer, large amount of cross-linking agent and an initiator. The template is leached out after the polymerization revealing imprints characteristic of the tagged template.

Electrochemical sensors have been prepared based on ion and molecularly imprinted polymers, Pombeiro et al. [15] reported a newly prepared copper selective electrode based on 1-Phenyl-2-(2-hydroxyphenylhydrazo) butane-1,3-dione, the electrode showed good selectivity for copper (II) ions over many metal ions and was successfully applied for direct determination of copper (II) in soil polluted by oil and as an indicator electrode in potentiometric titration of copper ion with EDTA. Copper-(II) selective potentiometric sensor based on porphyrin in PVC matrix has been prepared [5]. The sensor gave an excellent Nerstian value and good response time. Fakhari and Raji [16] reported Copper-selective PVC membrane electrodes containing carriers 2,2'_[1,2-ethandiyl-bis(nitrilomethylidine)-bis]*meta* cresole(I), 2,2'_-[1,2-ethandiyl-bis(nitrilomethylidine)-bis]*para* cresole(II) and 2,2'_-[1,2-ethandiyl-bis(nitrilomethylidine)-bis]*ortho* cresole(III) as ionophores, amongst the electrodes have been applied in direct determination of copper in urine samples. Mureseanu et al. [17] prepared chemically modified electrodes based on mesoporous silica and functionalized with tripeptide Gly-Gly-His and was used at low pH for direct determination of copper in tap water in which excellent performance was achieved. Copper selective electrode has been constructed using β-cyclodextrine and 1,4-bis(6-bromohexyloxy)benzene for determination of copper in pure and polluted water samples [18]. Săndulescu et al. [19] prepared a fast and highly responsive copper electrode using N,N'-bis(acetylacetone)ethylenediimine as a receptor, the electrode was Nerstian and gave a low detection limit.

In this work, a new electrochemical sensor using copper-carboxybenzotriazole complex based on PVC matrix membrane and copper ion imprinted polymer in which no previous research has exploited copper-carboxybenzotriazole complex for this application has been reported. Electrode parameters such as pH, selectivity, sensitivity, detection limit have been determined and used for determination of copper ions in synthetic and wastewater samples

2. EXPERIMENTAL

2.1. Apparatus

Potential measurements were performed using pH meter (TRANs, China) at 25±0.1 ∘C. The fabricated electrochemical sensor was used in conjunction with Ag/AgCl reference electrode (COLE-PARMER, US). All measurements were carried out in a 125ml plastic container with constant stirring.

FT-IR spectra were recorded with (Shimadzu IR Affinity-1, Japan) spectrometer. The FT-IR analysis was carried out between 400 and 4000cm^{-1}.

Atomic Absorption Spectrophotometer (AA-6200 Schimadzu) was used in the measurement of the absorbance samples for comparison with the proposed electrochemical sensor.

The surface morphologies of the prepared membranes, NIP, IIP and CU-CBT complex were examined using Scanning Electron Microscopy SEM (QUANTA FEG, USA)

The thermal stability of the prepared membranes was studied by Thermogravimetric Analyzer (TG 209 F1 Iris, NETZSCH).

All EMF measurements were carried out with the following electrochemical cell assembly: Ag/AgCl |internal solution, (0.1M) Cu(NO$_3$)$_2$|PVC membrane||test solution| Ag/AgCl, KCl (3 M).

2.2. Reagents

The following reagents from ACROS ORGANICS, UK were used as received: Bis(2-ethylhexyl)sebacate (BEHS) (97%), dibutylphthalate (DBP) (97%), Dioctylphthalate (DOP) (99%), acryl acid (AA) (99.5%), ethylenedimethacrylate (EDMA), dibenzoylperoxide (BPO) and methylalcohol. In addition, copper nitrate (REIDEL, India), hydrochloric acid (GCC, UK), tetrahydrofuran (TEDIA, USA), dimethylformamide (BDH, England), nitric acid (M&B, England), sodium hydroxide (extra pure) (LOBA, India) and high molecular weight polyvinylchloride (PVC) (PRETEST) were also used.

University of Colorado**,** Boulder (USA) provided the carboxybenzotriazole used in this research.

2.3. Synthesis of the Copper-carboxybenzotriazole Complex

Carboxybenzotriazole (0.22g, 1.35mmol) was dissolved in 1M sodium hydroxide (2ml) and stirred for 10minutes. Copper(II) nitrate trihydrate (0.164g, 0.68mmol) was dissolved in 1M nitric acid (5ml) and poured into a stirring solution of well dissolved caboxybenzotriazole and kept with constant stirring until a pale green product was obtained, the precipitate was filtered, dried grounded and passed through 90μm sieve .

2.4. Preparation of Copper Ion Imprinted Polymer

Copper ion imprinted polymer was prepared as reported by Moody et al. [20] with some modifications. Copper-carboxybenzotriazole complex (0.1g) and 3mmol acrylic acid (AA) as functional monomer were dissolved in dimethyl formamide (DMF) (0.5ml). 15mmol EGDMA as cross linker and 0.073g of dibenzoyl peroxide (BPO) as an initiator were transferred into the mixture, purged with N$_2$ for 10mins. Polymerization was started at 71^{0}C for 2hrs yielding a green rigid solid. The product was dried, grounded, screened and sieved to powder. The particles of the polymer were leached with 5M HCl acid at constant stirring for 24h to remove the copper ions. The imprinted

polymer was filtered and dried. Controlled polymer was prepared by the same protocol with addition of carboxybenzotriazole (ionophore) instead of the complex.

2.5. Membrane Preparation Fabrication of Electrochemical Sensors

Several membranes were prepared using the method described by Cragset.al. [21]. 0.02g of imprinted polymer was dissolved in 0.5ml of DMF and 5ml of THF, 0.3ml plasticizer and 0.17g PVC were added and stirred until a viscous homogeneous mixture was obtained. The final paste was poured into a 5cm diameter glass ring glued to a glass plate with PVC-THF solution. The evaporation was controlled by covering the ring with filter papers wad for 48hrs.

10mm in diameter of the evaporated membrane was cut and pasted on one end of a PVC tube with THF/PVC adhesive. The other part of the PVC tube was fixed to a glass tube and filled with internal filling solution (0.1M Copper-(II) nitrate). The optimized sensor was conditioned in 0.1M solution of Copper-(II) nitrate for 24hrs before the potential measurements.

2.6. Sample preparation

A 10mL aliquot of a well shaken wastewater collected from Jordan University of Science and Technology treatment plant containing copper ions was treated with 10mL of mol/L HNO_3 and heated to boiling for 15mins to decompose the metal complexes. The solution was quantitatively transferred to a 100mL measuring flask and completed to the mark with 10^{-2} mol/L acetate buffer pH 5.5 [22].

The fabricated copper sensor and the reference electrode were dipped into 50ml of prepared copper (II) ion solution and the concentration of the sample was determined by Standard addition method.

FT-IR spectra were recorded with (Shimadzu IR Affinity-1, Japan) spectrometer. The FT-IR analysis was carried out between 400 and 4000cm^{-1}. The surface morphologies of the prepared membranes, NIP, IIP and CU-CBT complex were examined using Scanning Electron Microscopy SEM (QUANTA FEG, USA)

Atomic Absorption Spectrophotometer (AA-6200 Schimadzu) was used in the measurement of the absorbance of the real samples which was used for the validation of the developed method.

3. RESULT AND DISCUSSION

3.1. FTIR Spectra

The FTIR spectrum of carboxybenzotriazole-CBT (Figure 1) resembles previously reported spectra by Mohan and Kenneth [23, 24]. The absorbance bands at 3441 and 3206 cm^{-1} represent O-H and N-H stretching of the carboxybenzotriazole (CBT). An absorbance band seen at 1701 cm^{-1} is

characteristic of carbonyl group stretching in the CBT. The bands at 1207 and 745 cm^{-1} are of particular importance due to high intensity, these bands represent C-H in-plane and out-of-plane bending for the benzene ring in CBT as seen in Figure 1.

The disappearance of the intense peak at 3206 cm^{-1} is quite noticeable. This could be due to the possible coordination of copper-(II) ion with the nitrogen of the CBT. New bands are seen in the spectrum of the complex at 1697, 1383 and 754 cm^{-1}. They are assigned to C=O stretching, C-H vibration and C-H out-of-plane deformation of benzene ring in CBT respectively. These bands are similar to the spectra reported by Tehrani et al. [25].
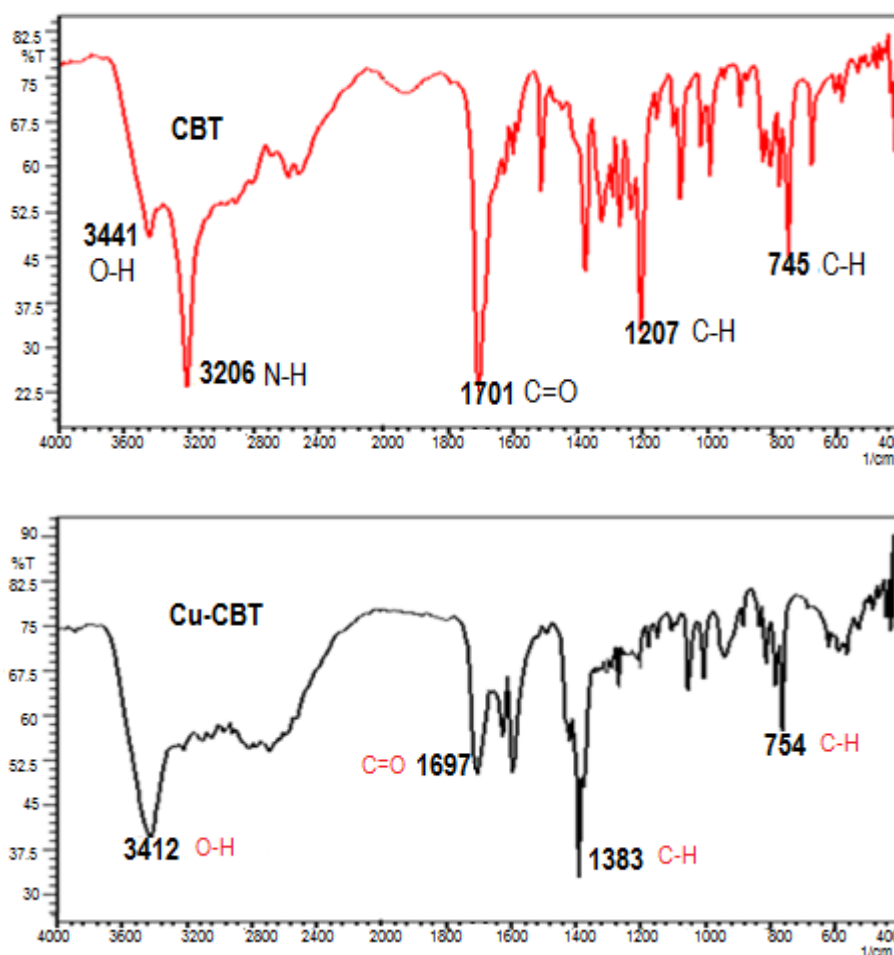

Figure 1. FTIR spectra for CBT and Cu-CBT complex conducted obtained by KBr pellet method

3.2. Calibration Curves for IIP and NIP

Non-imprinted polymer (NIP) membrane was prepared using the composition of the optimized IIP electrode. The membranes were tested and calibrated against the copper solutions. Figure 2 shows the plot of potential response of IIP and NIP in the concentration range of 1.0×10^{-6} to 1.0×10^{-1}.

As seen in figure 2, the potential response of IIP shows a better response to copper ion than for the NIP. The good response behavior of IIP over NIP as seen in Figure 2 could be attributed to the specific interaction of the copper ions with the imprints which are lacking in the NIP.

However, the poor response of the NIP membrane could be attributed to non-specific interaction on the surface of the NIP. This type of response characteristics for both IIP and NIP was observed by Tehrani [25] and Haginaka [26] for metoprolol and bisphenol A, respectively.
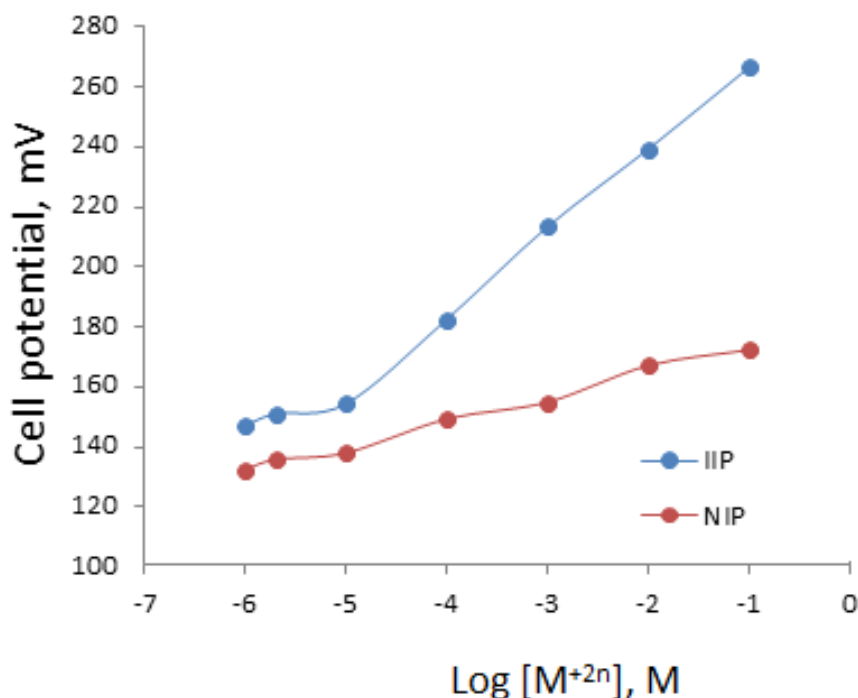

Figure 2. Comparison of potential response of IIP and NIP membrane based on DBP plasticizer as plotted against log [copper II ion] concentration

Several membranes containing different amounts of copper-(II) _ion imprinted polymer (0.01g, 0.02g and 0.04g) were prepared. Liquid sensors were designed and constructed with the prepared membranes as their sensing parts. The response behaviors of the sensors were studied and the results obtained are summarized (Table 1). As seen in Table 1 increasing the amount of the IIP from 0.01g to 0.02g resulted in improved response. However, further increase in the amount of IIP from 0.02g to 0.04g showed no clear advantage in terms of the slope values for the electrochemical sensors.

3.3. Effect of Plasticizer

Selection of the best plasticizer for the development of a polymeric membrane specific to a particular ion usually involves experimental tests. In this research three different types of plasticizers were used namely: Bis(2-ethyl hexyl)sebacate (BEHS), dibutylphthalate (DBP), and Dioctylphthalate (DOP).

Table 1. Effect of composition on the response behavior of the electrochemical sensors

Membrane	Plasticizer	IIP (g)	Slope (mV/dec.)	R^2	Detection Limit (M)	Response Time(s)
1	DBP	0.01	21.8	0.9886	5.0×10^{-6}	31
2	DOP	0.01	18.2	0.996	2.0×10^{-6}	53
3	BEHS	0.01	16.1	0.9794	3.0×10^{-6}	46
4 [a]	DBP	0.02	28.1	0.9992	2.0×10^{-6}	22
5	BEHS	0.02	20.2	0.9844	3.0×10^{-5}	48
6	DOP	0.02	22.3	0.9807	2.0×10^{-6}	59
7	BEHS	0.04	22.6	0.9837	6.0×10^{-6}	52
8	DOP	0.04	23.8	0.9956	3.0×10^{-6}	58
9	DBP	0.04	25.6	0.9974	4.0×10^{-6}	40

[a] optimized composition

Among the three plasticizers tested dibutyl phthalate, DBP has shown good behavior in terms of slope, linearity and fast response time. The observed behavior exhibited by DBP could be due its compatibility with the polymer components, low solubility and volatility in aqueous solution [27]. As seen in Table 1, electrochemical sensors coated with membranes (no. 1, 4 and 9) containing DBP as plasticizers showed good responses as compared to other sensors fabricated with the remaining plasticizers.

3.4. pH Effect

The effect of pH on the optimized sensor was studied using 1.0×10^{-3} solution of copper-(II) ion over a pH range of 2-10. The pH of the solutions was adjusted by adding small volumes of nitric acid or sodium hydroxide solutions. As shown in Figure 3, there was variation in the potential of the sensor at low pH values. This variation in potential could be attributed to the response of the sensor to hydrogen ions (H^+) in the solution.

The observed drift in the potential at higher pH could be due to precipitation formed at such higher pH values. The precipitate is attributed to the formation of copper-(II) complexes upon addition of small drops of sodium hydroxide to change the pH, this result was similar to the one obtained by Fakhari and Raji [15].

The potential remained almost constant at pH between 3 and approximately 8; the range at which the potential remained constant was considered as the pH range for the developed sensor.
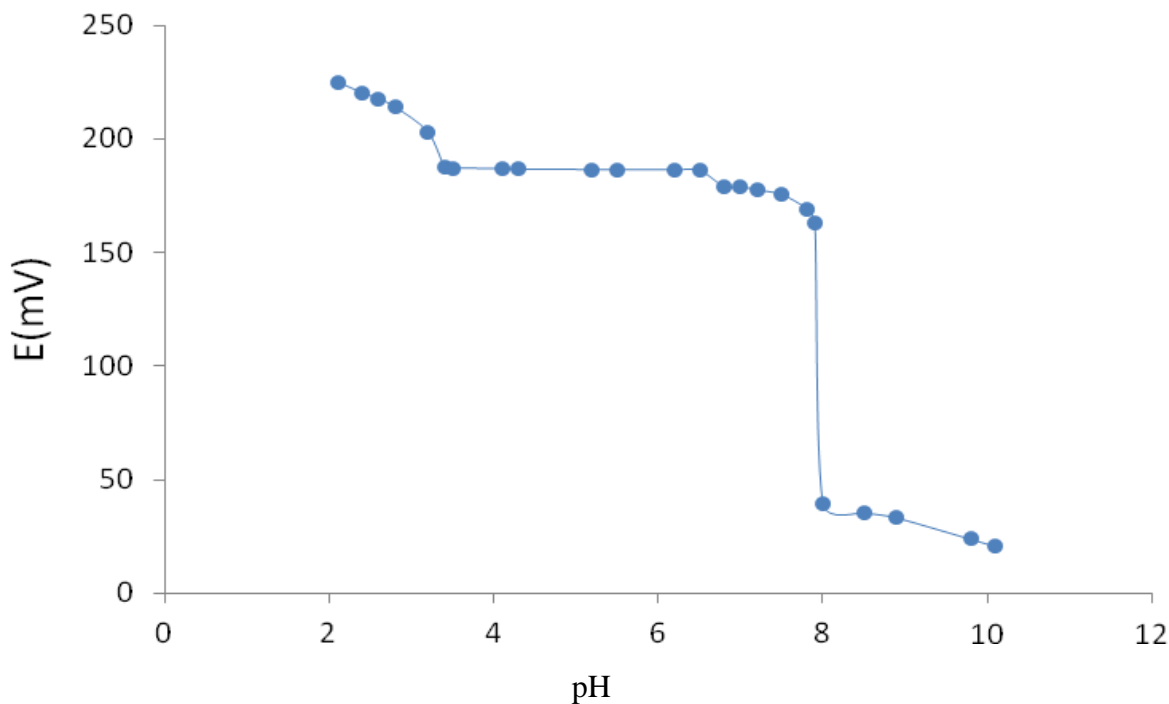
Figure 3. variation of potential with pH of the optimized sensor based on membrane no. 4 for solution of copper (II)-ion at 1.0×10^{-3}M

3.5. Response and Lifetime

Response time is defined as the length of time from which the electrochemical sensor and a reference electrode are brought into contact with the sample solution and the instant at which the potential has reached 90% of its final value [28]. The response time of the optimized sensor constructed based on membrane no.4 was determined to be around 22 seconds. It has been observed that the response time of the sensor increases as the value of the slope drifts from Nernstian. This behavior could be attributed to the degradation of the membrane with time.

Lifetime of the sensor was determined by studying variation of the electrode parameter (i.e. slope) with time (Figure 4). The sensor showed a near Nernstian value of 28.1 mV/ decade. Variation in the Nernstian value of the slope was very small after two month of its initial measurement; the time interval between each measurement was one week.

3.6. Potentiometric Selectivity

The selectivity of the optimized liquid sensor for copper ions based on membrane no. 4 over other metal interfering ions was studied using separate solution method (SSM) as described by Umezawa et al. [29].
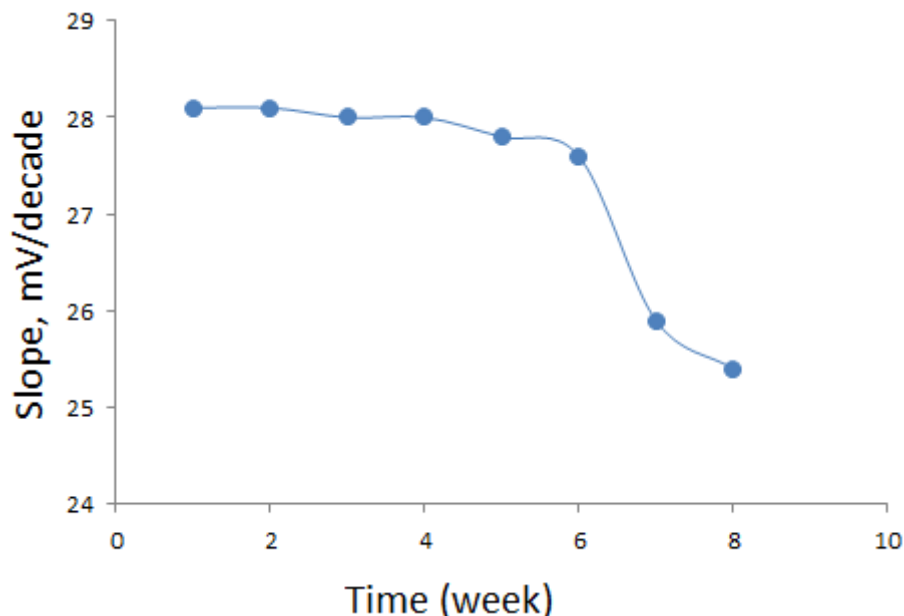
Figure 4. plot of slope values vs. time (per week) for the optimized sensor based on membrane no. 4 containing DBP as plasticizer.

The interfering effect of the following ions: Li^{3+}, Cr^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Na^+ and K^+ at concentration from 10^{-5} to 10^{-1}M were studied and the selectivity coefficients ($K_{A,B}^{pot}$) values obtained are summarized in Table 2. Nitrate salts of the interfering ions were used in all the measurements.

Table 2. Selectivity coefficient ($K_{A,B}^{pot}$) determined by using optimized liquid sensor designed with a membrane having the same composition as no. 4

Conc.	Cr^{3+}	La^{3+}	Mg^{2+}	Ba^{2+}	Ca^{2+}	Na^+	K^+
10^{-5}	7.2×10^{-2}	4.3×10^{-2}	4.6×10^{-1}	8.3×10^{-2}	2.4×10^{-1}	184.6	162.8
10^{-4}	1.5×10^{-1}	1.9×10^{-1}	5.2×10^{-1}	9.4×10^{-2}	3.7×10^{-1}	10.5	15.4
10^{-3}	2.2×10^{-1}	3.7×10^{-1}	5.6×10^{-1}	1.9×10^{-1}	3.9×10^{-1}	5.8×10^{-1}	6.9×10^{-1}
10^{-2}	6.3×10^{-1}	4.4×10^{-1}	6.8×10^{-1}	2.4×10^{-1}	5.4×10^{-1}	3.1×10^{-2}	1.1×10^{-1}
10^{-1}	7.8×10^{-1}	6.5×10^{-1}	7.6×10^{-1}	2.7×10^{-1}	6.3×10^{-1}	1.5×10^{-3}	6.2×10^{-3}

The selectivity coefficients were found to depend on the charge, mobility and specific and non-specific interaction. The result agrees with that reported by Shokrollahi et al. [30].

As seen in Table 2, increasing the concentration of the interefering ions causes increase in the selectivity coefficients $K_{A,B}^{pot}$ for trivalent and divalent ions, despite the increase of the values are all less than one. These values are good as they reflect the potential of the sensor to measure copper-II ions in the presence of trivalent and divalent ions (Cr^{3+}, La^{3+}, Mg^{2+}, $Ba2^+$, and Ca^{2+}). However, the

monovalent ions showed high selectivity coefficient values at low concentration, this behavior could be due to smaller size, high mobility as well as large stability constant for Na^+ and K^+ ions with CBT.

Similar results were obtained for monovalent ions by Kakhi, Al-Mheidat and Zayed [31,32,33] for sibutramine and uranyl electrodes based on carboxybenzotriazole as an ionophore.

3.7. Scaning Electron Microscopy –SEM

Surface morphologies of the ion imprinted polymer (IIP) and non-imprinted polymer (NIP) membranes were examined and their characteristic features before and after conditioning are shown in Figure 5. Figure 5 (A) shows smooth surface of the IIP membrane before conditioning with no imprints apparent.

Figure 5 (B) shows the same surface of the IIP after conditioning with clear imprints which could be attributed to copper(II) ion. The appearance of the imprints after conditioning indicates the need for the membrane to be conditioned before taking the measurements. Figure 5 (C) shows the NIP particles on the surface of the membrane before conditioning without imprints while figure 5 (D) shows the same surface after conditioning for 24 hours.
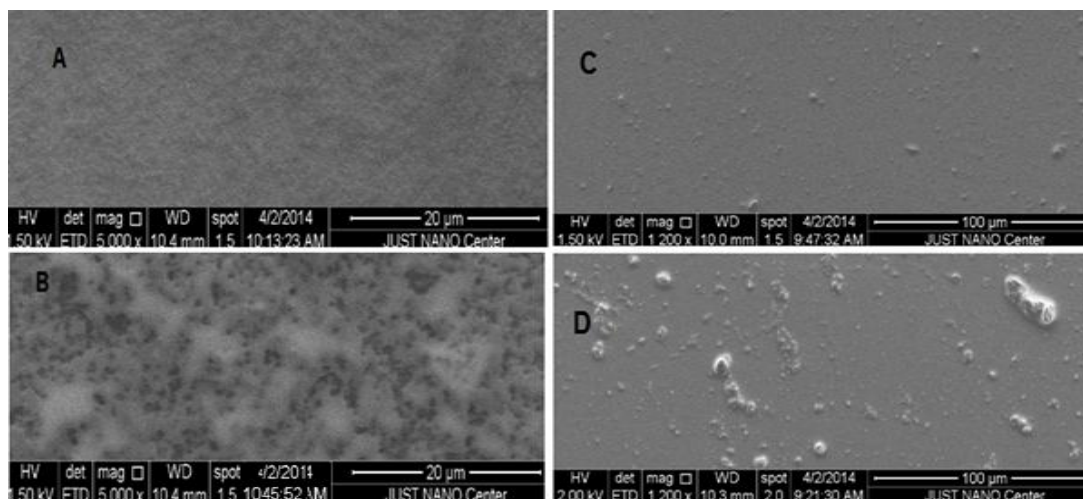

Figure 5. SEM images of (A) IIP membrane before conditioning, (B) IIP membrane after conditioning, (C) NIP membrane before conditioning and (D) NIP membrane after conditioning

3.8. Thermogravimetric analysis

The effect of temperature on the degradation of imprinted and non-imprinted polymer membranes was studied. Synthetic materials degrade in a number of stages; these steps can be seen in figure 6 and 7 which show the thermograms of the membranes prepared based on imprinted and non-imprinted polymers. The first stage is from room temperature to 180^0C which represents evolution of volatile matter (DMF) and evaporation of residual absorbed water.
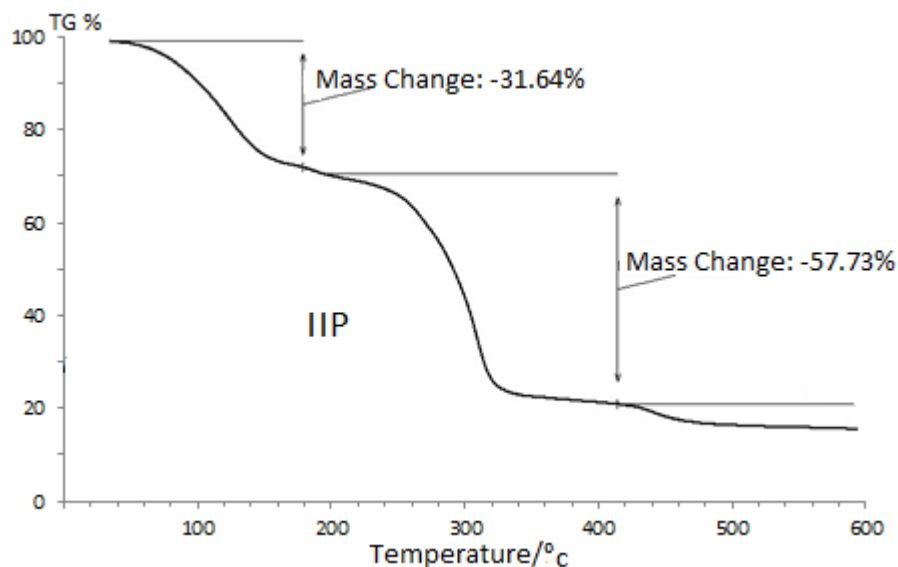
Figure 6. Ion imprinted polymer membrane (IIP) thermogram based on DBP plasticizer conducted under nitrogen atmosphere
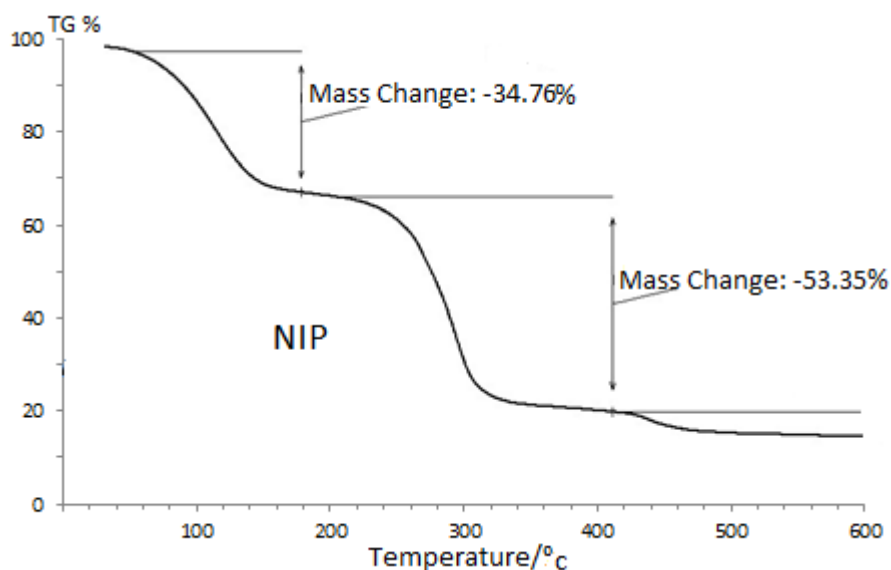

Figure 7. Non-imprinted polymer membrane (NIP) thermogram based on DBP plasticizer conducted under nitrogen atmosphere

The second stage starts from 180^0C to 420^0C which represents the main thermal degradation of the membranes. The third stage takes place beyond 420^0C indicating carbonation of the degraded material to ash. Another important feature observed on the thermograms is that, about 31.64% of the membrane prepared based on IIP consists of volatile matter or absorbed residual water while the membrane based on the NIP consists of almost 34.76%. This may be attributed to the presence of imprints on the imprinted membrane which allows fast evaporation of volatile materials than in the NIP membrane.

4. ANALYTICAL APPLICATION

The utility of the sensor based on optimized membrane (No. 4) was examined by applying the sensor in the determination of copper-(II) ions in synthetic and wastewater samples. The results obtained by the proposed sensor were in agreement with the results obtained by AAS. Excellent recoveries were achieved; these recoveries have shown the possibility of using the sensor in the determination of copper-(II) ions in other real samples.

Table 3. Determination of copper in synthetic and wastewater samples using AAS and Cu^{2+} sensor based on optimized membrane (No. 4)

Sample	Concentration of Cu^{2+} as Determined by AAS (ppm)[a]	Concentration of Cu^{2+} as Determined by proposed Sensor (ppm)[a]
SS1	13.3±0.31	11.9±0.17
SS2	1.3±0.21	1.4±0.32
Wastewater	2.1±0.10	2.0±0.20

[a]Average Value of three determinations ±standard deviation
SS= Synthetic sample

Table 4. Evaluation of recovery of the proposed method for the determination of copper ion in synthetic and real sample

Sample	Concentration of Cu^{2+} added (ppm)[a]	Concentration of Cu^{2+} found (ppm)[a]	Recovery (%)
1	1.3	1.4	109
2	2.1	2.0	95
3	12.7	11.9	94

[a]Average Value of three determinations

5. CONCLUSION

A new electrochemical sensor using copper-carboxybenzotriazole complex based on PVC matrix membrane and copper ion imprinted polymer has been successfully prepared and evaluated for copper ion determination in wastewater samples. The prepared sensor was found to be sensitive, selective and has wide pH range and stable shelf life for about two months. The investigation of the three different plasticizers: Bis (2-ethyl hexyl) sebacate (BEHS), dibutylphthalate (DBP), and Dioctylphthalate (DOP) have shown DBP to be the best plasticizer for the membrane preparation.

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