Full Paper

Electrochemical Determination and Recovery of Copper Ion in Water Samples by Supported Liquid Membrane using 2-Amino-N-(2-Pyridylmethyl)-Benzamide as Carrier

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Abstract- In the present study, copper ion has been separated from Phosphate Buffer Solution by 2-Amino-N-(2-Pyridyl Methyl)-Benzamide as an organic ligand through a flat type Supported Liquid Membrane (SLM). To this end, the organic ligand was dissolved in various solvents, and then the Polytetrafluoroethylene (PTFE) membrane was immersed in the resulting solutions for 24 h. Before extraction step, solvents with best performances including Ethanol and benzyl acetate were selected as solvent and as plasticizer, respectively. The optimized complexing reagent concentration on the membrane was 0.05 M. The adjusted pH was 4.5 and concentration of Cu solution was 1×10^{-3} M for feed solution, respectively. Copper ion was then determined using Fast Fourier Transformation Continuous Stripping Cyclic Voltammetry (FFTCCV) technique by a Carbon Paste Electrode (CPE). PTFE with 0.1 μm pore size have more permeability than 0.2 μm. Based on the obtained results, effective parameters imposing sensitivity of copper ion measurement were finally investigated at pH 3.2, at scan rate of 10 mV.s^{-1}, stripping time of 0.1s and potential of -600 mV. Limit of detection of 0.19 μM for copper ion in optimized condition was attained. Under the optimized conditions the recovery of Copper ions from real samples were studied and recovery percentage were 45.71%, 34.28% and 22.58% for tap water, river water and sea water respectively.

Keywords- Heavy metal ions, Copper, Supported liquid membrane, Organic ligands

1. INTRODUCTION

Heavy metals are not decomposable and tend to accumulate in living organisms and several heavy metal ions are recognized to be lethal or carcinogenic [1]. Thus, it is essential to remove these heavy metals from wastewaters effectively before their discharge into the environment [2]. Copper is a mandatory nutrient for plants and animals while its excessive quantities are poisonous [3]. It is well renowned that the free Cupric ions is highly toxic for aquatic organisms and therefore its determination importance has generated intense interest from analytical point of view [4].

Various methods have been developed for the removal of Copper Ions. It includes ion exchange, liquid–liquid extraction, supported liquid membrane (SLM), membrane filtration [5], complexation-ultrafiltration, electrolysis (EL), electrodialysis (ED) [6], adsorption [7] and etc. [8-10]. Therefore, it is essential to have simple and cost-effective procedures. Nowadays, modern electrochemical techniques are advantageous because of low cost of apparatus, simplicity of procedure, suitability for real-time detection and portability compared to other analytical methods [11]. Besides, these methods for example Fast Fourier Transform (FFT) voltammetric techniques have the potential to be more effective [12]. In this type of technique, the electrochemical and the background signal would be detached in frequency domain by a distinct FFT [13,14].

Solvent extraction based techniques have been mentioned in many recent records since they are easy, simple and quick [15-17]. On one hand, in most of conventional separation methods, presence of alteration between physical and chemical properties such as hydrophobicity, molecular weight and solubility [18,19]. On the other hand, chelate extraction is one of the analytical separation methods for the metal species in solution forms [20,21]. On this purpose, crown ethers, Schiff bases, oximes, amines and several phosphine oxides are some of examples that can be employed as chelating agent [16].

Liquid membrane (LM) has triggered intense attention for removal of heavy metals from aqueous samples [22,23]. Based on the configuration, three types of LMs are generally as Bulk Liquid Membrane (BLM) [22] Supported Liquid Membrane (SLM) [24,25], and Emulsion Liquid Membrane (ELM) [26,27].

SLM is defined as a dipped organic solvent in a supporting polymer, which was introduces in the 1990s. It is classified as greatly complex energy storage system due to small volume use of organic components in the membrane arrangement [28,29]. SLMs have advantageous features such as high separation efficiency, scale-up simplicity and low costs [30].

Herein, recovery of Copper ions from feed solution (PBS pH 4.5) using SLM with 2-Amino-N-(2-Pyridyl Methyl)-Benzamide (Scheme 1) as carrier was evaluated, in receive chamber (PBS pH 3.2) Copper ions were determined with CPE by FFTCCV technique each 30 min. Then the developed method was tested for its applicability with real samples.
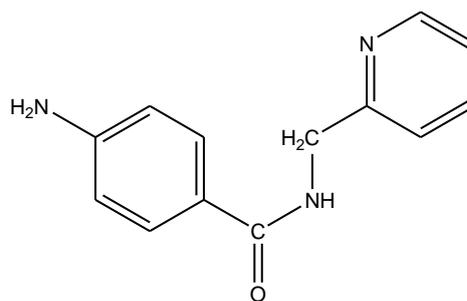
**Scheme 1.** Chemical structure of the organic ligand

2. EXPERIMENTAL

2.1. Chemical materials and apparatus

Graphite powder with average particle size of 1–2 μm and mineral paraffin oil, purchased from Aldrich, were used for carbon pastes preparation. The SLM sheets were provided from a local company. All solutions were prepared in phosphate buffer solution (PBS) that was made using 8.7 mL of phosphoric acid (85% m/v) in the constant volume of double distilled water following adjustment of the pH value to 2.0 with stock solution of sodium hydroxide. Electrochemical experiments were performed by a homemade ultra-voltammetry system designed in center of excellence electrochemistry at University of Tehran [31-33].

2.2. Extraction procedure

The following steps were performed for each extraction: First, PTFE membrane was immersed in the organic ligand (0.05 M) solution for almost 24 h. Then, the membrane was pulled out and inserted in to plasticizer solution for 10 seconds in order to preserve the ligand from being solved. The membrane was then placed in a glass vial cell (Scheme 2). 70 mL of copper solution (1 mM) (pH 4.2) was prepared and placed in the feed chamber (the feed chamber has 70 mL volume). 40 mL of 0.1 M PBS at (pH 3.2) and placed in the receive chamber (the receive chamber has 40 mL volume). The solutions in the chambers were stirred by magnets. Since extraction began, interaction between the copper ions and the organic ligand occurred in the feed chamber. Then, due to pH difference between the two chambers, copper ions were transferred to the receiving chamber.
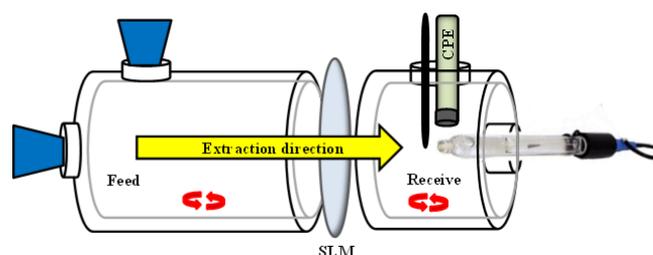
Scheme 2. Schematic shape of the extraction setup

To determine copper ions and the progress of extraction in receiving chamber, ions were measured electrochemically by a carbon paste electrode using FFTCCV technique each 30 min.

2.3. Electrode preparation

In order to make carbon paste electrodes, 0.07 g of graphite powder and 0.03 mL of paraffin oil (70/30) (w/w) was thoroughly mixed till a uniformly-wetted paste was attained. Finally, it was packed into a plastic syringe. Copper wire, at the opposite site, made the electrical contact. The electrode surface was renewed on a clean paper and rinsed prior to each measurement.

2.4. Effective factors

The final analyte concentration to the receiving chamber ($C_{f,a}$) ratio and the initial concentration of analyte ($C_{i,s}$) in the feed chamber is considered as the preconcentration factor (PF):

$$PF = \frac{C_{f,a}}{C_{i,s}} \tag{1}$$

Where $C_{f,a}$ is obtained from the calibration curve. The extraction recovery (ER %) is distinct as the portion of the extracted moles of analyte in the receiving phase to those originally was in the feed solution:

$$ER\% = \frac{V_{f,a}}{V_{i,s}} PF \times 100 \tag{2}$$

Where $V_{f,a}$ and $V_{i,s}$ are the receiving phase volume and the initial sample solution volume, respectively. Based on the data's that attained from experiments PF intended 0.943 and ER% calculated to be 53.87%, respectively.

3. RESULT AND DISCUSSION

3.1. UV spectra of copper and organic ligands

In order to find the most appropriate complexing agent for copper ion, 1.0×10^{-5} M solution of organic ligand was prepared. 150 µL of 1×10^{-3} M Cu^{2+} solution was inserted into a UV cell containing 3.0 mL of the ligand solution. After insertion the color was changed from drab to yellow which could be a sign of a complexation formation. The UV spectra of ligand shows two λ_{max} for the ligand solution at almost 350 and 290 nm and adding Cu^{2+} ions to the ligand solution has displaced λ_{max} 350 nm to 330 nm while decreased intensity of λ_{max} 290 nm which can again be considered as indicator of the interaction.

3.2. Effective parameters

3.2.1. Effect of pH on Cu electrochemical determination

As copper reduction mechanism which is affected by the pH, electrochemical behavior of Cu^{2+} in 0.1 M PBS in different pH was studied by cyclic voltammetry. Since Cu^{2+} ion deposits as sediment in pH 6-7, therefore the pH range of 2-5 was selected for the experiment. Due to the competition between Cu^{2+} and H^+ ions in pH<3 and pH increase shifted anodic and cathodic peaks to the more negative values, but in pH=4 and 5 the current response has decreased intensively. Based on these observations, the pH=3.2 was chosen as the optimized pH for Cu^{2+} determination in phosphate buffer.

3.2.2. Effect of scan rate

The electrochemical response of the CPE in the existence of Cu^2+ (1.0×10^{-3} M) in PBS (pH 3.2) possibility to be influenced by the scan rate was investigated at 0.01–14 mV/s range. Figure 1 shows the obtained results under stated condition; the CPE shows the maximum sensitivity at the sweep rate of (10 mV/s) and as it is displayed that both cathodic and anodic peak current linear relation enhances as the scan rate grows. The position of the cathodic peak slightly shifted towards the negative potential (-200 mV) and the anodic peak shifted a little towards positive direction (+50 mV) with the increase of scan rate.
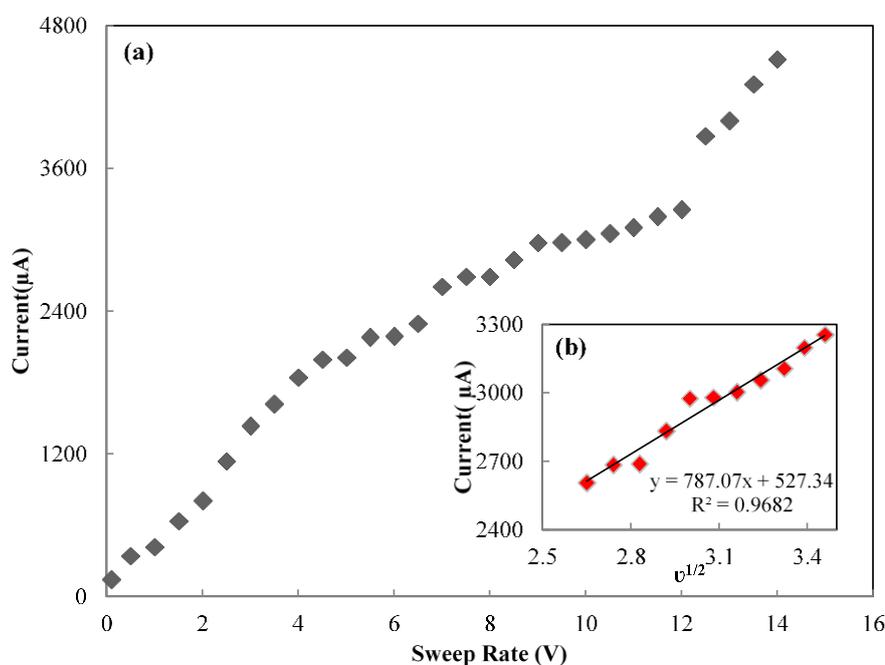

Fig. 1. Effect of sweep rates 0.01 to 14 V/s on electrochemical determination of Cu (10^{-3} M) in PBS 0.1 M (pH 3.2) (a); Anodic peak currents versus square root of scan rates (b)

On this approach, as potential scan rate can affect the method sensitivity, high sweep rates should be used for analyte detection on the electrode surface Fig. 1a shows anodic current response of Cu oxidation versus sweep rate. The linear relationship (R^2=0.968) between I_{pa} and sweep rate in the range of 7 to 12 mV/s indicated that Cu^{2+} electrochemical reaction is a diffusion-controlled type (Fig. 1b).

3.2.3. Effect of accumulation time and stripping potential

As accumulation time and stripping potential can intensively affect the sensitivity of the determination method, thus their influence was then investigated [34]. To examine these two parameters, a 1.0×10^{-3} M Cu solution in 0.1 M PBS with pH=3.2 was used. The stripping potential in the range of -600 to +800 mV and the accumulation times of 0.01, 0.1 and 1 s were fluctuated, and the response signal was recorded. Based on the results displayed in Fig. 2a and 2b, the time 0.01 s and potential -600 mV were chosen as optimized accumulation time and potential, respectively. The longer time leaded to electrode surface saturation and thus intensive decrease in current response. Fig. 2b shows the accumulation potential effect on Cu solution 10^{-3} M in PBS 0.1 M pH 3.2.
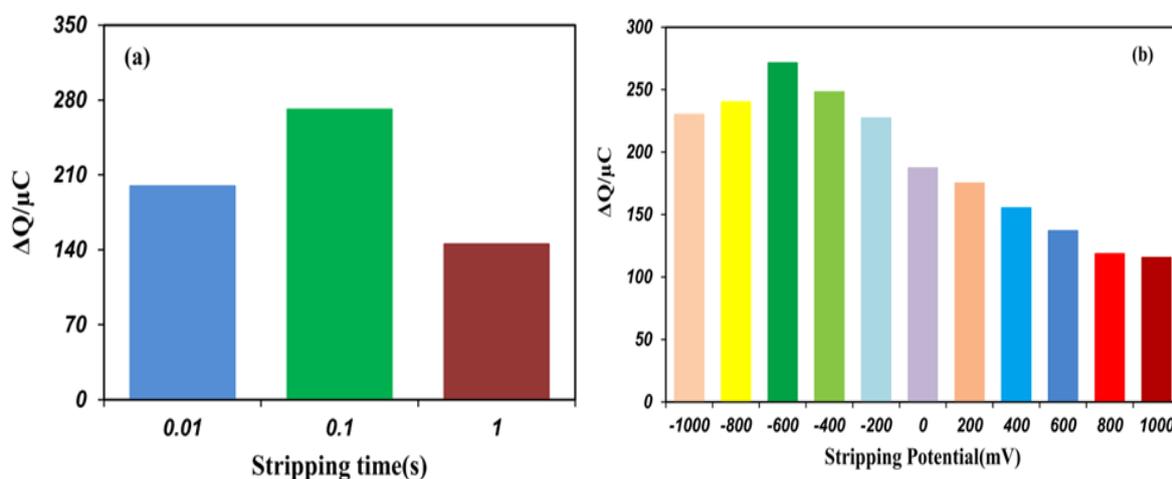

Fig. 2. Stripping time effect on electrochemical determination of Cu (10^{-3} M) in PBS 0.1 M (pH 3.2) with scan rate of 10 mV/s (a); Stripping potential effect on electrochemical determination of Cu (10^{-3} M) in PBS 0.1 M (pH 3.2) at sweep rate of 10 mV/s (b)

3.2.4. Effect of diluent on Cu^{2+} extraction

The solvent type could affect the extraction parameters including the efficiency and the selectivity. The organic solvent should be water immiscible and compatible with the membrane. According to the earlier findings, the chemical nature of the SLM is highly important for the success of extraction and long-chain alcohols with high number of H-donor

functionalities are appropriate solvents for the extraction of acidic compounds [35,36]. To study the effect of solvent type on ligand for Cu extraction, Ethanol, Benzyl acetate, Methanol, Acetone, Dichloromethane, Acetonitrile, Toluene, Ethyl acetate, Dibutyl phthalate and Dimethyl sulfoxide were studied. A 1.0×10^{-2} M of ligand solution was prepared in each solvent. As the two chambers were containing aqueous solutions, in order to avoid the dissolution of the ligand, plasticizer was used. The membrane was then immersed in each solution for 24 hours and finally the extraction process was done (Fig. 3). Ethanol, Methanol and Acetone could easily solve the ligand. Also, these solvents had the ability to permeate into the membrane texture, thus extraction with these solvents could provide more satisfactory results. As Fig. 3 shows ethanol was selected as the optimized solvent (and Benzyl Acetate as plasticizer) for the Cu ion extraction.
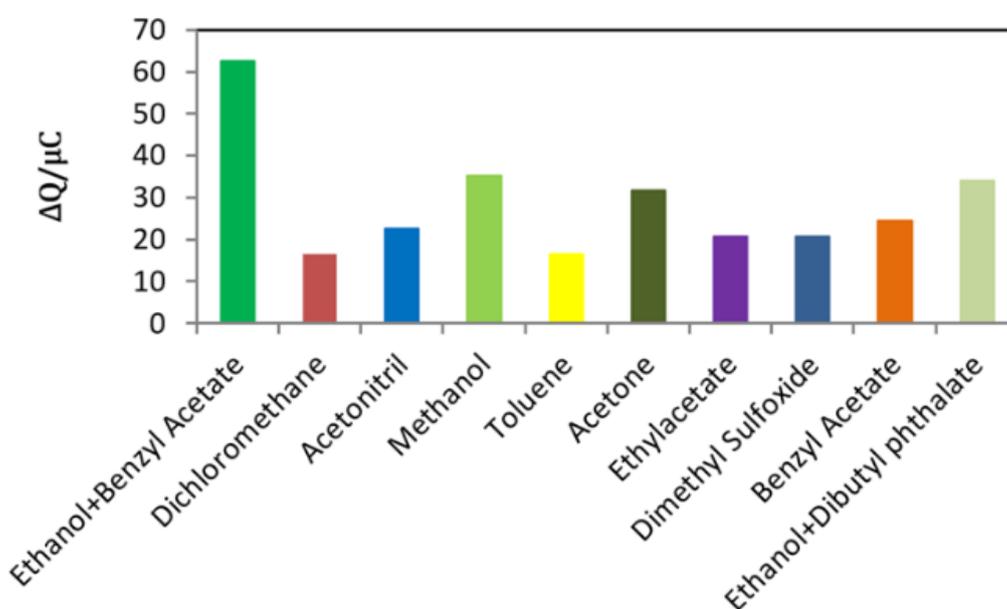

Fig. 3. Solvent type effect on ligand (10^{-2} M) solubility for optimizing Cu (10^{-3} M) extraction in PBS 0.1 M (pH 4.5)

3.2.5. The complexing reagent concentration

In blank experiments with no organic ligands on PTFE membrane no recovery of Copper ions were observed. The PTFE membrane with two different pore sizes of 0.1 μm and 0.2 μm were selected for comparison. The voltammetry studies show that the PTFE membrane with pore size 0.1 μm had more transportation of Cu^{2+} ions. Zha et al., 1995 observed that the membrane with the smaller pore size obtained the slowest mass transfer rate. They further detected that the use of hydrophobic membranes increase the mass transfer resistances [28]. According to the higher recovery percentage for further studies PTFE membrane with 0.1 μm pore size was used. Since bare PTFE membrane which had no ligand being posited on was not

able to transport Cu ions, therefore concentration of the ligand on the membrane was an imposing factor on copper extraction from aqueous phase.

On this purpose, the PTFE membrane was immersed into the ligand solution 0.01, 0.05, 0.1 and 0.5 M concentrations. Cu^{2+} ion was determined by FFTCCV on the carbon paste electrode for each solution in the receive chamber. The recorded results are shown in Fig. 4. As it can be seen in the figure, with increase of complexing reagent concentration from 0.01 to 0.05 M the extraction enhanced and in the concentration range of 0.1 to 0.5 M the extraction decreased. So, the optimized concentration is 0.05 M.
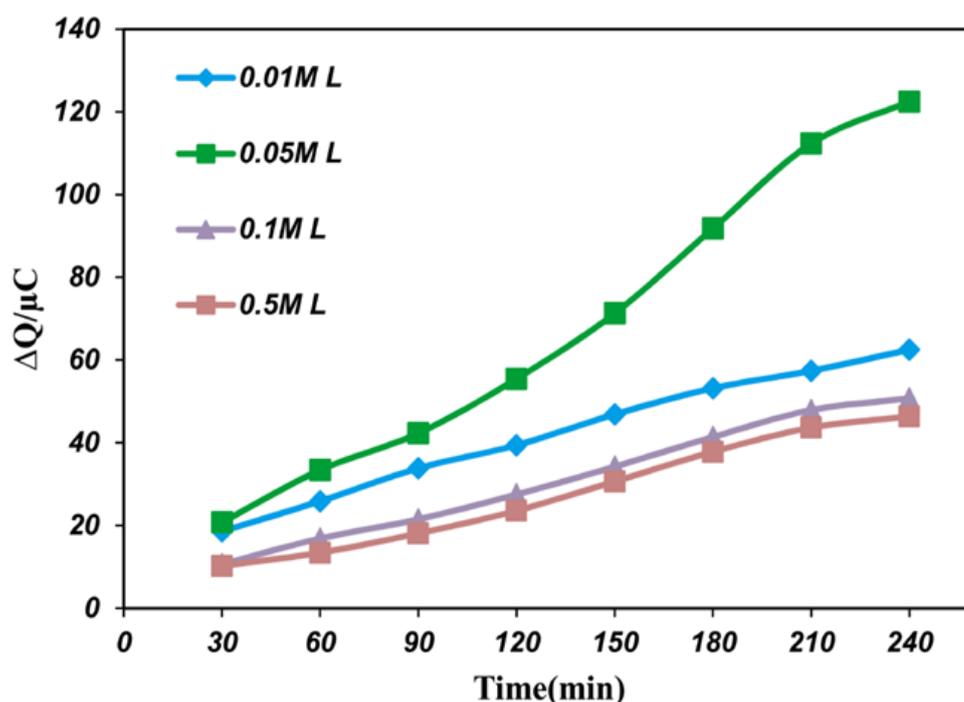
Fig. 4. Effect of Ligand 0.01, 0.05, 0.1 and 0.5 M solutions on Cu (10^{-3} M) extraction in PBS 0.1 M (pH 4.5)

3.2.6. pH of the feed solution

In order to investigate the stimulus of pH of the initial solution on the transport of Copper ions, the studies were accompanied with pH was alerted in the range 2.0–5.0. The effect of pH on recovery of Cu is shown in Fig. 5. The permeability of Cu^{2+} increased with rise in pH of the initial solution. From the results, it is clear that decrease in hydrogen ion concentration causes increase in the rate of connotation of Cu with the carrier. The difference of pH in the feed and receive chamber is one driving force of the extraction. Since the 2-Amino-N-(2-Pyridyl Methyl)-Benzamide was an acidic extracting agent; cation transport could be done through switching the proton and replacing a number of extracted molecules with the equal electrical charge. As it shown in the following equation:

$$M^{n+} + nHL_{org} \rightleftarrows ML_{org} + nH^+ \tag{3}$$

Therefore it was expected that increasing the initial solution pH could accomplish the proton conversion in the more appropriate path [37].
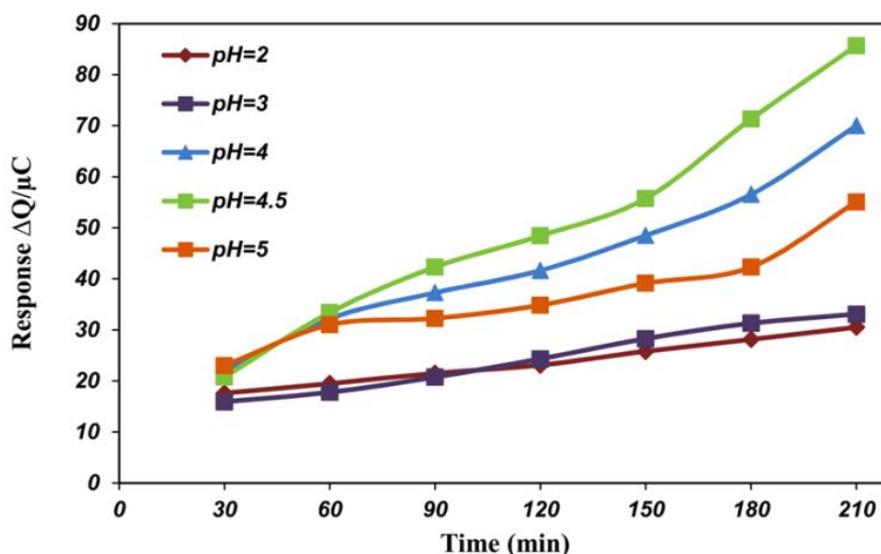

Fig. 5. Effect of initial feed solution PBS pH (2, 3, 4, 4.5 and 5) on Cu (10^{-3} M) extraction

It can be concluded that decrease of the H^+ concentration in the initial solution, could enhance the ligand ability to exchange protons with the analyte molecules. As shown in the Fig. 5, the optimized pH for initial solution was 4.5 as no significant interference from possible ions in the selected range.

3.4. Calibration curve

In order to achieve the linear range for the Cu^{2+} ion determination, analyte solutions were prepared in the range of 10^{-3} to 10^{-11} M. The current response of the solutions was recorded in optimized conditions. It was observed that the electrode signals varied exposed to different concentration of the Cu^{2+} ions, and the response current corresponding to the Cu^{2+} reduction increased with Cu^{2+} concentration at a range of 10^{-3}–10^{-11} M. Fig. 6a shows the obtained results. As it can be seen in the Fig. 6b linear range was attained in the range of 10^{-3} to 10^{-7} M. This linear relationship can be used to find out the unknown amounts of Cu^{2+} in the specified concentration range.
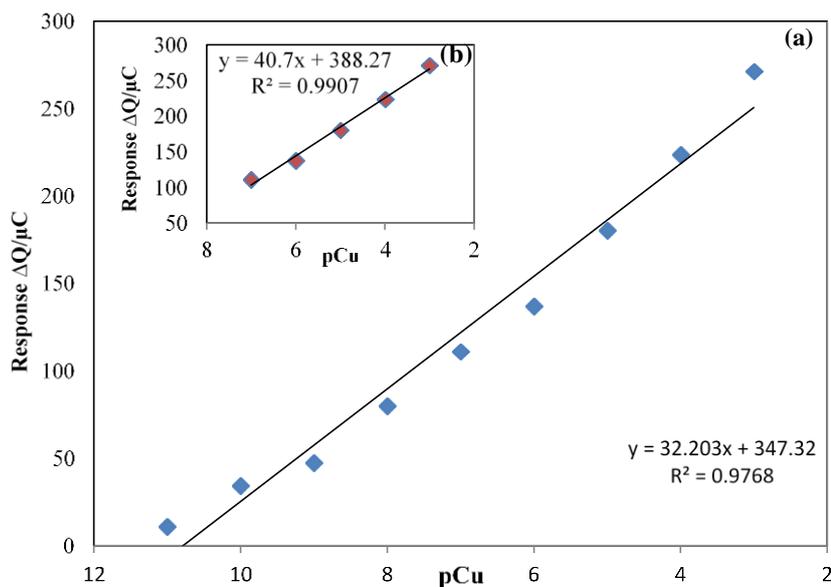
Fig. 6. The signal *vs.* pCu from 10^{-3} to 10^{-11} M (a); the linear range from 10^{-3} to 10^{-7} M (b)

Table 1. Some recent reports compared by the method for Cu^{2+} electrochemical determination

Electrode	Technique	LOD	Linear Range	Refs.
Biochar	DPAdSV[a]	0.4 μM	1.5×10^{-6}-3.1×10^{-5} M	[34]
L-cys/GNP/GCE[b]	CV[c]	Not Reported	10^{-6}-5×10^{-4} M	[38]
BGCE[d]	CV/DPV[e]	10^{-5} M	10 μM-2 mM	[39]
CPE	FFTCCV	0.19 μM	10^{-7}–10^{-3} M	This work

[a] Differential pulse adsorptive stripping voltammetry
[b] L-cysteine on gold nanoparticles/Glassy carbon electrode
[c] Cyclic Voltammetry
[d] Bare glassy carbon electrode
[e] Cyclic voltammetry / differential pulse voltammetry

Besides, the limit of detection (LOD) and the limit of quantification (LOQ) were obtained based on the following equations;

$$LOD=3\times S_b/m \tag{4}$$
$$LOQ=10\times S_b/m \tag{5}$$

Where S_b is the standard deviation of the blank signal, and m is the slop of the calibration curve. As explained, the LOD and LOQ values were 0.19 and 0.64 μM, respectively in the prespecified concentrations (10^{-7}-10^{-3} M). Relative standard deviation of 4.2% was achieved for three successive measurements of 10^{-3} M copper ions as mentioned without renewing of the electrode surface between runs. Moreover, the prepared electrode showed adequate operational stability. Table 1 depicts a comparison between the performed research and some other recent records in the same area.

3.5. Real sample analysis

Finally, the prepared electrode applicability for Cu ion separation and electrochemical determination was used for some real samples. At this point, tap water, river water and sea water were chosen as real samples. 1.0×10^{-3} M solutions of Cu^{2+} were prepared by these real samples. The extraction of Cu^{2+} was then carried out as mentioned in the previous sections. The result is shown in Fig. 7 for Cu^{2+} extraction from tap water, river water and sea water. The recovery percentages of Cu ion in the real samples are shown in the Table 2. The relative error of 4.4%, 5.2% and 5.6% was calculated for tap water, river water and sea water respectively.
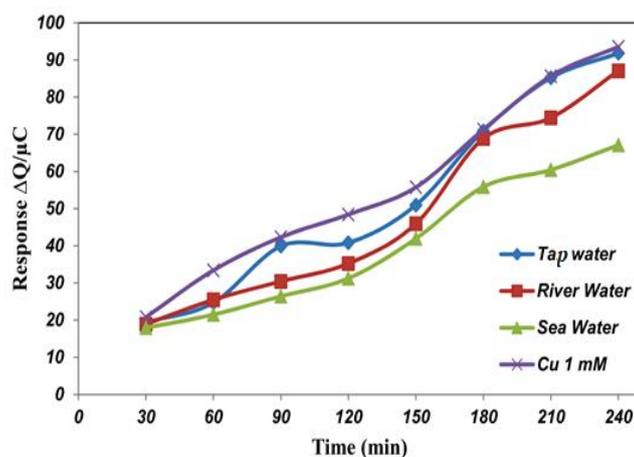

Fig. 7. Extraction and electrochemical determination of Cu (10^{-3} M) in tap water, river water and sea water

Table. 2. Recovery percentage of Cu (10^{-3} M) in tap water, river water and sea water

Real Sample	Recovery (%)
Tap water	**45.71**
River Water	**34.28**
Sea Water	**22.85**

4. CONCLUSION

In the present work, Cu^{2+} ions were separated through a PTFE membrane by 2-Amino-N-(2-Pyridyl Methyl)-Benzamide as an organic ligand. Ethanol and benzyl acetate were selected as optimized solvent and as plasticizer, respectively. The desired deposited concentration of ligand on the membrane was 0.05 M. The adjusted pH was 4.5. Copper ion was then electrochemically determined using FFTCCV technique on the carbon paste electrode surface. According to the achieved results, some effective parameters on Cu^{2+} measurement

were finally investigated and pH 3.2, potential scan rate of 10 Vs^{-1}, stripping time of 0.1 s and potential of -600 mV, were optimized. Limit of detection of 1.0×10^{-11} M for copper ion in optimized condition was attained.

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