

Full Paper

Application of FFT Cyclic Voltammetry for Monitoring Removal of Mercury Ions from Aqueous Environment using New Adsorbent based Modified Mesoporous Silica (SBA-15)

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Abstract- As the electrochemical method, the Fast Fourier Transform (FFT) Stripping Cyclic Voltammetry detection method was designed for measurement and monitoring of adsorbed mercury ions by new modified adsorbent based on mesoporous silica as a new adsorbent. In this respect, SBA-15 as mesoporous silica and 1, 3, 5 Trithiane as effective modifier ligand were chosen, and the modification process was carried out physically. Continuing research application of modified mesoporous silica for the removal of mercury ions (Hg^{2+}) from the aquatic environment in different pH, the weight of adsorbent and, stirring time as the major parameters were investigated and analysis of flow-injection was used as the major method for determination of adsorbed mercury ions by modified SBA-15. Also, a special computer numerical technique is used to calculate Hg response based on the total charge exchange at the electrode surface, where the currents were integrated into the range of reduction of Hg. The time for stripping was less than 300 ms. The results showed that the best Hg^{2+} ions removal conditions were achieved at the 15.0 mg of modified adsorbent, pH 5.0 and stirring time 15 min; Also the maximum percentage removal of Hg^{2+} ions and the capacity of the adsorbent were found to be 85% and 10.6 mg of Hg^{2+} ions /g modified SBA-15, respectively.

Keywords- Fast Fourier transform stripping cyclic voltammetry; Mercury ions; Mesoporous silica; Adsorbent; Wastewater; Modified SBA-15; Trithiane ligand

1. INTRODUCTION

In recent decades, Mercury ions (Hg^{2+}) are considered as one of the highly toxic materials that are presented in a wide range of industrial wastewaters such as chemical, mining and refining petrochemical [1-3]. Due to their harmful effects on vital organs such as heart, brain, liver, and fatty texture, these ions are considered as one of the chemical main sources of pollution even at low concentrations [4,5]. Therefore nowadays removal of Hg^{2+} ions from the aqueous environment is one of the major challenges for hygienic management system of human societies [6]. In this respect different physical and chemical methods such as membrane technologies, membrane separation, vacuum evaporation, chemical precipitation, ion exchange, and adsorption have been developed and used to remove Hg^{2+} ions from the aquatic environment [1,7-10]. But some of these methods due to common different problems such as low mechanical and thermal stability and a weak chemical union with the Hg^{2+} ions, are often inefficient or costly to removing Hg^{2+} ions from the aqueous environment [1,10,11].

Hence require using of a new efficient method to remove Hg^{2+} ions from the environment felt strongly [10,12]. In this regard for determination and removal of metal ions [13-17] the development of modified mesoporous materials such as SBA-15 and MCM-41 [18], has generated considerable interest. But, at the first, a method to determination and monitoring Hg^{2+} is required that so, on the one hand, can be used to determine the concentration of the Hg^{2+} ions in the aquatic environment and on the other hand can be surveyed the impact of the adsorbent used and the concentration of mercury ions that removed. Nowadays different methods and techniques such as Atomic Emission Spectrometry (AES) [19], Atomic Fluorescence Spectrometry (AFS) [20,21], Cold Vapor Atomic Absorption Spectrometry (CVAAS) [22,23], Inductively Coupled Plasma-Atomic emission Spectrometry (ICP-AES) [24] and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [25, 26] have been used to detection mercury ions in aquatic samples. Although, these techniques and methods perform well, those have common limitations such as requiring complicated, time-consuming sample preparation and treatment, and high cost of the measurement equipment [27]. Therefore, a simple, rapid, and low-cost method is required. Fast stripping voltammetric techniques can offer a simple, low-cost, and rapid method for detection and monitoring of Hg^{2+} ions in aqueous environments with considerable sensitivity in the low parts-per-billion (ppb) range [28]. Also, using the application of potential sweeping techniques (for example square wave voltammetry or cyclic voltammetry) that is associated with a potential waveform for electrode conditioning (or cleaning) can be actual helpful [29].

Moreover, EC conditioning allows the maintenance of an active and clean electrode surface for a reasonably long period of time [30]. Hence and as will be discussed later, in voltammetric measurements useful information about the changes in the double layer at the electrode surface and the processes of adsorption, can be provided by the background current [30]. For example,

due to the adsorption of species on gold Ultra Micro Electrode (UME), the change in the double layer capacitance in square wave voltammetric measurements was used for the determination of anion acid [31].

This research work describes a simple, rapid, and low-cost stripping voltammetric detection technique in a flow-injection system, by which (Hg^{2+} ions) heavy metal ions can be non-selectively or selectively measured. For noise reduction and calculating the analyte signal, a special computer numerical technique is introduced here. Also, the signal has been calculated based on the total charge exchange and net partial at the electrode surface by integrating currents at a selected potential ranges at the Cyclic Voltammogram (CV) [30]. The detector can be used in the determination of (Hg^{2+}) heavy metal ions in various chromatographic analysis techniques (e.g., capillary electrophoresis) depending on applied conditions [30]. Furthermore, the sensitivity of the method as an important parameter significantly was improved depends on the mode of data processing used in the calculation of the detector response [30].

2. MATERIALS AND METHODS

2.1. Reagents and chemicals

In this scientific research work all reagents and chemicals that used such as reagents in preparation of the stock eluent solution for flow-injection analysis (0.05 M H_3PO_4 and 1 M NaOH were used for adjusting pH of the eluent), were analytical grade and purchased from Merck Company (Darmstadt, Germany). Also, all solutions were prepared in doubly distilled deionized water (Corning Mega-Pure System, MP-6A, and D-2). By mixing 14.8 ml 0.2 M acetic acid with 35.2 ml 0.2 M sodium acetate trihydrate and volume with doubly distilled deionized water to 100 ml, A stock standard acetate buffer solution with pH 5.0 were prepared. A stock solution (1000 mg L^{-1}) of Hg^{2+} was prepared by dissolving the appropriate amounts of $\text{Hg}(\text{NO}_3)_2$ in doubly distilled deionized water. Also, solutions in all experiments were made up in the background electrolyte solution and were used without the elimination of dissolved oxygen.

2.2. Synthesis of SBA-15

SBA-15 as non-functionalized mesoporous material was prepared according to the procedure in the literature [32].

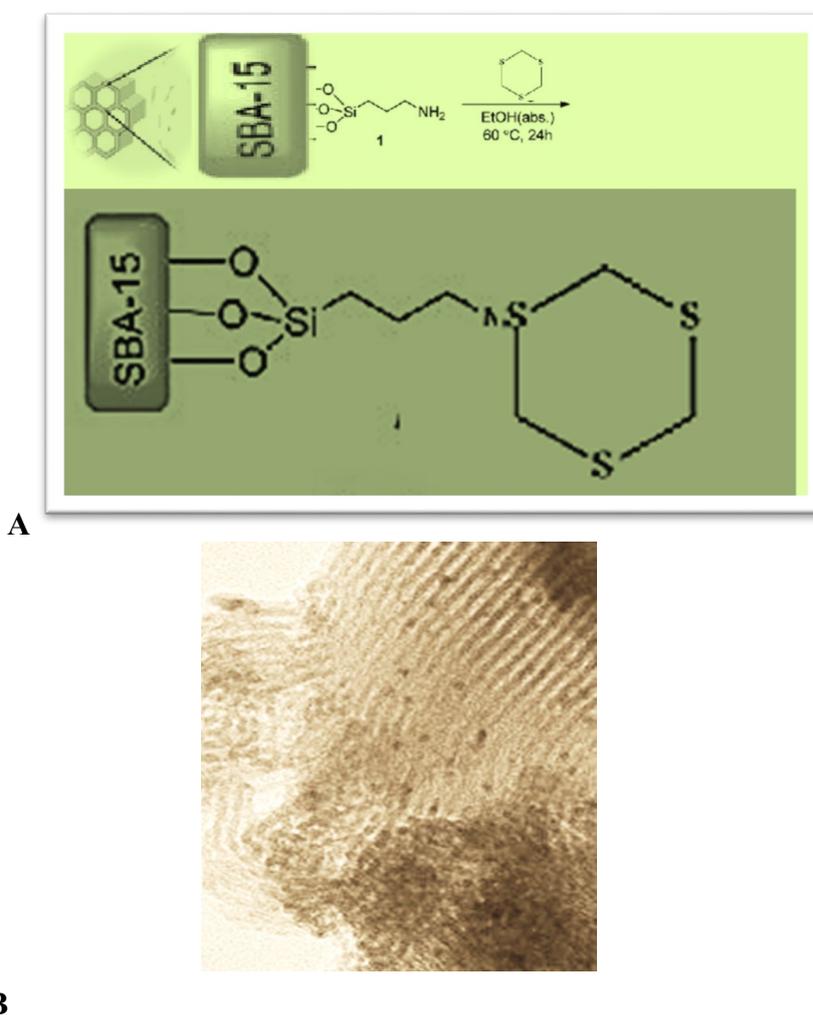
2.3. Synthesis of 1, 3, 5 Trithiane as Modifier Ligand

For modification base adsorbent (SBA-15) in this research work that has not the acceptable ability to removing Hg^{2+} ions from the aquatic environment, 1, 3, 5 Trithiane as an organic ligand was used. Hence, this modifier compound was prepared according to the

procedure in literature [33].

2.4. Modification of SBA-15

In this research work, the prepared SBA-15 was modified with 1, 3, 5 Trithiane ligand by 1.5 modification ratio (Ligand / SBA-15 w/w). In this respect, 60 mg of Trithiane ligand was dissolved in an adequate amount of acetonitrile and 40 mg of SBA-15 was added and mixed for 15 min, after filtration the functionalized product was exposed to the atmosphere and was used as a modified sorbent. The Scheme 1A shows the over-all procedure for preparation of SBA-15-functionalized, and the obtained TEM is shown in Scheme 1 B.



Scheme 1. The over-all procedure for preparation of SBA-15-functionalized, B) TEM image of SBA-15 material

2.5. Flow Injection Setup

For flow injection analysis a 10 roller peristaltic pump and a four-way injection valve

(Supelco Rheodyne Model 5020) with a sample injection loop (200 μL) were used. In this regard by means of a plastic syringe, target solutions were introduced into the sample loop. In Figure 1B, the electrochemical cell used in flow injection analysis is shown. Also, the volume of the cell was 50000 μL . The flow rate of the eluent solution was 200 $\mu\text{L/s}$ in all experiments described in this paper.

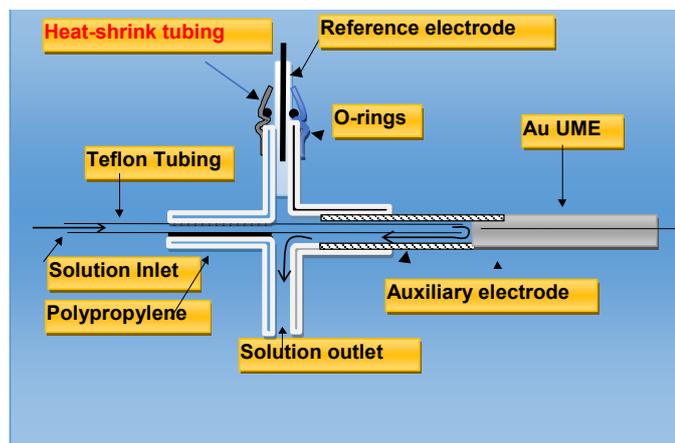


Fig. 1. The diagram of the electrochemical flow cell

2.6. Electrode preparation

By sealing metal micro-wires (Good fellow Metals Ltd., UK) into a soft glass capillary, gold UMEs (with 12.5 and 10 mm in diameter) were prepared. The capillary was then cut perpendicular to its length to expose the wire. Also, electrical contacts were made of using silver epoxy (Johnson Matthey Ltd., UK). As the main procedure, in this research work before each experiment, the electrode surface was polished for 1 minute using extra fine carborundum paper and then was polished for 10 minutes with 0.3 mm alumina. Prior to being placed in the cell, the electrode was washed with doubly distilled deionized water. Also in all measurements, an $\text{Ag(s)} \mid \text{AgCl(s)} \mid \text{KCl (aq, 1 M)}$ reference electrode were used and an auxiliary electrode was made of a Pt, 1 cm length and 0.5 mm in diameter.

2.7. Data Acquisition and Processing

In this research work, all of the electrochemical experiments were done using a setup comprised of a PC PIV Pentium 900 MHz microcomputer equipped with a data acquisition board (PCL-818HG, Advantech. Co.) and a custom made potentiostat [34]. In Figure 2, the diagram of the applied potential waveform during cyclic voltammetric measurements is shown. According to this figure, the potential waveform contains three potential time sections for; a) electrochemically cleaning the electrode surface, b) accumulating of the Hg^{2+} (metal) ions, and c) scanning potential (current measurement) [30]. In the first section in the experiment phase, the surfaces of the electrode cleaned electrochemically by applying to potential steps [30].

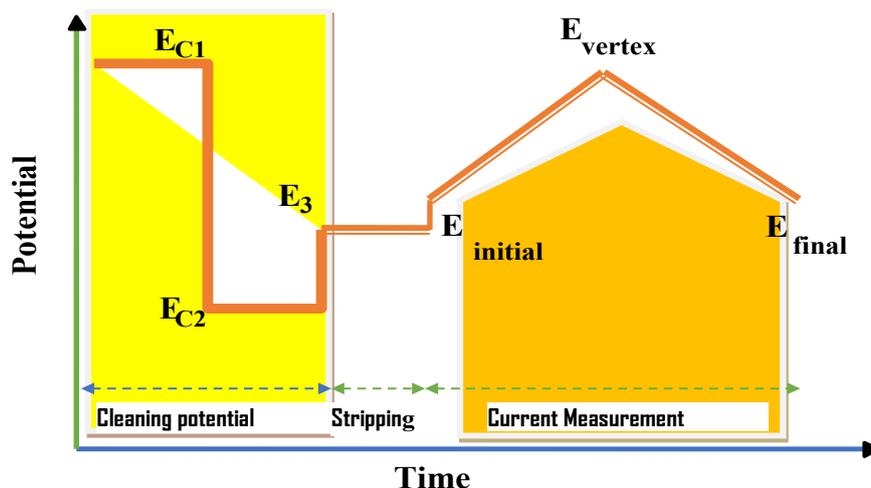


Fig. 2. Diagram of potential waveform used in the experiment

At the first step the surface of electrode is strongly oxidized by applying very positive potential ($E_{Ec1}=1600$ mV, for 100 ms), in this time all the adsorbed Hg^{2+} (metal) ions are removed from the surface, and at the next step, by applying a negative potential ($E_{Ec2}=-400$ mV, for 100 ms), the surface of the electrode is recovered [30]. In the second section of the potential waveform (E_s), (which is typically between 0.05 to 0.1 s) accumulation of the injected Hg^{2+} (metal) ions takes place. In fact, within this process, that length of it depends on the type of analyte (or its rate of adsorption) the Hg^{2+} (metal) ions were adsorbed at the surface of the electrode. Finally, the third section of the potential waveform is a potential ramp. During this time the current data were collected. All data acquisition and data processing programs were developed (by Delphi 6 ® program) in this laboratory.

2.8. Metal Adsorption Experiments

In this research work, the general procedure for removal of Hg^{2+} ions by the modified SBA-15 was as follows: A batch system was employed for the removal of Hg^{2+} ions and removing was performed in a beaker containing Hg^{2+} ions in 10 mL acetate buffered solution (pH=5.0); then 15 mg modified SBA-15 was added to the solution and the mixture was stirred for 15 min to remove Hg^{2+} from the solution. Finally, filtration was performed and Hg^{2+} ions concentrations were determined by FFT cyclic voltammetry method.

3. RESULTS AND DISCUSSION

3.1. Signal calculation for monitoring the Hg^{2+} concentration

For monitoring the mercury ion concentration the solution during the removal, a FIA setup with FFT cyclic voltammetry was used. Where, for calculating the analyte signal, integration

of current between potential E_1 to E_2 was done in the recorded cyclic voltammograms. Actually, in order to see the influence of the adsorbed Hg^{2+} ions on the oxidation and reductions peaks of the gold surface, the scan rate must be set at very high rates (e.g, 20 to 100 V/s).

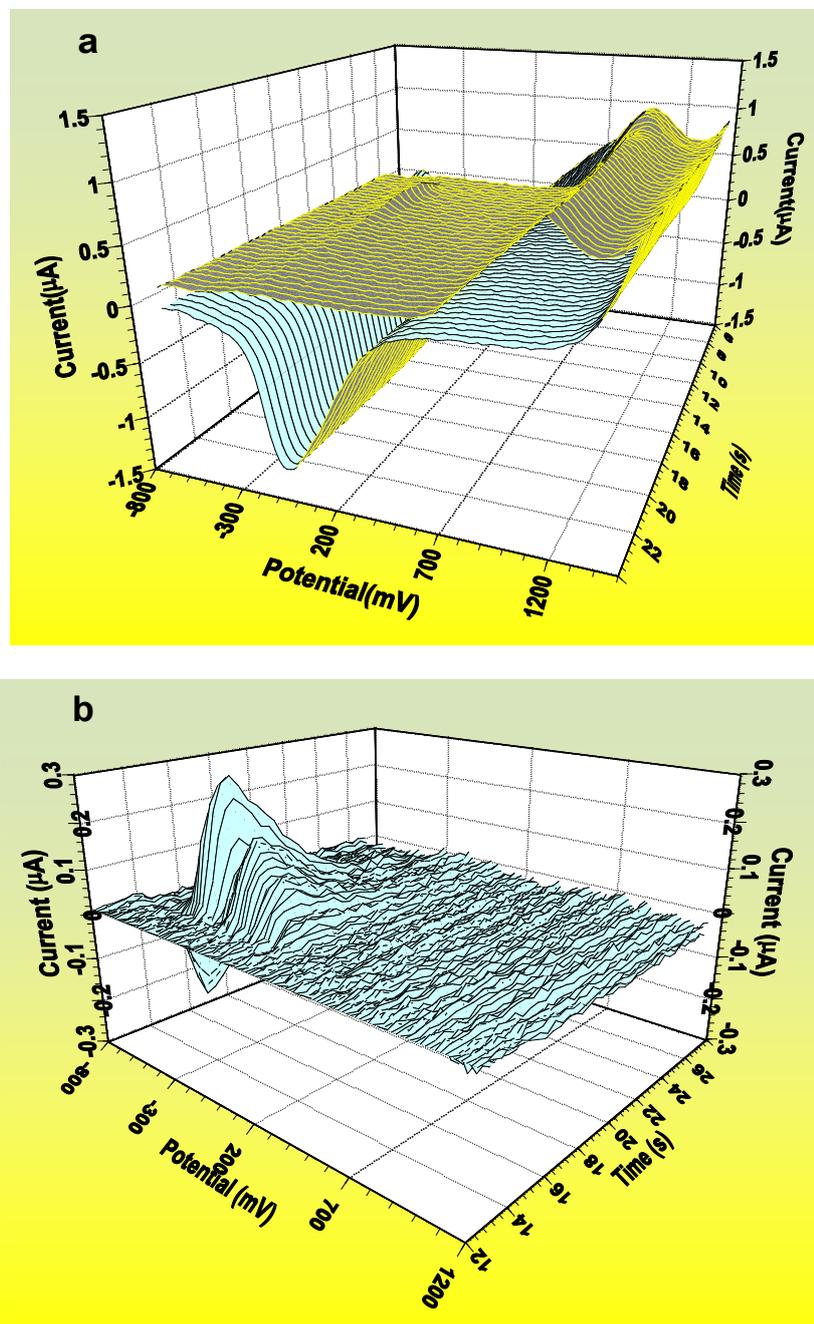


Fig. 3. (a) Cyclic voltammograms at a 50 μm Au electrode during a Flow- Injection experiment. These CVs are at the optimum condition. (b) Curve result from the subtraction of a CV refinance from the following CVs in (a). The eluent was 0.05 M H_3PO_4 , the flow rate was 200 $\mu\text{L}/\text{s}$, and the scan rate was 70V/s. Cleaning time was 160 ms (at 1690 mV) and 200 ms (at -440 mV) conditioning and stripping period, respectively. The injected solution (500 μL) contained 1×10^{-6} M Hg^{2+} , in 0.05 M H_3PO_4 . The stripping time was 300 ms at -200 mV.

Also the signal, depending on the rate of the electrochemical processes and scan rate, the amount of the adsorbed Hg^{2+} ions on the surface could be changed. But, under optimum conduction the important point here is that part of the adsorbed Hg^{2+} ions still remains on the electrode surface to influence the cathodic and anodic current peaks of the redox process of the electrode surface [32].

Therefore, the detector response, which is based on the integration of the current changes at range E_i and E_f , can be seen for all the injected Hg^{2+} ions, and the calculated ΔQ is non-selective [32]. Also to calculate the signal of Hg^{2+} in the injected solutions, it was necessary to remove background currents from the recorded CVs.

The current integration over a potential range, E_1 , and E_2 , was calculated by this equation, in the computer program:

$$\Delta Q(s, \tau) = \Delta t \left(\sum_{E=E_1}^{E=E_2} i(s, E) - \sum_{E=E_1}^{E=E_2} i(s_r, E) \right) \quad (1)$$

where $i(s, E)$ represents the CVs during the k -th sweep Δt is the time difference between two following points on the CVs, s, τ is the scan number, is the time period between subsequent sweeps, and $i(s_r, E)$ is the reference CV curve. By averaging a limited CVs at the start of the experiment (i.e. before injection of the analyte) the reference CVs was gotten; typically, the averaging of CVs included the 5 to 11 curves.

These equations show that for the same FIA experiment, the analyte signal can be gotten using an integration limits. Nevertheless, the sensitivity of Hg^{2+} signal was extracted in terms of ΔQ , which strongly depends on the the integration boundaries.

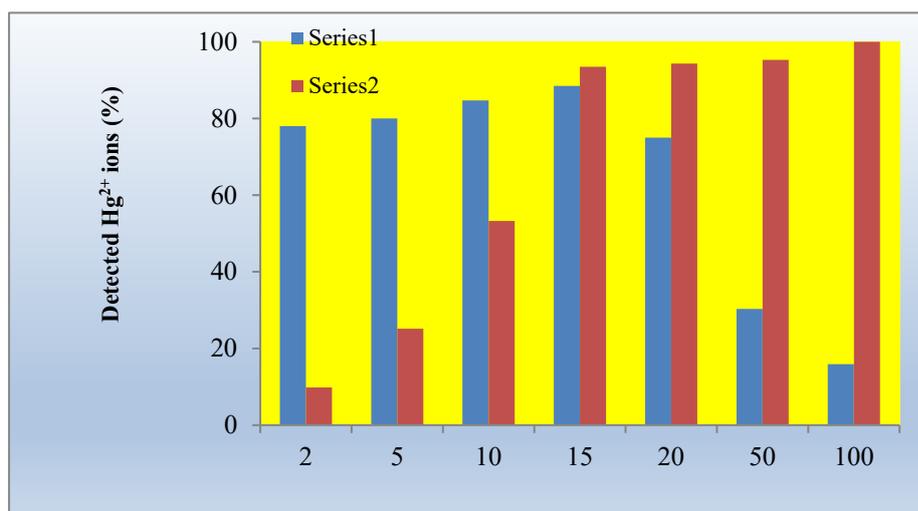
Fig. 3a shows a sequence of the recorded CVs during the FIA of 200 μL of 1×10^{-6} Hg^{+2} (in 0.05 M H_3PO_4) into the eluent solution containing 0.05 M H_3PO_4 . On the graph, the potential axis symbolizes potential applied to the working electrode. Also, the time passing between the beginning of the flow injection experiment and the beginning of a particular sweep (i.e. it represents a quantity proportional to the sweep number) determined with the time axis.

The eluent was 0.05 M H_3PO_4 , the flow rate was 200 $\mu\text{L}/\text{s}$, and the scan rate was 70V/s. Each scan was preceded by 160 ms (at 1690 mV) and 200 ms (at -440 mV) conditioning and stripping period, respectively. The stripping time was 300 ms at -200 mV. The injected solution (500 μL) contained 1×10^{-6} M Hg^{2+} , in 0.05 M H_3PO_4 . b) Curves result of subtraction of an average CVs (in absent of the analyte) from the test of the CVs in According to the above figure, as can be seen, in the absence of Hg^{+2} ions the shape of the CV curves is typical for a polycrystalline Au electrode in acidic media. The characteristic element of CVs at the gold electrode is a set of peaks associated with the formation and dissolution of a surface oxide layer at about 1270 and -135 mV (when potential sweep rate is 700 V/s), respectively. The process is also initiated by the electrosorption of the hydroxyl ion, which at more positive potentials undergoes deprotonating and structural rearrangement. The surface oxidation can be initiated

by adsorption of the water molecule and then at more positive potential AuOH forms leading to the formation of a two-dimensional phase of gold oxide (Au_2O_3).

Fig. 3b demonstrates the absolute current changes in the CVs after subtracting the reference CV (in absent of the analyte). As shown in the figure, this mode of presentation of the electrode response provides more details information about the effect of the adsorbed Hg^{2+} ions on oxidation and reduction peak currents of the CV. Likewise, these curves show that current changes mainly happen at two potential regions; potential region of the oxidation and reduction of the gold surface, and potential region of reduction and oxidation of Au_2O_3 .

In present of Hg on the electrode surface (which can deposit on the electrode), the oxide layer of Au_2O_3 process becomes strongly inhibited. In reality, the inhibition of the surface process causes a significant change in the peak currents and consequently, the overwhelming changes in the shape of CVs happen. As mentioned above the calculated ΔQ , which includes the charge exchange the potential regions, is non-selective and does not depend on the type of the adsorbed metal ions.



Series 1: Performance of Hg^{2+} ions detection
Series 2: Concentration of Hg^{2+} ions

Figure 4. The effect of amount of Hg^{2+} ions on the performance of detection. The eluent was 0.05 M H_3PO_4 , the flow rate was 200 $\mu\text{L}/\text{s}$, and the scan rate was 70V/s. Cleaning time was 160 ms (at 1690 mV) and 200 ms (at -440 mV) conditioning and stripping period, respectively. The injected solution (500 μL) contained 1×10^{-6} M Hg^{2+} , in 0.05 M H_3PO_4 . The stripping

However, in order to a larger S/N the integration range was set all over the voltammogram. The universality of the detector in this mode is very advantageous for chromatographic analysis, where a mixture of metal ions presents in the sample. A few points must take into consideration in this detection method. Theoretically, the analyte response can be affected by

the thermodynamic and kinetic parameters of adsorption, the rate of mass transport, and the electrochemical behavior of the adsorbed species. In this research work and in order to achieve maximum performance of the detector, the effect of experimental parameters was tested and optimized.

3.2. Effect of Concentration of Hg²⁺ Ions

In this research, the optimum concentration of Hg²⁺ ions in the samples for taking the maximum efficiency was investigated by analyzing different samples with different concentrations of Hg²⁺ ions (2, 5, 10, 15, 20, 50, and 100 mg/l). Results are given in Figure 4; as can be seen, the percentage of adsorption of Hg²⁺ ions on modified SBA-15 is increased with increasing the concentration of samples from 2 to 15 mg/l significantly and in the range of 15 to 100 mg the percentage of removing was decreasing significantly.

4. CONCLUSION

A new electrochemical technique for monitoring of Hg²⁺, and effective modified mesoporous silica removal of Hg²⁺ presented, also, the adsorbent was prepared and tested in batch mode experiments for removal of Hg²⁺ ions from aqueous samples. Obtained results demonstrated that the successful application of modified SBA-15 for the effective removal of Hg²⁺ ions as a rapid and easy method. Moreover, the presented results in this research paper indicated that the adsorption voltammetry associated with selective (or non-selective) detection of metal ions at UME can serve as a fast and reliable technique for trace analysis of heavy metal ions in flowing solution. Also, the gold UME provides a stable response for several hours without any chemical and mechanical treatment. For example, a 48-hour test involved replicate measurements of the response for 1×10^{-6} M Hg²⁺ on a gold electrode in a continuously flowing 0.05 M H₃PO₄, the relative standard deviation of the results was 4.6% and there was not any definite drift in the electrode sensitivity. The Hg²⁺ signal, however, can be reliably expressed in terms of the total absolute difference only if the baseline drift is small (say, less than 1% during the entire experiment) such a situation is commonly encountered in flow-injection experiments. Also the maximum percentage of removal of Hg²⁺ ions from samples have happened at pH equal to 5.0 and 15 min as stirring time, also use of 15 mg modified adsorbent. According to this point that adsorbents will use in full scale, therefore, prepared the applicable form of an adsorbent such as specific column and determination of its effective parameters will need; so authors in future work will be focused on these targets.

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