Original Article

Removal Mercury(II) Ions in Aqueous Solutions by Using {Poly(Styrene Alternative Maleic Anhydride)} Modified with Melamine and Modified Melamine with Thio Propanedioic Acid and Propanedioic Acid and Spectrophotometric Method for the Determination of Mercury(II) Ions

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ABSTRACT

A cheap and simple and precise method was developed and validated for determining of trace Hg^{2+} ions in real samples. The method was based on the reaction of Hg^{2+} ions with the novel reagent modified poly (styrene alternative maleic anhydride (SMA)) with melamine ($C_3H_6N_3$)(M)and melamine-propanedioic acid ($C_6H_8N_6O_3$) (MA)and melamine-thio propanedioic acid($C_6H_8N_6O_2S$) and after completing the adsorption the mixture was filtered and mercury(II) ions concentration was determined in filtrate after adding KI, NH_3 and KOH by UV the formed complex (K_2HgI_4) is pallid yellow but in presence ammonia is deep yellow shows an absorption maximum at λ_{max}=350 nm in borate buffer of pH = 9.6. The corrected absorbance of the formed complex at λ_{max} was gotten employing β-correction spectrophotometric method. Beer's–Lambert law of the colored Hg–reagent complex was obeyed in the concentration range of 0.05–20μgmL^{-1} Hg^{2+} ions, with a relative standard deviation in the range of 1.2±0.78%. The detection limits (D.L) and quantification limits (Q.L) of the method were 0.012 and 0.040μgmL^{-1} Hg^{2+}, respectively. The method is sensitive ($\varepsilon = 8.37\times10^4$ $Lmol^{-1}$ cm^{-1}), cheap and less toxic than most of the reported extractive spectrophotometric methods .The validation of the method was examined by comparison with the data gotten by the inductively coupled plasma-mass spectrometry (ICP-MS). The statistical procedure of data in terms of Student's t-tests and variance ratio f-tests has allocated no significant differences.

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Keywords: ICP-MS spectrometry; SMA(styrene alternative maleic anhydride); β-correction spectrophotometric method.

INTRODUCTION

Metal ions are not only valuable intermediates in metal extraction, but also important basic materials for technical applications. Accordingly, complexation of metal ions is an important technique for recovering metals from different sources (hydrometallurgy) and for their elimination from streams in civic and industrial waste. As a result, complexation, separation, and elimination of metal ions have become increasingly absorbent areas of research and have led to new technological developments. Metal-chelating and ion exchange polymers were used in hydrometallurgical utilizations such as recovery of rare metal ions from seawater and elimination l of traces of radioactive metal ions from wastes[1]. These methods have found widespread usability because their selectivity. A polymeric ligand is applied to selectively bind a specific metal ion in a mixture to isolate important metal ions from wastewater and aqueous media[2-5]. A polymeric ligand is usually applied in an insoluble resin form to separate a specific metal ion from a liquid containing a mixture of metal ions. Mercury is one of the most toxic heavy metal in the earth and it exists in nature at trace and ultra trace amounts in three valence states[12]. Mercury (0, I, II) species and are can be combine with most inorganic and organic ligands to form different complexes, e.g.HgX_4^{2-} (where X= Cl, Br and I) and methyl mercury[12,13]. Mercury can assemble in animals and plants and also enters into human body through the food continuum causing damage to centeral nervous system[14]. Due to the toxicological affects and potential accumulation of mercury onto human bodies and aquatic organisms, the determination of Hg^{2+} or organo Hg^{2+} has seen anjump of interest in the last few years[15]. According to WHO, the accepted limits of mercury in drinking water are less than 1.0 $ngmL^{-1}$ [16]. The determination ofslight concentrations of mercury is a basic task. Therefore, considerable efforts and progress have been carried out to develop accurate, low cost and reliable methods for mercury measurement in polluted samples without any complicated processing steps[17]. The most general techniques in natural samples are ICP-MS[13-14]; atomic fluorescence[18,19]; cold vapour atomic absorption[20-22]; GC[23]; stripping voltammetry[24,25]; X-ray fluorescence spectrometry[26]; neutron activation analysis[27] and atomic fluorescence spectrometry[28]. The measurement and chemical speciation of Hg^{2+} and/or methyl mercury in a series of complicated matrices, e.g. Mushroom from Tokat-Turkey, water and fish have been reported by Tuzen *et al*[29,30]. Moreover, the use of Lichen (Xanthoparmelia conspersa) biomass and Streptococcus pyogenes loaded Dowex optipore SD-2 has been reported as efficient materials for the elimination of Hg^{2+} and methyl mercury from aqueous solution[31,32]. Among these techniques, visible absorption spectrophotometry represents the most convenient technique because of the availability of the tool, simplicity, speed, precision, accuracy and low cost. A series of chromogenic reagents has been reported for mercury(II) determination in various samples[33-37]. Most of these methods are suffered from the without of sensitivity due to the significant interference of the amplitude of chromogenic reagent with the analyteat λ_{max}. This problem was solved by using the β-correction spectrophotometric method to calculate the real absorbance of the complex[38,39]. A recent literature on the analytical applications of the entitled poly (styrene alternative maleic anhydride(SMA-MS)) (Scheme. 1) has revealed no study on the use of the reagent for mercury (II) determination and/or other trace metal ions. Therefore, the aims of the present manuscript are focused on the synthesis and spectroscopic characterization (UV–Vis, IR and 1H NMR) of the SMA- MS reagent. Moreover, the stiochiometry of the formed Hg^{2+}- SMA- MS chelated was illustrated in a try to develop an accurate method for the analysis of mercury (II)-ions in different water and other real samples. The affect of different parameters that control the absorbance of the formed complex was determined.

EXPERIMENTAL

Reagent and Material

Analytical-reagent grade $HgCl_2$, KI, KOH, NH_3 and other inorganic chemicals, including HCl and NaOH, were purchased from Merck (Germany) and were used without further purification. Melamine, Thiopropanedioicacid, propanedioicacid, styrene, maleic anhydride and the organic solvents, such as triethylamine(TEA), tetrahydrofuran (THF) and normal hegxane, were also purchased from Merck and were used without further purification. The aqueous solutions were provided by the dissolution of metal salts in deionized water.

Equipment

IR spectra were measured with a Fourier transform infrared spectrophotometer (Nexus-670, Thermo Nicolet, USA). The Xray diffraction (XRD) spectra were recorded on an X'pert Philips X-ray photoelectron spectrometer (The Netherlands) with nonmonochromated Mg Ka radiation as the excitation source. The UV–Vis (200–800 nm) and IR (180–4000cm^{-1}) spectra were recorded on a Perkin Elmer (Lambda 25, Shelton, CT, USA) and a Perkin Mattson 5000 FTIR spectrophotometers, respectively. The absorbance measurements of the reagent and its mercury (II) complex were also measured with a Perkin Elmer (Lambda 25, USA) spectrophotometer (200–800 nm) with 10mm(path width) quartz cell. ABruker NMR(model VanceDPX400 MHz)was used for recording the proton NMR spectra of the reagent and its mercury (II) complex in deuterated DMSO solution using TMS as internal standard. A digital micro-pipette (Volac), an Orion pH-meter (model EA 940) and the scientific melting point SMP1 (UK) were used for the preparation of the standard and test solutions, pH measurements and melting point, respectively. De-ionized water was gotten from Milli-Q Plus system (Millipore, Bedford, MA, USA) and was used for the preparation of all solutions. Carbon, hydrogen, nitrogen and sulfur content was determined by a Perkin Elmer 2400 C series elemental analyzer, USA. A Perkin Elmer ICP-MS spectrometer (model Elan DRC II, USA) was used under the optimum experimental conditions.

Figure 2(A) displays the FTIR spectra of the SMA–M, SMA–MA, and SMA–MS copolymers. The comparison of the SMA–M spectrum with the SMA spectrum shown that the intensity of anhydride peaks decreased, and the formation of amide groups took place at about 1676 cm^{-1}. In the case of the SMA–MA and SMA–MS copolymers, the FTIR spectra revealed that the grafting reaction was efficient and the anhydride peaks disappeared, and instead, the spectrum showed the characteristics of the absorption peaks of the carbonyl of amide at a lower frequency of about 1622 cm^{-1} and the carbonyl of carboxylate anion at about 1560 cm^{-1}. All of the pendant carboxylic acids of the resins were converted to free carboxylate ions because of the existence of amino groups in the neighborhoods .It is known that mercury complexation to a certain polymeric ligand causes changes in the absorption spectra of the starting polymer. FTIR spectroscopy has been used for the characterization of polymer–mercury complexes because the frequency at which a characteristic group of the polymer absorbs is modified by mercury-ion complexation, the shift or absence of a certain band present in the starting ligand, and the presence of new bands. Therefore, the first information about the structural changes caused by the complexation of the obtained chelated resin with Hg^{2+} was provided by the FTIR spectra. The shift of infrared absorption bands for the free carbonyl bond (C=O) of the carboxylate groups illustrated whether the bonding between the ligand and each mercury ion in the solid phase was covalent or ionic. The more covalent it was, the higher the frequency shift was for the free carbonyl bond absorption. Figure 2(B) represents the FTIR spectra of the mercury ions adsorbed in the resins. In this study, the absorption band for C=O in the chelating group shifted to higher frequencies with increasing covalent nature of the carbonyl band in the results of complexation with ionic mercury and appeared about 1680–1720 cm^{-1}.

Recommended procedure

Dynamic adsorption experiments were exerted by mixing 50 mg of chelating resin with 50 mL of the mercury-ion solution (50 ppm) in a flask with a magnetic stirrer at 25Ĉ for 16 h. The pH values of the solutions were adjusted to 2.5, 5.5, 9.6 and 11.2 by the addition of aqueous hydrochloric acid or sodium hydroxide solution. When the adsorption experiment was complete, the mixture was filtered, and the residual metal-ion concentration was measured by UV as described above. In a series of volumetric flasks (10 mL), an appropriate concentration (0.01–50μgmL^{-1}) of Hg^{2+} solution was added to the reagent solution (2mL of KI 0.005M and 2mL of KOH 2.5M and 1mL of NH_3 30 w/w%). To the test solution, an approximate volume (4mL) of buffer of pH= 9.6 was added and finally the solution was made up to the mark with distilled water. The solution mixtures were allowed to stand at room temperature for 15min before determining the absorbance at 350nm.

Synthesis of the Grafted SMA Copolymer by melamine(M) (SMA–M) and modified melamine with propanedioic acid(MA) and thiopropanedioic acid(MS)

The SMA copolymer was prepared by the free-radical polymerization of 1.88g(0.0192mol) maleic anhydride and 2g (0.0192mol)styrene at a ratio of 1 : 1 were poured into a flask 50 mL of THF as a solvent at 70 Ċ in the presence of 0.018g (0.0000768mol) benzoyl peroxide(BPO) as an initiator(Scheme 1)[48]. For synthesis of the grafted SMA copolymer, 1 g (0.005 mol) of SMA copolymer and 0.47g (0.004 mol) of melamine (M) at a ratio of 1 : 0.5 were poured into a flask (and repeated with MA and MS at 80 Ċ for 4h).Then, 0.5 mL (0.004 mol) of tri ethylamine (TEA) as a catalyst and 50 mL of THF as a solvent were charged in a three necked, round-bottom flask equipped with a condenser, magnetic stirring bar, inlet and outlet for inert gas, and ultrasonic irradiation probe. The reaction mixture was refluxed under these conditions for 6 h. The precipitations were completed by the addition of n-hexane as a nonsolvent and were separated by filtration and washed by n-hexane several times. The product was dried in a vacuum oven for 24 h at 60 ĉ (yield = 98%).The synthesis process of the first chelating resin is shown in Scheme 1.

Analytical application

Determination of mercury (II) in tap and mineral water .Tap water collected from the laboratories of Chemistry Department, Urmia University, Khoy and salmas city and mineral water, commercially available in Urmia market, were filtered through 0. 5µm cellulose membrane filter prior to analysis and stored in LDPE sample bottles (250 mL). The recommended general spectrophotometric procedure used to prepare the standard curve was followed and the concentration of mercury (II) ions was then determined from the standard curve using the equation:

$$\text{Mercury (II) concentration} = C_{std} \times A_{samp}/A_{std} \quad (1)$$

Where C_{std} is the standard concentration and A_{samp} and A_{std} are the corrected absorbance of the sample and the standard, respectively.

Alternatively, the standard addition method was employed as follows: transfer known volume (5.0 mL) of the unknown water samples to the volumetric flask (25.0 mL) adjusted to pH 9.6 with B–R buffer (10 mL). An accurate volume (2mL of KI 0.005M and 2mL of KOH 2.5M and 1mL of NH_3 30 w/w%) of the reagent was then added to the test solution and the reaction mixture was then made up to the mark with distilled water. Repeat the same procedures after adding various concentrations (0.2–1.0µgmL^{-1}) of mercury (II). Measure the true absorbance displayed by the test solutions before and after the addition of the standard (0.2–1.0µgmL^{-1}) mercury (II) solution employing β-correction spectro-photometry method. The concentration of mercury (II) was then determined via the calibration curve of the standard addition procedure.

Analysis of mercury in dental-unit (DU) wastewater

DU wastewater samples were assembed from dental chair, Farhangian Hospital, Urmia city, at the end of working day. An accurate volume of sample was digested by UV-digester in the presence of suitable volumes of both concentrated HNO_3 and H_2O_2 (30%) for 1 h. the obtained solution was neutralized by NaOH (5 mol L^{-1}) and 10mL of this solution was treated under the conditions of recommended procedure.

RESULTS AND DISCUSSION

Optimization of the system

To take full profit of the method, the reagent concentrations and reaction conditions must be optimized. Various experimental factors were studied in order to optimum conditions. These parameters were optimized by setting all parameters to be constant and optimizing one each time.

The sorption behavior of mercury-ion on the resins at various pH values was tested with a batch equilibration technique, and the results are summarized in Table 2. The pH of the mercury-ion test solution was determined during the sorption process. After equilibration with the resin, an increasing acidity of the solution was observed. This was attributed to the release of protons from the resin. In general, the adsorption of mercury-ion increased with increasing pH and reached a limiting value in each instance, which was followed by a decrease in adsorption beyond the limiting value. It is well known that the adsorption of heavy-metal ions by resins depends on the pH; this effects the chelation extremely as well as the physisorption processes. Thus, the effect of pH on the adsorption capacities needed to be further investigated. The SMA–M resin was dissolved completely in water at pH 10 because of its non cross linked nature, and its hydrophilicity was increased because of the deprotonation of its functional group and SMA- MA and SMA-MS resin was dissolved completely in water at pH 10.5and 11.2 respectively. Maximum adsorption mercury-ions on resins was at pH=5.5, and also maximum absorption by K_2HgI_4 complex was pH=9.6 (fig.5) and concentration of KI, KOH were respectively 0.005mol$L^{-1}$and 2.5 mol L^{-1} respectively.

Determination of the Adsorption Capacity for Mercury(II) Ions

Dynamic adsorption experiments were performed by the mixture of 50 mg of chelating resin with 50 mL of the metal-ion solution(50 ppm) in a flask with a magnetic stirrer at 25ºC for 16 h. The pH values of the solutions were adjusted to 2.5, 5.5, 9.6 and 11.2 by the addition of aqueous hydrochloric acid or sodium hydroxide solution. When the adsorption experiment was complete, the mixture was filtered, and the residual metal-ion concentration was determined by UV after was added 2mL of KI 0.005M and 2mL of KOH 2.5M and 1mL of NH_3 30 w/w%. The adsorption capacities (q's; mmol Hg^{2+}/g resin) under various conditions were calculated as follows:

$$q = \frac{(C_o - C_f)V}{W} \qquad (2)$$

Where C_o and C_f are the initial and final concentrations (mmol/L) of metal ions in the aqueous solution, respectively; V is the volume of the metal-ion solution (0.05 L); and W is the weight of the resin (0.05 g).

Desorption of Mecury Ions in Acidic Media

For the desorption of mercury ions, aqueous 0.2M HCl was used. The resin–mercury-ion complexes in which adsorption was carried out at pH 5.5 were immersed in the 0.2M HCl solution with a magnetic stirrer at 25ºC for 1 h. After filtration, the final mercury- ion concentrations in the solution were estimated by UV. The desorption ratio (D %) was calculated as follows:

$$D\% = \frac{\text{Millimoles of mecury ions desorbed to the HCl solution}}{\text{Millimoles of mecury ions adsorbed onto resin}} \times 100 \qquad (3)$$

Analytical performance

At the optimum experimental conditions of the reaction of the reagent (mixture of 2mL KI 0.005M, 2mL KOH 2.5M and 1mL NH_3 30%) withHg^{2+} in the aqueous solution of pH 9.6,the effective molar absorptivity (ε) calculated from Beer's–Lambert plot and the Sandell's sensitivity index[35] [35] of theHg(II)–complex with and lack the use of β-correction spectrophotometry were found to be equal to 8.37×10^{4} $Lmol^{-1}$ cm^{-1} and 2.5×10^{4} $Lmol^{-1}$ cm^{-1} and 0.004μgcm^{-2} and 0.009 μgcm^{-2} respectively. The plot of the absorbance's of the Hg (II) complex at 505nm versus mercury (II) concentrations employing β-correction spectrophotometry was obeyed Beer's–Lambert law in the concentration range of 0.05–20ppm. The regressions of the linear plots without and with the use of β-correction spectrophotometry were given by Eqs. (4) and (5), respectively:

$$A = 0.053C + 0.074 \qquad r^2 = 0.999 \qquad (4)$$

$$A_c = 0.21C + 0.014 \qquad r^2 = 0.998 \qquad (5)$$

The effective concentration range of Hg^{2+}ions as evaluated by the Ringbom's plot was obeyed in the range 0.1–15ppm. The precision and accuracy of the developed procedure was evaluated by the recovery studies of four replicate measurements of Hg^{2+}in distilled water at concentration level of 1.0μgmL^{-1} using β-correction and the ordinary single wavelength spectrophotometry methods. The relative standard deviation and the relative error of the developed β-correction method were 1.2% and 1.0% while 2.2% and 2.7% for the single wavelength spectrophotometry, respectively. The level of precision was found suitable for the routine analysis of the mercury (II) in various water samples. Under the conditions established for mercury (II) ions, the lower detection limits

(D.L) and quantification limits (Q.L) of Hg^{2+} were measured by using the equations:

$$LOD = \frac{3\delta}{b} \qquad (6)$$

$$LOQ = \frac{10\delta}{b} \qquad (7)$$

Where δ is the standard deviation (n = 6) of the blank and b is the slope of the calibration plot. The values of D.Land Q.Lof the developed method lack using β-correction absorbance values were found are 0.16 and $0.52 \mu g mL^{-1}$ mercury (II), respectively. Such limits were improved to lower detection and quantification limits of 0.012 and $0.040 \mu g mL^{-1}$ Hg^{2+}, respectively using the developed β-correction method at the optimum experimental conditions. Such limits are comparable to most of the spectrophotometric methods involving pre concentration step on solid sorbent. The analytical properties of theoffered method were also compared with many of extractive spectrophotometric methods. The data given in Table 1 revealed that, the developed method is simple, less toxic, reliable and free from interference of the ions Al^{3+}, Ag^{+}, Co^{2+}, and Ni^{2+} Cd^{2+} , pb^{2+} and the excess reagent compared to the reported methods ICP-MS method in terms of Student’s t-test (2.14– 3. 95) and f-test (0.45–0.89)[46] [46]. The results summarized in Table 7 revealed that, the percentage recoveries of both methods were in good agreement and always higher than 95% confirming the accuracy of developed procedure and its independence from matrix. The correct absorbance of the examine solutions calculated by the offered dual-wavelength β-correction spectrometry was drawn against the concentrations ofHg^{2+} added. The spiked mercury (II) concentration was measured by the standard addition curve and the outcomes were successfully compared with the value of Hg^{2+} measured by ICP-MS (Table 7).

CONCLUSIONS

The method described obtained a simple and valuable means of measurement of trace amounts of Hg^{2+} ions in aqueous solution by spectrophotometry. The prepared chelating resins are good candidates for removing of mercury ions from aqueous solutions. The removal of mercury ions from wastewater in this study was efficient, and it can be said that nearly complete adsorption was achieved in the case of Hg^{2+}. The method is sensitive ($\varepsilon = 8.37 \times 10^{4}$ $L mol^{-1}$ cm^{-1}), inexpensive and less toxic than most of the reported extractive spectrophotometric methods[47,6-8]. Moreover, the method also has the advantage of virtual freedom from interference from extraneous ions. Thus, it can act as an alternative approach to the widely used flameless AAS and ICP-OES in rapid and precise determination of trace amounts of mercury in natural water and industrial effluent samples[40-45][40-45]. On the other side, a calibration matrix constructed with β-correction spectrophotometric method has been successfully used for the analysis of Hg^{2+} ions in real samples. The method requires no complex pretreatment of chromatographic separations and/or preconcentration of the analyte[49-51].

ACKNOWLEDGEMENTS

The authors would like to thank Prof. Dr. Peyman Najafi Moghadam & Dr. Reza Hasanzadeh(Urmia university) for their help in providing reagents for the synthesis of polymers.

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Table 1: Analytical features of some spectrophotometric methods employed for mercury determination

Reagent/Ref.	λ_{max}	pH	Linear dynamic Range (µgmL^{-1})	Molar absorptivity (L mol^{-1} cm^{-1})	Remarks
Thiobenzoylacetone/[6]	345	4	0.6–12	1.7×10^4	Sensitive but interference from Ag$^+$ and excess of chromogenic reagent. Using toxic organic solvents.
Variamine Blue B/[7]	605	2.5–4	0.64–4.4	4×10^4	Sensitive but using toxic organic solvents. Time-consuming.
Phenanthroline and eosin/[8]	550	4.5	0.2–1.2	8×10^4	Sensitive, but interference from Al^{3+}, Co^{2+}, Ni^{2+} and excess of dye. Thiacrown ether and
Bromocresol Green/[9]	420	–	0.5–12	–	Less sensitivity and interference from. Cu^{+2}, Cd^{2+}and Ag$^+$. Time-consuming.
Diphenylthiocarbazone/[10]	488	Acidic media	0.1–25	2.5×10^4	Low sensitivity
6-hydroxy-3-(2-oxoindolin -3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)[11]	505	4–6	0.2–2	4×10^4	Sensitive, selective and free from the interference of Al^{3+}, Ag$^+$ Co^{2+}, Ni^{2+} and excess chromogenic reagent. No need for organic solvent.
This work	350	2-11	0.05-20	8.37×10^4	Very sensitive, selective and free from the interference of Al^{3+}, Cd^{2+}, Co^{2+}, Ni^{2+} and excess chromogenic reagent.,

Table 2: Optimized parameters

Parameters	Proposed method
pH[a]	9.6
Amount of KI	2mL(0.005M)
Amount of KOH	2mL(2.5M)
Amount of NH_3	1mL(30%)
Time[b]	15min
Time[c]	16h
pH[d]	5.5
RSD[e]	1.2±0.78
Molar. A[f]	8.37×10^4
R[g] R.E[h]	0.9995
LOD[i]	0.012
LOQ [j]	0.040
L.D.R[k]	0.05-20ppm

[a]pH for the formation of K_2HgI_4, [b]Time for the formation of K_2HgI_4 , [d]pH for the adsorption with resins ,[c]Time for the adsorbtance completion Hg(II) ions with resins,[f] Molar absorptivity, [h]Regression Equation (A=0.053C + 0.074),[k]Linear Dynamic Range(ppm), [i]Limit of Detection , [j]Limit of Quantification

Table 3: Adsorption of mercury-ions at Various pH's (2.5, 5.5, 9.6 and 11.2)

Resin	pH			
	2.5	5.5	9.6	11.2
SMA-M	0.801	0.202	0.921	-
SMA-MA	0.721	0.121	0.712	-
SMA-MS	0.687	0.092	0.624	-

Table 4: Adsorption Capacity for Mercury Ions at Various pH's (2.5, 5.5, 9.6 and 11.2)

Adsorption capacity (mmol/g)				
	2.5	5.5	9.6	11.2
SMA-M	0.362	0.475	0.17	-
SMA-MA	0.377	0.490	0.380	-
SMA-MS	0. 384	0.495	0.395	-

Table 5: Adsorption Percentage for Mercury Ions at Various pH's (2.5, 5.5, 9.6 and 11.2)

Adsorption percentage (%)				
	2.5	5.5	9.6	11.2
SMA-M	74.56	95.16	68.04	-
SMA-MA	75.58	98.22	75.92	-
SMA-MS	76.90	99.32	79.24	-

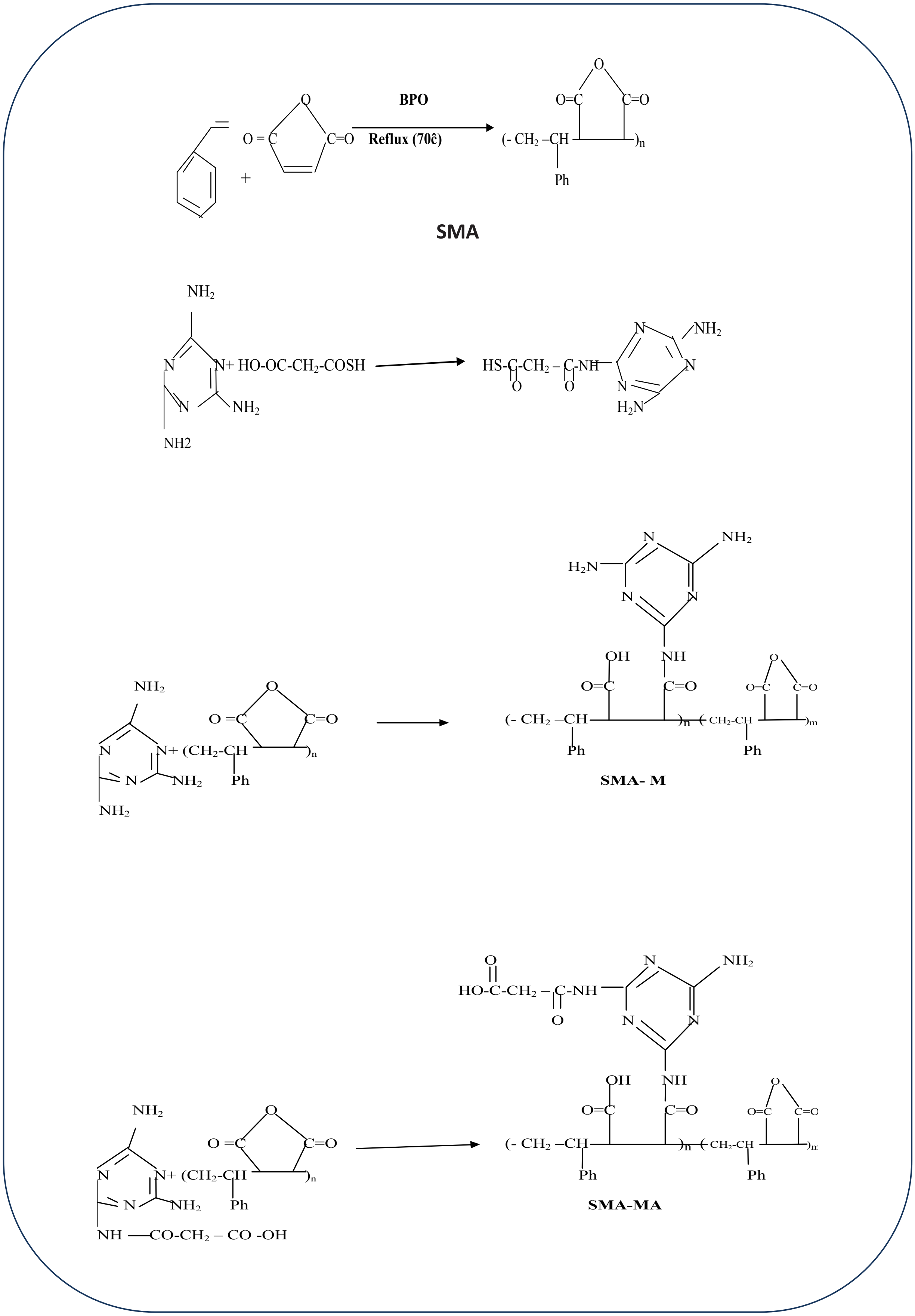
Table 6: Percentage of Desorption for Mercury(II) Ions

SMA-M	98.64
SMA-MA	98.54
SMA-MS	98.41

Table 7: Analysis of mercury (II) ions in tap, mineral and DU wastewater samples by the developed (A) and the ICP-MS (B) methods

Water sample	Mercury(II) added, (μgmL^{-1})	Mercury(II) found (μgmL^{-1})^{a}		Recovery(%)	
		A	B	A	B
Tap water	-	ND	ND	-	-
Tap water	1.5	1.57±0.05	1.56±0.04	104±0.03	106±0.02
Mineral water	-	ND	ND	-	-
Mineral water	3	2.99±0.25	3.11 ±0.07	99.8±1.65	105 ±1.75
DU waste water	-	3.5±0.14	3.6±0.15	-	-
DU waste water	2	5.54±0.16	5.65±1.85	97.8±1.15	102.7±1.2

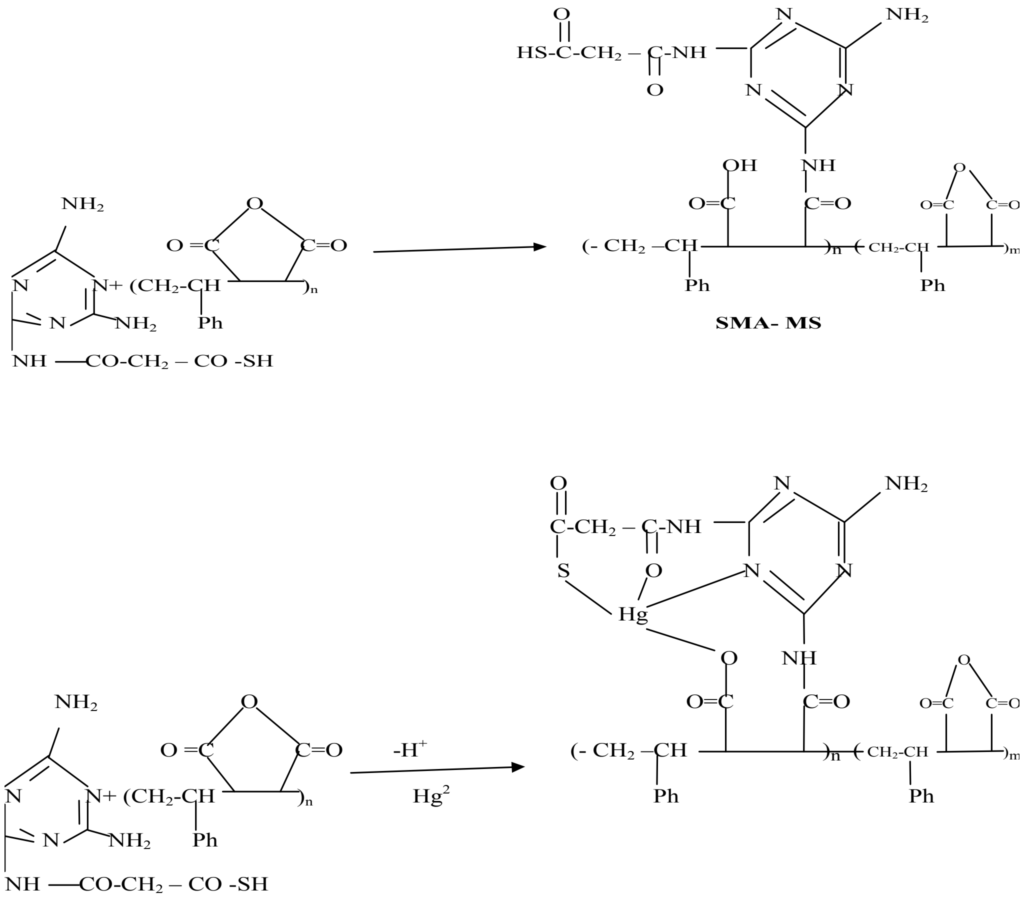
[a] Average of six measurements±standard deviation



SMA

SMA- M

SMA-MA



Scheme 1: Chemical structures of the reagent SMA- M & SMA- MA & SMA- MS {poly(styrene alternative maleic anhydride – modified melamine) and the proposed structure of its mercury (II) complex.

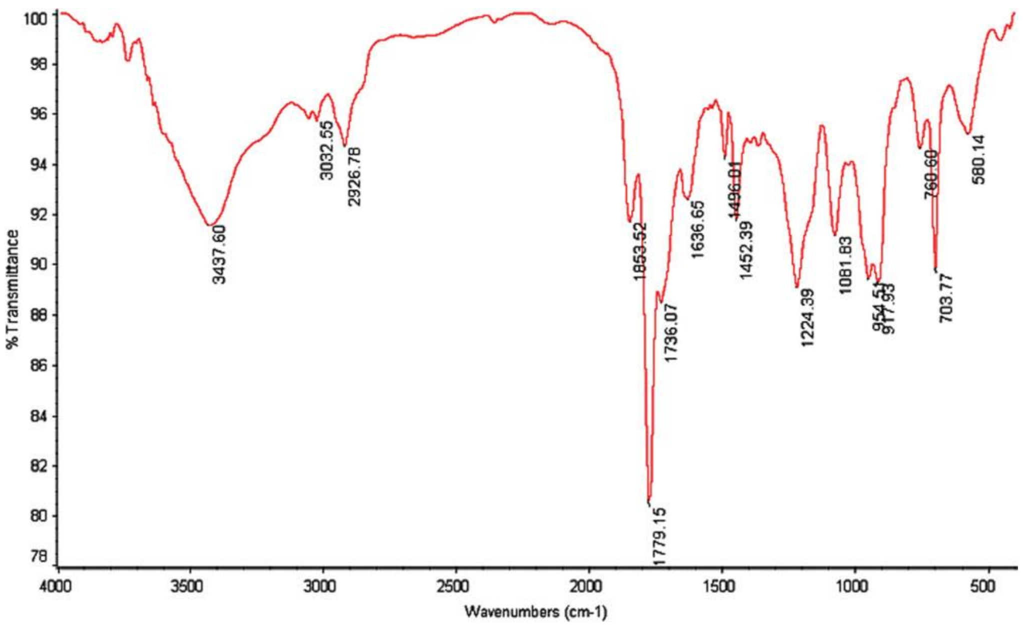


Fig. 1: FTIR spectrum of the SMA copolymer.

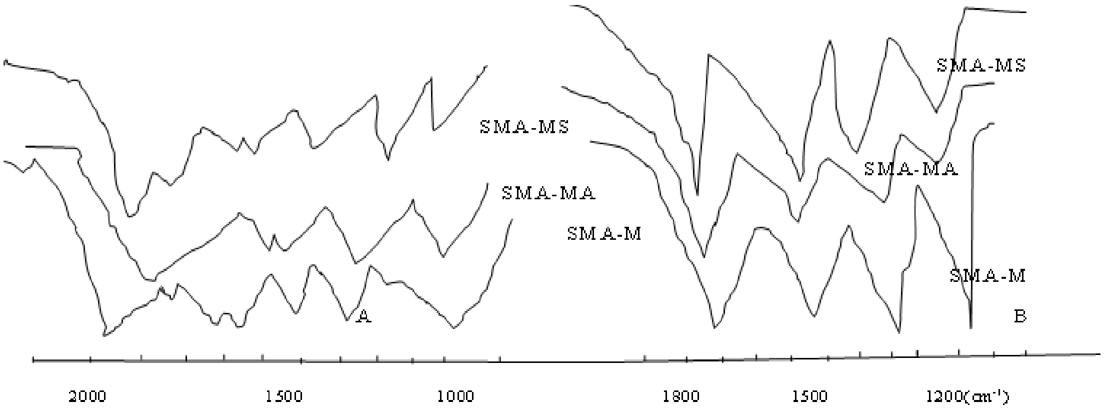


Fig. 2: FTIR spectra of the SMA–M, SMA–MA, and SMA–MS copolymers (A) before complexation.

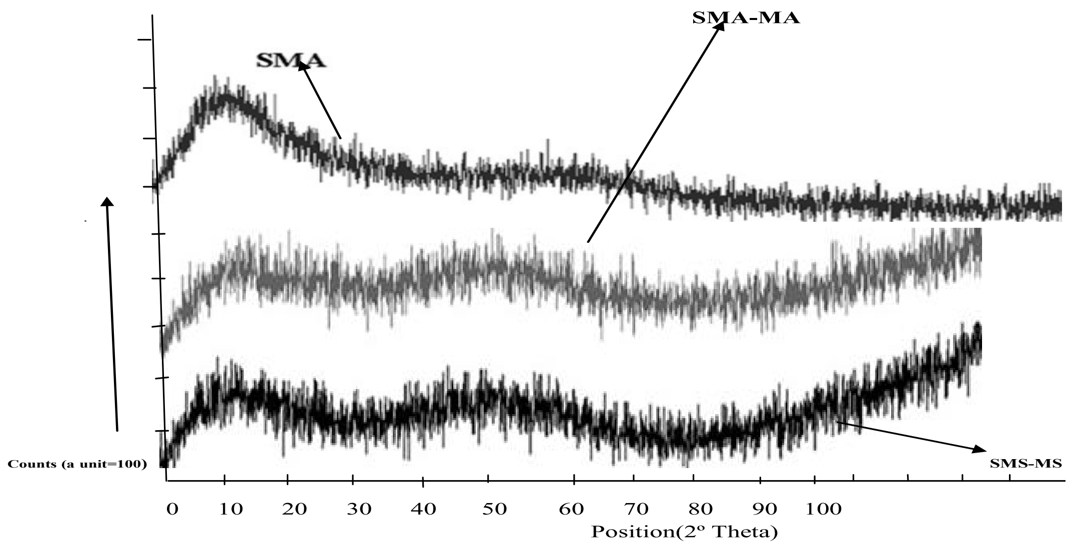


Fig. 3: XRD patterns of the synthesized copolymers.

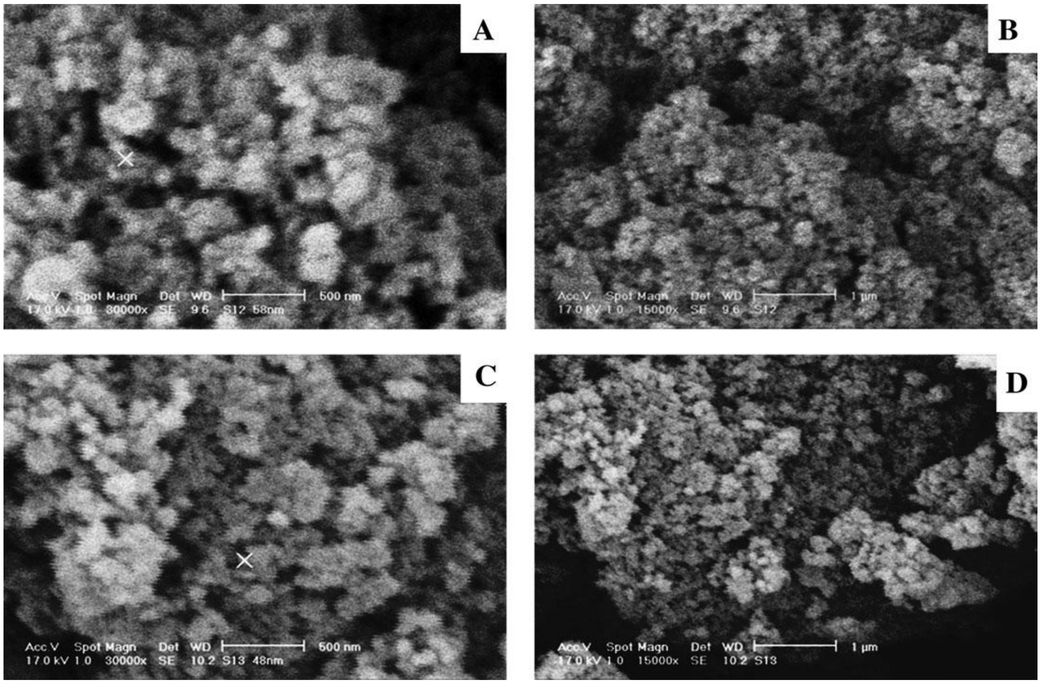


Fig. 4: SEM images of the chelating resins (A) SMA–MA (scale = 500 nm), (B) SMA–MA(scale = 1µm), and (C) SMA–MS(scale = 500 nm) and(D) SMA–MS (scale = 1 µm).

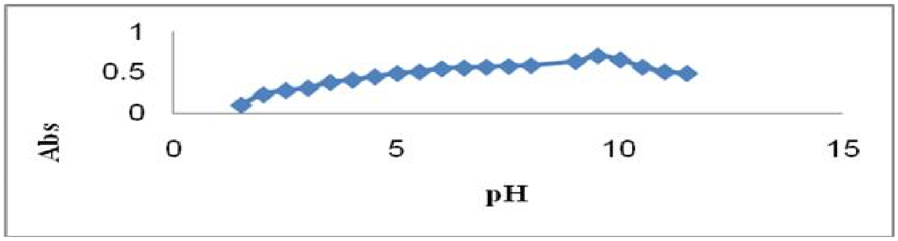


Fig. 5: Effect of borate buffer solution on the complexation of Hg(II) with I^- for the formation K_2HgI_4.

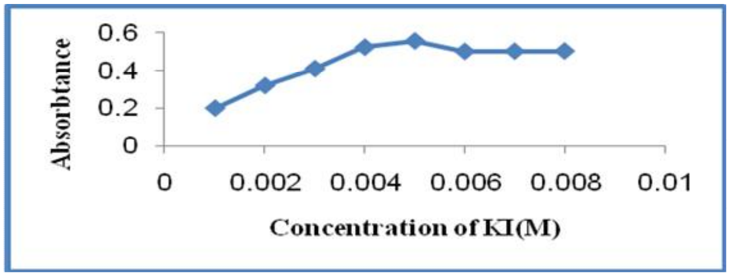


Fig. 6: Effect of concentration of KI on the complexation of Hg(II) with I^- for the formation K_2HgI_4.

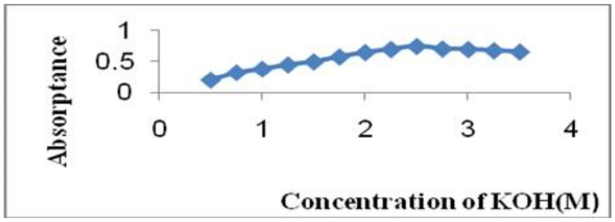


Fig. 7: Effect of concentration of KI on the complexation of Hg(II) with I^- for the formation K_2HgI_4.

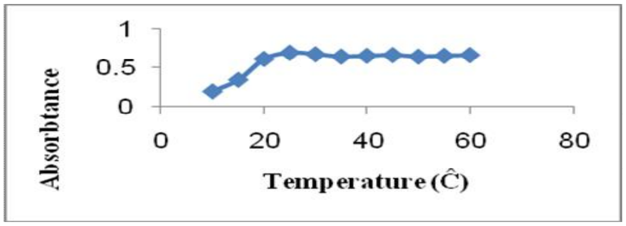


Fig. 8: Effect of Temperature on the complexation of Hg(II) with I^- for the formation K_2HgI_4.

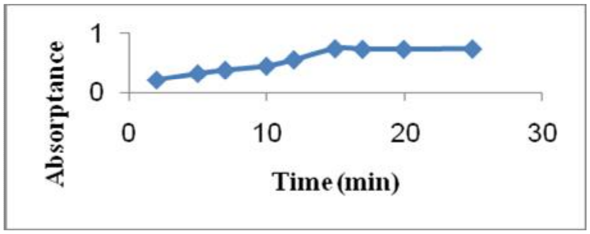


Fig. 9: Effect of Time on the complexation of Hg(II) with I^- for the formation K_2HgI_4.

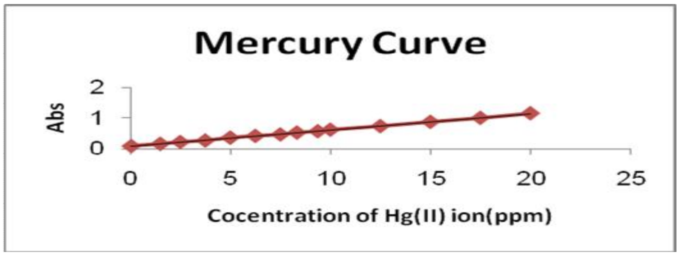


Fig. 10: Calibration curve for the determination of Hg(II) ions.