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SEPARATION, PRECONCENTRATION AND DETERMINATION OF INORGANIC MERCURY IN ENVIRONMENTAL WATER SAMPLES

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ABSTRACT

A new and relatively green methodology for determination of traces of mercury ions in water samples has been developed .The method depends on two steps (processes), the first one was carried out by the sorption of the Hg(II) ions on the surface of modified cellulose (CELLSAL), The second process, using cold vapor atomic absorption technique (CVAAS) for determination of the Hg(II) ions. This method showed high recovery and good sensitivity. Batch extraction technique has been employed to investigate the effect of the experimental factors influencing the sorption and separation process for example interfering ions, shaking time and change of pH value. Successful application of the proposed method for determination of Hg(II) ion in different binary mixtures and in several environmental water samples has been investigated .

Keywards: Separation- Preconcentration- Determination-Inorganic mercury

INTRODUCTION

Mercury and its compounds are human, plant and animal hazard due to their protoplasmic poisons [**Niboer *et al.*, (1980)**]. The tolerance limit of inorganic mercury in aqueous solution is 1 μg l^{-1}. Mining, recovery, use in a variety of products, industrial waste and accumulation in human body via food are the major sources of poisoning mercury. Mercury has a tendency to amalgamate on various surfaces and capable to form relatively stable complexes with many reagents [**Versieck *et al.*, (1980) and Faust *et al.*, (1986)**]. Low levels of mercury in environmental samples necessitate a preconcentration process before its determination. Several solid-liquid separation systems such as activated carbon [**Huang *et al.*, (1984) and Mcbay *et al.*, (1987)**], inorganic metal oxides [**Rauf *et al.*, (1989)**], ion exchange resins [**Kenawy *et al.*, (2010) and Becker *et al.*, (1993)**] and immobilized reagents such as diethyldithiocarbamate [**Arpadjan *et al.*, (1997)**], 8-hydroxyquinoline [**Abbas *et al.*, (1989)**] and dithizone [**Porta *et al.*, (1991)**] have been employed. Solid phase extraction (SPE) was also investigated using polymer chemically modified chloromethylated polystyrene-PAN(ion-exchanger) [**Akl *et al.*, (2004)**], The problem associated with ion-exchange resins is that matrices have limited adsorption capacity and selectivity [**Kenawy *et al.*, (2010)**].

Here in, CELLSAL has been applied for selective separation and preconcentration of Hg(II) prior to its determination from environmental waste samples. Characterization of the modified cellulose and its Hg(II) compounds is achieved using different techniques.

EXPERIMENTAL

Reagents:

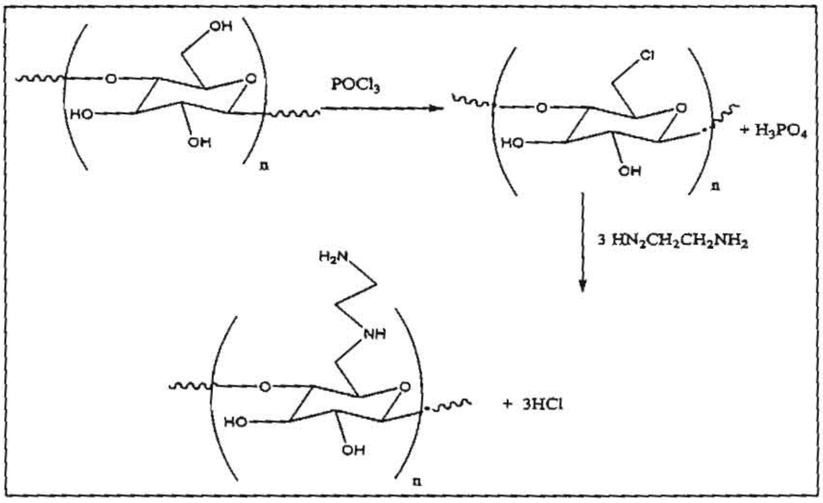
A stock solution of Hg(II) (1000 $\mu g\ ml^{-1}$) was prepared by dissolving appropriate amounts of $HgCl_2$ (Aldrich, USA) in deionized water. All other reagents (BDH, England) were of Analytical grade.

Equipment:

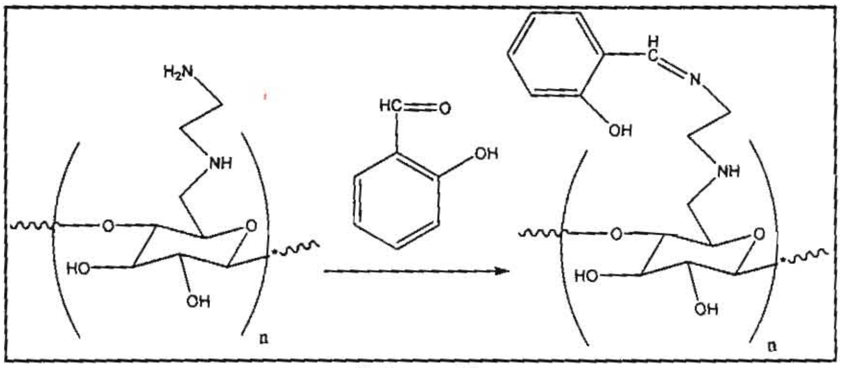
A Perkin-Elmer model 2380 Atomic Absorption Spectrometer (USA) with hydride technique was used. The IR spectra were carried out using Mattson 5000 FTIR Spectrophotometer in the range 4000-200 cm-1 as KBr disc. UV–Visible measurements were performed on a Unicam 2001 UV-Vis Spectrophotometer using a 1 cm quartz cell. The pH values were measured using a pH-meter (Hanna Instruments, 8519, Italy) with accuracy of ±0.01 and standardized with 0.05 mol l^{-1} potassium hydrogen phthalate (pH 4.01) and standard tablet (pH = 9.2) at 25°C.

Preparation of cellulose functionalized with salicylaldehyde :

Synthesis of chlorodeoxycellulose [**Veivi *et al.*, (1990)**] and ethylenediamine-cellulose [**Roselleta (1998)**] has been slightly modified. Whatman cellulose powder (10 g) was preswollen during 30–60 min in DMF. The mixture of 400 ml DMF and 12 ml $POCl_3$ was heated to 90°C (scheme 1). The preswollen cellulose powder is added to the solution and is heated at 90°C for 15 min. The mixture was cooled down, filtered and washed successively with DMF (100 ml), 5% NaOH (100– 200 ml), bidistilled water, 5% acetic acid and bidistilled water again. Then the product was air-dried. The Cl-functional group was substituted by heating the prepared cellulose under appropriate stirring with 100 ml ethylenediamine in a water bath at 100°C for 2 h at reflux (scheme 1). After filtration the formed ethylenediamine-cellulose powder was washed with ethanol and bidistilled water and air-dried. Then 5g of ethylenediamine cellulose was refluxation with 15 ml salicylaldehyde in a little amount of absolute ethanol and few drops of glacial acetic acid over a water bath for 4 hours. The prepared yellowish brown modified cellulose (scheme 2) was filtered off, rinsed several times with bi-distilled water, dried and stored in a polyethylene bottle.



Scheme (1)



Scheme (2)

Batch method:

A sample solution (100 ml) containing known concentration of Hg(II) (25 μg/ml) was transferred to a stoppered glass bottle (250 ml) and 50 mg of the modified cellulose was added after adjusting the pH to 5. The mixture was shaken for 30 min, filtered and washed with bidistilled water. The sorbed Hg(II) was eluted with 5 ml of 0.1 mol l^{-1} HNO_3 and the resulting solution was completed to 100 ml and determined using cold vapor atomic absorption technique.

Column method:

The modified cellulose (1.0 g) was first swollen for 24 h in bidistilled water and packed in a glass column (40 X 6 mm). A sample solution (100 ml) of 25 μg/ml Hg(II) buffered at pH = 5 was passed through the column at optimum flow rate. After the sorption step, the column was washed with 100 ml of bidistilled water to remove any uncomplexed Hg(II) from the modified cellulose bed. The stripping of Hg(II) from the modified cellulose was carried out by 5ml 0.1 mol l^{-1} $HN0_3$ solution. The eluate solution was collected in a 100 ml calibrated flask and analyzed.

RESULTS AND DISCUSSION

In order to verify the presence of the active functional groups of the functionalized cellulose, the spectra of the chlorodeoxycellulose, ethylenediamine-cellulose and CELLSAL were recorded. The IR spectra of chlorodeoxycellulose exhibited a characteristic band at 701 cm^{-1} which may attributed to C–Cl band and showed also the presence of a broad band attributed to OH stretching at 3400 cm^{-1} due to the presence of water.

Upon modification of chlorodeoxycellulose with ethylendiamine (scheme 1), there are additional bands at 3160 cm^{-1} corresponds to NH_2 band. Also, the sharp decrease in the intensity of the band located at 701 cm^{-1} was taken as an evidence to the progress of the reaction through ester link.

Upon modification of ethylenediamine-cellulose with salisaldehyde (scheme2), there are additional bands at 1640 cm^{-1} corresponds to -C=N- band. Also, the sharp decrease in the intensity of the band located at 3160 cm^{-1} was taken as an evidence to the progress of the formation of chief base **[Smits *et al.*, (1980)].**

Metal- CELLSAL complex was confirmed by 1) the shift in C=N band to lower wavenumber by 20 – 30 cm^{-1}; and 2) the disapperance of OH- phenolic and NH bands. This behavior confirmed the complex formation between CELLSAL and Hg^{2+} ion.

Also, the shifts of pH-metric titration curves Fig. (1) for CELLSAL with Hg^{2+} ion from those of Ethylendiamine-cellulose solely was taken as a further support to indicate that, sorption of metal ion takes place through complexation with CELLSAL.

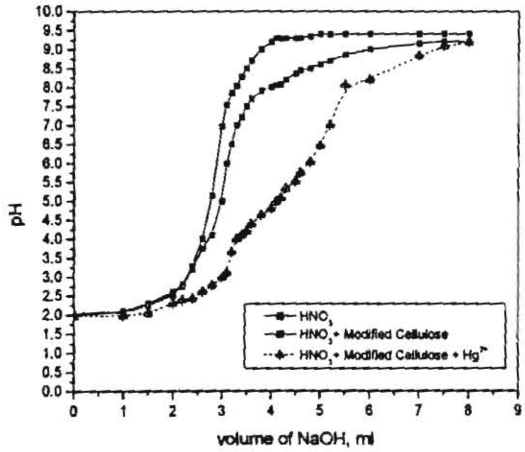


Fig. (1): pH – metric titration of modified cellulose with Hg(II).

Batch technique:

Effect of pH:

The effect of pH on the sorption of the studied metal ion has been investigated in the pH range 1-8 by batch equilibrium experiments [1-2.5 HCl/ KCl and 3-8 acetic/ acetate]. The experiment was elaborated by shaking the solution containing the ion with the modified cellulose of variable pH for sufficient equilibrium time. The pH was adjusted using acetic- acetate buffer solutions. From data represented in Fig. (2), it could be concluded that, the maximum sorption efficiency of CELLSAL for Hg(II) ion was achieved in the pH range of 5- 6.5. For subsequent experiments the working media is adjusted at pH 5 for sorption of Hg(II) ion.

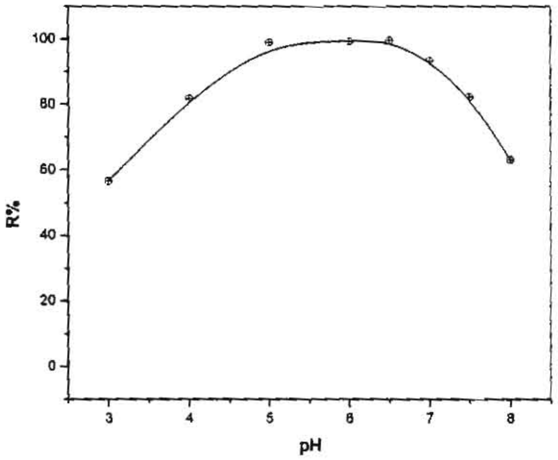


Fig. (2): Effect of pH on the recovery % of Hg(II) usin CELLSAL and stirring time = 40 min at 25±1°C.

Determination of sorption capacity:

The sorption capacity of the modified cellulose towards Hg(II) was determined by shaking excess Hg(II) with 50 mg of CELLSAL at pH 5. The data indicate that 32 mg g^{-1} is the maximum sorption capacity for Hg(II) with CELLSAL

Effect of shaking time:

To determine the rate of sorption of Hg(II) on CELLSAL, batch experiments were elaborated by shaking 50 mg of the modified cellulose with 100 ml of feed solution containing Hg(II) at room temperature (25±1°C) using A Sturat scientific mechanical shaker (USA) with a speed of 200 strokes/minutes. Aliquots of 1ml solution were taken for analysis at pre-determined intervals. The concentration of Hg(II) in the supernatant solution was determined and the amount of Hg(II) sorbed on CellSal was calculated by mass balance.

The sorption half-time ($t_{1/2}$) defined as the time needed to reach 50% of the total sorption capacity, was 11 min. was estimated from Fig. 3. It was observed that, the maximum sorption of Hg(II) with CELLSAL reached its equilibrium time after 40 min.

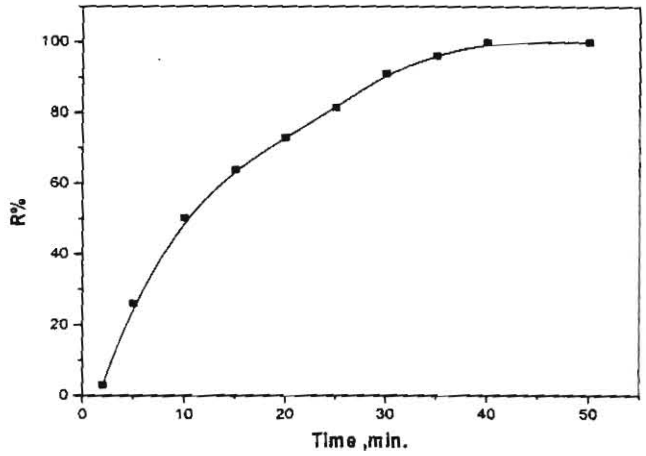


Fig. (3): Effect of stirring time on the recovery % of Hg(II) using 50 mg CELLSAL, pH = 5 at 25±1°C.

Choice of eluent:

Choice of the effective eluent for the quantitative stripping of the retained Hg(II) on CELLSAL is of special interest. The Hg(II) sorbed on CELLSAL is eluted with different acid solutions (HCl, HNO_3 or H_2SO_4) as well as EDTA into the aqueous phase. Literature survey showed that, atomic absorption spectrometry (AAS) may be handicapped by the presence of a complex organic matrix that causes severe suppression of Hg(II) signal. So, the use of acid solution is analytically preferred. 0.1 mol l^{-1} of HNO_3 affords quantitative elution of Hg(II) from the modified cellulose.

Interferences:

The influence of several cations and anions on the sorption and determination of Hg(II) is summarized in Table 1. Most of the examined cations and anions did not interfere; Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+} and especially Co^{+2} interfered only in the determination process. The interference is eliminated or reduced using EDTA [**Tashiro *et al.*, (1982)**] which forms a stable complex with most interfering ions, but with Hg(II) the modified cellulose has the ability to replace Hg(II) from its EDTA complex and the metal ion determined in the eluent.

Table (1): Influence of interfering cations and anions on the recovery % of 10 $\mu g\ ml^{-1}$ Hg(II) ion using 100 mg of CellSal at pH =5.0 and 25±1°C.

Coexisting ions	Concentration ($\mu g\ ml^{-1}$)	Hg(II) (Recovery %)
K^+, Cl^-, NO_3^-, NH_4^+,	500	100.00
CH_3COO^-, F^-	350	100.00
Ca^{2+}, Al^{3+}, Mg^{2+}	200^a	99.82
Ni^{2+}	200^a	99.64
Mn^{2+}, Co^{2+}	200^a	99.80
Cu^{2+}	200^a	99.55
Fe^{3+}, Zn^{2+}	200^a	99.45
Pb^{2+}	200^a	98.68
Cd^{2+}	200^a	99.80

^{a} in presence of 2ml of 10^{-3} $moll^{-1}$ EDTA .

Column technique:

Effect of flow rate:

The effect of flow rate on Hg(II) sorption was investigated at different flow rates (0.5 - 10 ml min^{-1}) under the optimum conditions. It is found that, the optimum flow rate for the maximum sorption percentage of Hg(II) is 2 ml min^{-1}. Using flow rate > 2 ml min^{-1}, Hg(II) ions do not reach equilibrium. The relatively rapid sorption of Hg(II) is taken as an indication for its high reactivity with modified cellulose .

Breakthrough capacity:

It used to evaluate the amount of Hg(II) sorbed per gram on the modified cellulose under the operating conditions. To obtain a breakthrough capacity, a glass column packed with 1.0 g of the modified cellulose and the Hg(II) solution (25 $\mu g\ ml^{-1}$) at pH = 5 was passed through the column at 2 ml min^{-1} flow rate. The receiving effluent after 5 minutes was fractionalized into 5 ml portions and the Hg(II) in each was determined. The breakthrough capacity presented in Fig. (5) indicates that, the column is exhausted with 29 mg Hg(II) per one gram cellulose.

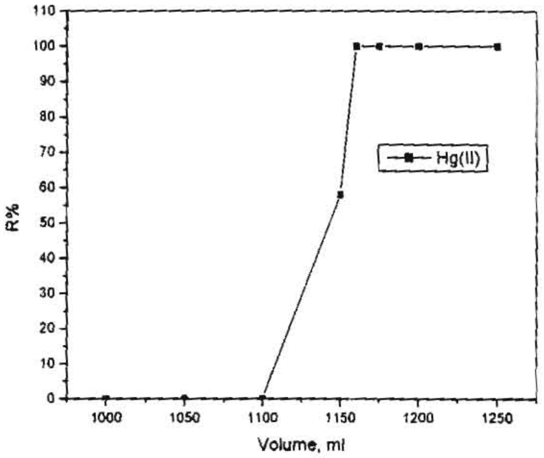


Fig. (5): Breakthrough curve of Hg(II) with flow rate 2 ml min^{-1} at 25 °C.

Column reuse:

To test the long-term stability of the column containing the modified cellulose, successive sorption and desorption cycles were subjected by passing the Hg(II) solution through the column at 2 ml min^{-1} flow rate. The sorbed Hg(II) is then eluted from the resin with 5 ml of 0.1 mol l^{-1} HNO_3. The procedure was repeated several times and the stability of the column was assessed by monitoring the change in the recoveries of the sorbed Hg(II). The results of fifty sorption/desorption cycles indicated that, the recovery decreases by 2–3 % for Hg(II), which reflect good stability of the modified cellulose.

Effect of volume and preconcentration factor:

To the column, 0.1 - 1.5 L aqueous solution containing 5 µg of Hg(II) was passed, eluted with 5 ml of 0.1 mol l^{-1} HNO_3 and determined. It is found that, Hg(II) could be removed quantitatively from volume up to 1350 ml, then the recovery decreases remarkably. Therefore, a practical maximum of 270 folds preconcentration factor for Hg(II) was obtained using 5 ml of 0.1 mol l^{-1} HNO_3.

Detection limit of Hg(II):

It means the lowest concentration of Hg(II) below which its quantitative sorption by the modified cellulose is not perceptibly seen. It was investigated for Hg(II) at 10^{-1} - 10^{-3} µg ml^{-1} passed through the column at 2 ml min^{-1} flow rate. The limit of detection (LOD) for Hg(II) ion is 0.5 ppb, showing high sensitivity of the modified cellulose for preconcentration of trace Hg(II).

Applications:

Selective separation of Hg(II) from binary mixtures:

To investigate the selective separation and determination of Hg(II) from its mixture with diverse metal ions (column mode), an aliquot of aqueous solution (500 ml) containing 1 mg Hg(II) and 25 mg of another cation was taken and the recommended procedure was followed (column mode). The results summarized in Table 2 showed that Hg(II) in the binary mixtures is almost sorbed by the modified cellulose up to 25 mg of the diverse ions. It is interesting to note that, no effect on the recovery of Hg(II) in the presence of EDTA under the recommended experimental conditions.

Table (2): Separation of Hg(II) from binary mixtures.[a].

Diverse ion	Recovery% of Hg^{2+} ion
Na^+	100.0 (0.056)[b]
Mg^{2+}	99.7 (0.210)
Ca^{2+}	99.4 (0.553)
Co^{2+}	99.5 (0.480)
Ni^{2+}	100.0 (0.380)
Cu^{2+}	99.6 (0.850)
Zn^{2+}	99.2 (1.180)
Pb^{2+}	100.0 (0.652)
Cd^{2+}	99.6 (0.800)

[a] Initial sample containing 1 mg Hg^{2+} , 25 mg of diverse ions in 500 ml water (column mode)

[b] Values in parentheses are RSD's based on three replicate analyses.

Selective separation of Hg(II) from natural water:

Surface water samples were collected from Nile river water (Mansoura, Dameitta, and Ras EL-Bar) and tap water from Mansoura city. All samples were filtered using a sintered glass G4 and the suspended matter is determined (Table 3). The pH, total dissolved salts (TDS), dissolved oxygen (DO) and total alkalinity (mg $CaCO_3$ l^{-1}) were determined according to the previous methods **[Tashiro *et al.*, (1982)]**. The samples were acidified with concentrated HNO_3 to pH ~ 2 and preserved in polyethylene vessel. The organic matter was digested prior to the separation process. In a 500 ml calibrated flask, 0.5 g of $K_2S_2O_8$ and 5 ml of 98% (w/v) H_2SO_4 were added and completed to the mark with water sample and heated for 30 min at 95°C. After cooling to room temperature, 1 ml of 5 x 10^{-3} EDTA solution was added to the sample and the pH was adjusted to 5 and passed through the column. The sorbed Hg(II) was then eluted by 5 ml of 0.1 mol l^{-1} HNO_3, to give a concentration factor of 270 folds and the elute was analyzed as previously described.

The quality of waters is mentioned in Table (3). Tap, Nile and Sea water samples were analyzed for Hg(II) by the described procedure. Preliminary investigation showed that the method is selective to sorb Hg(II) with high efficiency. Samples of waste water from Talkha (Table 4) showed high concentration of Hg(II); this area is relatively polluted by agricultural effluents and domestic sewage and was chosen because many water creatures were dead. The RSD % was found 0.92 – 1.65. Hg(II) was not found in Tap water of Mansoura city. In other water samples, Hg(II) was detectably low or present in the permissible level.

Table (3): Water quality measurements for the water samples collected from different locations.

Location	Parameters			
	pH	TDS (gl^{-1})	TDO (mg O_2 l^{-1})	Alkalinity (mg $CaCO_3$ l^1)
Tap water (Mansoura city)	7.22	0.12	6.38	130.00
Nile river (Mansoura city)	7.83	0.50	5.54	145.00
Wastewater (Talkha from Meat Antar)	8.25	0.55	7.85	190.00
Nile water (Dameitta city)	8.20	29.20	5.56	183.00
Wastewater (Ras El-Bar from Elborg)	8.14	14.30	6.24	155.00
Sea water (Port Said from Suez canal)	8.19	46.10	5.74	125.00

Table (4): Analysis of water samples using CVAAS for determination of Hg^{2+} in ng ml^{-1} (otherwise indicated) after preconcentration with CELLSAL at pH 5, stirring time 30 min at 25±1 °C (column mode).

Sample location	Experimental value, ($\overline{X}$)	RSD (%)
Tap water (Mansoura city)	ND	-
Nile river (Mansoura city)	0.12	1.0
Wastewater (Talkha from Meat Antar)	0.32	1.68
Nile water (Dameitta city)	0.05	1.52
Wastewater (Ras El-Bar from Elborg)	0.25	1.62
Sea water (Port Said from Suez canal)	0.02	1.50

ND: not detected

CONCLUSION

The newly modified Cellulose (CELLSAL) showed good potential for trace enrichment of Hg (II) ion. The methodology described offers a very simple and fast mean for selective sorption and preconcentration of this metal ion. The elution step does not involve use of organic solvents or higher concentration of acids as other procedures do. In comparison with other types of modified cellulose, the main advantages of CELLSAL were: 1) higher preconcentration factor; 2) higher sorption capacity; 3) low matrix effect; and 4) good precision. obtained Results showed that, CELLSAL can quantitatively sorb very low concentrations of the Hg (II) ion. Beside its stability in different media, it could be recycled for many cycles without any change in its sorption properties. The short loading time ($t_{1/2}$) of CELLSAL is another advantage. It has been demonstrated to be suitable for preconcentration of Hg (II) ion in samples with complicated and variable matrices like seawater. From the economic point of view, the sorption capacity of CELLSAL, after its versatile uses, has been found to be practically unchanged.

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لملخص العربي

تم تعيين اثار من عنصر الزئبق السام باستخدام طريقة تعتمد على السليولوز المحمل بالساليسالدهيد حيث ان السليولوز ناتج من النباتات الطبيعية وهى تعتبر طريقة خضراء كذلك باستخدام طريقة طيف الامتصاص الذرى لبخار الزئبق على البارد وهذه الطريقة حساسة جدا للزئبق كذلك تم دراسة العوامل المؤثرة على طرق التحميل مثل تركيز ايون الهيدروجين والزمن والتداخلات الكيميائية وتم تعيين الزئبق فى مخاليط ثنائية مختلفة وفى المياه الطبيعية.