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Solid phase extraction of Hg (Π) in water samples by nano-Fe_3O_4 encapsulated-dioctylphthalate and linked- diethylenetriamine

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ABSTRACT: A cold vapor atomic absorption spectrophotometric (CVAAS) method for the determination of trace Hg(II) after adsorption of magnetic nano- Fe_3O_4 -DOP- DTA has been developed. The as magnetic nano- Fe_3O_4-DOP-DTA have a good capacity to retain Hg^{2+}, but the raw and purified as magnetic nano-Fe_3O_4-DOP- DTA are found not to adsorb Hg^{2+} ions. This was treated with diethylenetriamine (DTA) in another solvent-free procedure for the formation of a novel nano-Fe_3O_4-DOP-DTA. Cold vapor atomic absorption spectrometry (CVAAS) was utilized for determination of Hg^{2+}. The effects of solution pH solution, elution conditions on pre-concentration of trace Hg^{2+} were studied and the effect of interfering ions was also investigated. Preconcentration factor was 200 .The method was successfully applied to the recovery of Hg^{2+} in different type of water samples. Graphene oxide and its derivate such as magnetic nano- Fe_3O_4 -DOP- DTA in this study is full of potential to use as an excellent adsorbent in the extraction method like solid phase extraction (SPE) and solid phase micro extraction (SPME).

Keywords: *CVAAS, Dioctyl phthalate (DOP) Encapsulate nano-Fe_3O_4, Hg^{2+}, Nano-Fe3O4-DOP, Preconcentration, SPE.*

INTRODUCTION

The properties of nano magnetic particles have attracted many studies on their functionality as magnetic carrier. This characteristic make these elements a fit candidate in a wide range of heavy metal ions application in biology and water samples [1,2], also in medical imaging uses such as magnetic resonance imaging (MRI) [3,4], in isolating substances and materials in anions– cations pre-concentration [5]. In recent years, SPE method have been well used for determination of Hg (II) ions in numerous environmental samples [6,7] because of its simplicity, rapidity, minimal cost, low consumption of reagents and its ability to combine with different detection techniques either in on-line or off-line mode [8]. The main part of the SPE is the sorbent material that determines the selectivity and sensitivity of the technique. Though, the commonly used SPE sorbents, such as C18 silica and graphitic carbon, are often the only suitable option for a limited number of analytes. Reusability of the SPE column is also a prob-

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lem. Thus, developing new SPE sorbent material is important [9]. Carbon derivate is well known for their high adsorption capacity. They have been established to possess excessive potential as adsorbents for removing many types of environmental pollutants such as heavy metals [10,11]: carbon nanotubes (CNTs) [12,13] , Fullerenes can be used as chromatographic stationary phases to offer high selectivity for specific compounds [14,15] or as sorbent materials for on-line clear up and preconcentration [16,17]. Mercury has been considered as a human health hazard because it may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defects [18]. Mercury and mercury compounds are included in all lists of priority pollutants and different regulations and guidelines have been developed limiting their levels in water and sediments [18]. But it plays an important role in science and technology, and inevitably exists in the environment [18]. The detection of mercury has long held the attention of the analytical community and, as such, a large number of protocols have arisen [18]. On the other hand, the toxicity level of mercury is becoming lower and lower, the direct determination of mercury at sub-microgram per liter level is suffered from the matrix interferences. It is evident that the use of separation and preconcentration procedures is still often necessary before the determination step, despite recent advances in analytical instrumentation [18]. Recently, CNTs have been shown to be excellent classes of sorbent materials for SPE [18]. Since the first application of CNTs in SPE by Cai et al that he use multi-walled carbon nanotubes (MWCNTs) [18], In recent years many reports have been distributed focusing on progress of use CNTs-based SPE methods for a great variety of analytes, including phenolic compounds [19], insecticides [20], pharmaceuticals [21,22], inorganic ions [23], organometallic compounds [24]. The one of the important advantage of CNTs for SPE adsorbents is their high surface spaces, which endue CNTs with high sorption capacities. Then, the selectivity of adsorbent (CNTs) can be controlled by covalently or non-covalently modification of the CNTs functional groups. Also, inherent properties of CNTs such as well chemical and thermal stability make them appropriate to be used as adsorbents for SPE column. Other carbon allotropes, for instance graphite and diamond, have also been established as adsorbents in SPE or SPME [25]. Graphene oxide is a novel two-dimensional nanomaterial or in fact can be mention graphene oxide is graphene but with more chemically reactive functionalities [26,27] which can be more functionalized [28,29]. Graphene oxide surface has a significant amount of the sp2-hybridized carbon backbone structure remains intact [30], allowing the nano plate to retain a high degree of planarity, as proven in thin-film deposition and fabrication experiments [31,32], and a consistently high surface to volume ratio [33]. The extraordinary properties of graphene and its derivate like graphene oxide make it a greater candidate as an adsorbent for SPE technique. Firstly, graphene has a large surface area (theoretical value 2630 $m^2 g^{-1}$) [34], suggesting a high sorption capacity. Exactly, both sides of the planar sheets of graphene are accessible for molecule adsorption, while for CNTs and fullerenes, steric hindrance may exist when molecules access their inner walls. Secondly, graphene can be simply modified with functional groups, particularly via graphene oxide which has many reactive groups [35]. Functionalization may more enhance the selectivity and sensitivity of SPE. Thirdly, CNTs usually contain trace amounts of metallic impurities that originate their synthesis and using the metal catalysts. These impurities could have negative effects on the applications of CNTs [36]. Nevertheless, graphene and graphene oxide instead, can be synthesized from graphite without the using metal catalysts. In fact, graphene is a layer of graphite, which does not use of any metal catalysts in its synthesis and exfoliation process. Accordingly, the pure material would be obtained [38]. Separation technique, in general, deal with the separation of components of mixtures to enhance the purity of substances while in preconcentration technique, one of the analytes or species have been selectively retained on a solid phase and then eluted with an appropriate eluent, and detected and quantified by an appropriate detection technique [36]. Actually, the SPE technique using graphene and derivate of graphene such as functionalization graphene oxide as a novel and great adsorbent [39]. Chemical modification of graphene oxide has been a promising way to achieve mass production of chemically modified graphene (CMG) platelets. Graphene oxide contains a range of reactive oxygen functional groups, which renders it a good candidate to use in the above-mentioned applications. In the present work, nano-Fe_3O_4-DOP-DTA was employed for production of solid phase. The synthesized and characterized new sorbent nano-Fe_3O_4-DOP-DTA was utilized for preconcentration of Hg (II) from water samples. Determination of Hg (II) concentration was achieved by CVAAS after preconcentration procedure.

EXPERIMENTAL

Apparatus

The concentration of the metal ion solutions was determined by using the Varian model spectra AA-240 (Mulgrara, Victoria, Australia). The pH-measurements of the metal ion and buffer solutions were carried out by an Orion 420. The size and morphology of graphene oxide was observed by scanning electron microscopy (SEM model LEO 440i), before taken image with SEM the surface of sample was coated with gold. X-ray diffraction (XRD) measurements were carried out with Hg Kα radiation (40 kV, 60 mA, 2ϴ from 5-115). Fourier transform-infrared (FT-IR) spectra were taken in KBr pressed pellets on a FT-IR Thermo hgcolet (USA).

Materials and reagents

All the necessary materials and reagents were of analytical grade and were purchased Merck, Aldrich and Sigma Company. All the dilutions were prepared by ultrapure deionized water. BDH Limited, Poole, England. Dioctyl phthalate, DOP, (purity> 99.55%), sodium hydroxide (NaOH) and diethylenetriamine (DTA) was purchased from BDH, UK.

Synthesis of magnetic nano-Fe_3O_4 sorbent

The magnetic nano-iron oxide was first synthesized according to a previously reported method [2]. A 6.1 g sample of $FeCl_3$-$6H_2O$ and 4.2 g $FeSO_4$-$7H_2O$ were dissolved in 100 mL of distilled water. A total of 25.0 mL of 6.5 M-NaOH was slowly added to the above solution. The reaction mixture was stirred for 4 h using a magnetic stirrer. After the complete addition of NaOH, the formed black precipitate, nano-Fe_3O_4, was then washed several times with distilled water, collected in a pure form by the assistance of an external magnetic field and dried in an oven at 70 °C.

Synthesis of nano-Fe_3O_4-DOP sorbent

The Fe_3O_4-encapsulated-DOP nano-sorbent was prepared by the addition of 20.0 mL of DOP to 10.0 g of nano- Fe_3O_4 sorbent. This mixture was heated under stirring at 80-90 °C for 3 hands the product nano-Fe_3O_4-DOP sorbent was filtered, washed with methanol, collected in a pure form by a magnetic field and dried in an oven at 70 °C until complete dryness.

Synthesis of magnetic nano-Fe_3O_4-DOP-DTA sorbent

A 10.0 g sample of nano-Fe_3O_4-DOP addition to 5 mL of DTA and these two reactants were combined together by heavy grinding and mixing in a mortar for 5 h. The produced nano-Fe_3O_4-DOP-TETA sorbent was heated to dryness in an oven at 60 °C.

Preparation of Solid Phase

Sorption characteristics of Hg(II) ions by magnetic nano-sorbents by the batch equilibrium technique. The applicability of magnetic nano-Fe_3O_4-DOP-DTA sorbent for extraction of Hg(II) ions was studied by the batch equilibrium technique under several experimental controlling factors. These include the effect of pH, contact time, sorbent dosage, initial metal ion concentration and interfering ions.

General procedure

100 ml solution with 50 ngml^{-1} Hg content was prepared as a sample. This solution was added to the magnetic nano-Fe_3O_4-DOP-DTA sorbent and by using buffer solution, its pH was modified to 3.0, followed the container was shaken for 25 min in order to allow easier Hg ions absorption of the nano-Fe_3O_4-DOP-DTA sorbent [36]. At the end of this stage, the nano-Fe_3O_4-DOP-DTA sorbent which had been formed on the bottom layer of the beaker was removed through applying external field with1.4T magnetic powers and was immediately decanted outside the supernatant. 1 mL of 1 molL^{-1} ion of eluent was injected into CVAAS for measurement of Hg(II) ions concentrations.

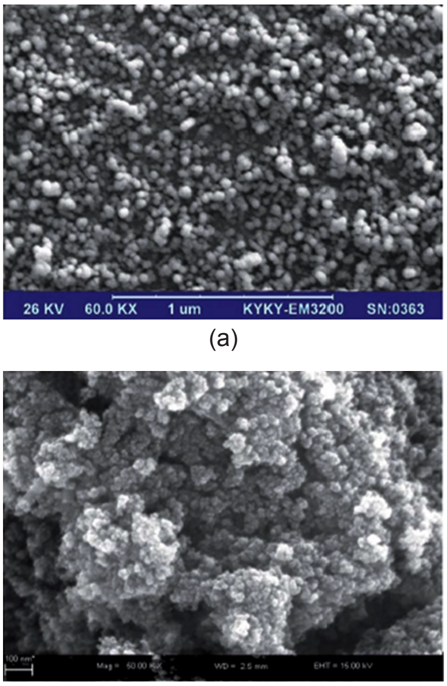
RESULTS AND DISCUSSION

Fig. 1a and b show the morphology and size of magnetic nano-Fe_3O_4-DOP- DTA sorbent as shown in Fig. 1a and b. The particles of nano-Fe_3O_4-DOP-DTA 339 sorbent retained a homogenous distribution in the range of 340 5.0–20.0 nm.

Optimization of SPE procedures

Effect of pH

The metal chelate stability constant and its chemical stability considerably influence the SPE recovery. The pH plays a very important role on metalchelate formation and following extraction. Therefore, pH was the first optimized parameter. pH of the analyte solutions was adjusted to desired values with diluted hydrochloric acid (0.1 mol L^{-1}) and/or ammonia solution (0.1 mol L^{-1}) The variation in recovery of Hg(II) with pH is shown in Fig. 2. According to the results shown in Fig. 2 up to pH 4.5-6.0, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in an acidic solution the protonation of magnetic nano-Fe_3O_4-DOP- ED occurs and there is a weak tendency for retention between Hg (II) and magnetic nano-Fe_3O_4-DOP- DTA, whereas at higher values (pH>6), Hg (II) reacts with hydroxide ions to produce $Hg(OH)_2$. Accordingly, pH 5.0 was selected for subsequent work and real sample analysis.



(a)

(b)

Fig. 1. Images of (a) Scanning Electron Microscopy (SEM) and (b) Transmission Electron Microscopy (TEM) of magnetic nano- Fe_3O_4 -DOP- DTA

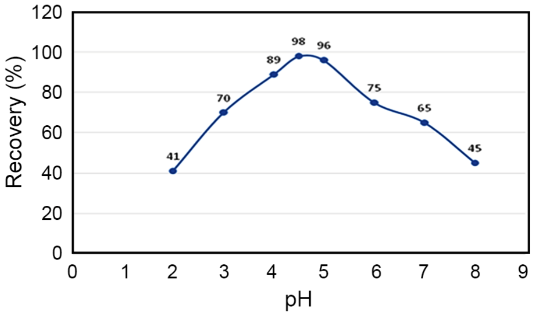


Fig. 2. Influence of sample pH on the percentage recovery of Hg (II), conditions: 100 mg adsorbent, 50 mL of 5 mg/L of Hg ions.

Stability studies

The stability of the newly synthesized magnetic nano-Fe_3O_4-DOP- DTA phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1 M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined revealed that the highest one corresponds to Hg(II), this ion was used to evaluate the stability measurements for the magnetic nano-Fe_3O_4-DOP- DTA phase. The results of this study proved that the magnetic nano-Fe_3O_4-DOP- DTA is more resistant than the chemically adsorbed analog especially in 1.0, 5.0 and 10.0 M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively. Thus, these stability studies indicated the suitability of phase for application in various acid solutions especially concentrated hydrochloric acid and extension of the experimental range to very strong acidic media which is not suitable for other normal and selective chelating ion exchangers based on a nano polymeric matrix. Finally, the magnetic nano-Fe_3O_4-DOP-DTA phases were also found to be stable over a range of 1 year during the course of this work.

Effect of shaking time studies

The effect of shaking time on the percentage extraction of metal ions at various equilibration time intervals (1, 5, 10, 15, 20, 25 min) was also studied and evaluated as

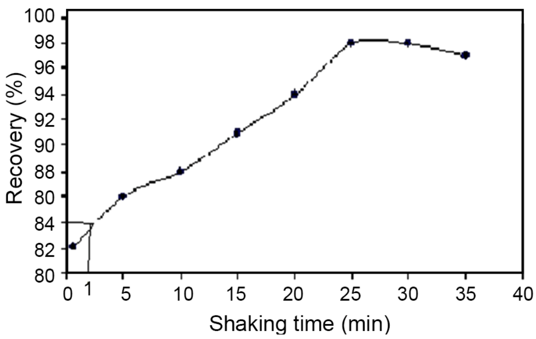


Fig. 3. Effect of shaking time (min) on the percentage extraction of Hg(II) by the magnetic nano-Fe_3O_4-DOP- DTA phases.

μmol g^{-1} and correlated to that determined at 30 min shaking time. Fig. 3 represents the percentage extraction versus shaking time in min and clearly reflects the rapid exchange equilibrium between magnetic nano-Fe_3O_4-DOP-DTA phase and Hg(II). One minute shaking time was found to be sufficient to establish 84% of the determined μmol g^{-1} value at 30 min whereas 10 min shaking time led to 90% extraction. The data and results presented in this section reveal the superiority of magnetic nano-Fe_3O_4-DOP-DTA phase as previously declared in the stability studies.

Distribution coefficient (K_d)

The distribution coefficient (K_d) data of the tested metal ions with the two newly magnetic nano-Fe_3O_4 -DOP- ED phase are summarized in Table 1. It is evident that Hg(II) is the strongest sorbed metal ion by magnetic nano-Fe_3O_4-DOP- DTA phase. The distribution coefficient values of Hg(II) by the loaded magnetic nano- Fe_3O_4 -DOP- DTA phase were found to be much higher than those reported for ion exchange resins containing magnetic nano- Fe_3O_4 -DOP- DTA derivatives [37]. In addition, the K_d values for Hg(II) by magnetic nano-Fe_3O_4-DOP- DTA phase were found to come on the second place after Hg(II) which behavior can be interpreted on the basis of the affinity of both nitrogen and hidroxyl donor groups present in magnetic nano-Fe_3O_4-DOP- DTA for binding with Hg(II) [38-49]. On the other hand, the various tested metal ions as shown in Table 1 were found to exhibit lower tendency to bind with magnetic nano-Fe_3O_4-DOP-DTA phase judging from the comparable low distribution coefficient values determined for these metal ions. The higher K_d value for Hg(II) and the lower ones for the other metal ions, except Hg(II), provide an additional evidence for the suitability of these two newly magnetic nano-Fe_3O_4-DOP- DTA phase for selective extraction of Hg(II) from aqueous solutions. It is also noteworthy that the conclusion drawn from the evaluation of the K_d values by magnetic nano-Fe_3O_4 -DOP- DTA phase is consistent with the reported data.

Table 1. Distribution coefficient (Kd) values of various metal ions.

Metal ions	K_d
Mn(II)	77
Fe(III)	88
Co(II)	69
Cd (II)	50
Cu(II)	84
Ni(II)	553
Cu(II)	263
Hg (II)	2100
Pb(II)	920

Preconcentration of Hg (II) from natural water for off-line CVAAS

This study was undertaken in order to evaluate the potential application of magnetic nano-Fe_3O_4-DOP-DTA phase for pre-concentration of trace levels of Hg(II) in natural water samples. Drinking tap water was used without prior treatments as an example and compared with double distilled water (DDW) to evaluate and investigate the matrix effect. Both drinking tap water and DDW (2 l) were spiked with 20 pg ml^{-1} of Hg(II). Several pre-concentration reagents are well known and extensively examined for desorption of the bound metal ions from the surface of the stationary phase and these include mainly, hydrochloric and nitric acid, thiourea HCl [49]. However, some of these reagents are usually characterized by adsorption on the surface of magnetic nano-Fe_3O_4-DOP- DTA which lead to severe change in the nature of packing material as well as non-reproducible results if the column used in future applications. The efficiency of metal ion preconcentration especially Hg(II), by 10.0M HCl acid is found to be high without causing any notable change to the chemical nature of the organic magnetic nano-Fe_3O_4-DOP- DTA. Therefore, 10.0 ml of 10.0 M HCl was used for the elution of the adsorbed Hg(II) from the column bed. The preconcentration factor targeted

Table 2. Effect of foreign ions on the percent recovery of 5 ppm Hg in water samples.

Ions	Amount taken (mg)	%Recovery
Na^+	10	101 (2.5)[a]
K^+	10	101 (2.5)
Ca^{2+}	10	100 (3.2)
Mg^{2+}	10	99 (3.8)
Fe^{3+}	8	2.2))100
Cr^{3+}	8	2.2))99
Co^{2+}	5	2.2))100
Cl^-	5	2.0))100
Br^-	2.5	2.5))97
F^-	2.5	100 (2.3)
Mn^{2+}	2.5	2.2))99
Zn^{2+}	2.5	2.7))97

Table 3. Analytical figures of merits for Hg.

Parameters	
RSD% n=10	0.88%
LOD(µm/L)	0.25
LOQ(µm/L)	0.883
Enrichment factor	200
calibration equation	Y = 0.06x - 0.0002
correlation coefficient	0.999

from this study is 100 as given. As the results indicate, the off-line detection results of the eluted and pre-concentrated Hg(II) are very good with a satisfactory preconcentration factor which can be further increased to 200-fold. Moreover, natural tap water sample was found to give very close results to that reported for DDW sample and this comparison indicates that the matrix effects of the dissolved inorganic and organic matters played an insignificant role in the aimed selective extraction, removal and preconcentration of Hg(II) by magnetic nano-Fe_3O_4-DOP- DTA phase.

Effect of foreign ions

Effects of foreign ions were also investigated on the measurements of Hg (II). Here a certain amount of foreign ion was added to 50 ml of sample solution containing 100 ng of each Hg (II) with a pH of 4.5. The amounts of the foreign ions and the percentages of the recovery of Hg (II) are listed in Table 2. As it is seen, it is possible to determine lead without being affected by the mentioned ions.

Figures of merits in method

In calibration curve was linear dynamic rang 1.0 ng/ml to 7.0 mg/ml for Hg. As analytical figures of merit, limit of detection (LOD), limit of quantification (LOQ) defined as $3S_B/m$ and $10S_B/m$, relative standard deviation (RSD) for the proposed preconcentration and speciation method have been determined and listed in Table 3.

Determination of Hg in natural tap water samples

In addition, the effect of packing amount of silica gel phase is also evident in Table 4, where the near completion of Hg(II) removal was accomplished by the use of 5 mg phase. The results of the preconcentration of Hg(II) from aqueous solutions are presented in Table 4 of Hg(II) from DDW and natural tap water samples. Real samples marked 1 to 5, were collected at the at the distances of 5, 100, 250, 350 and 500 metres of the total waste water of electroplating plants in the eastern parts of Varamin, respectively. The total

Table 4. Determination of Hg in real water samples.

Sample	Taken amount (µg)	cold vapor atomic absorption spectrometry (CVAAS) (µg)	%Recovery
Tap water (Tehran, Iran)	0	2.8)[a])4.2	-
	30	2.9))33.08	98.5
Tap water (Pakdasht, Tehran, Iran)	0	2.8))1.2	-
	30	3.5))33.1	100.5
Mineral water (Damavand Company)	0	N.D[b]	-
	30	3.2))30.09	98

a) Values in parentheses are RSD based on four replicated analyses.

b) No adsorption, passes through column

Table 5. Comparison of the total results of the proposed method with ICP-AES [a].

Sample	Hg^{2+} (mg.mL^{-1}) SPE- CVAAS	Hg^{2+} (mg.mL^{-1}) ICP-AES	F-test [c]	T-test [d]
1	16.5±0.5[b]	16.6±0.7	3.1	0.5
2	14.6±0.3	14.7±0.5	1.8	0.8
3	7.9±0.8	8.1±0.7	2.7	0.9
4	3.6±1.3	3.5±1.1	2.0	0.6
5	1.8±0.9	1.7±0.9	2.1	0.7

a All real samples were diluted 50 times before analysis.
b Mean ± standard deviations based on five individual replicate analyses.
c Tabulated F-value for (4,4) degrees of freedom at p (0.95) is 6.39.
d Tabulated T-value for 8 degrees of freedom at p (0.95) is 2.306.

Table 6. Comparison of published results of several on-line or several methods for determination of Hg^{2+}.

Technique	Sorbent	RSD(%)	Duration of SPE	Enhancement factors	LOD (µg /L)	Ref.
SPE & CVAAS	Dimethylglyoxim/sodiumdodecyl sulfate-immobilized on alumina-coated magnetite nanoparticles (DMG/SDS-ACMNPs)	1.9%	15	25	4.6	49
SPE & CVAAS	2-{4-[2-(1H-Indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl}-N′-(pyrrol-2-ylmethyliden) acetohydrazide (ICOTPA)	4.0%	25	30	0.27	50
SPE &VAAS	as magnetic nano- Fe_3O_4 -DOP- DTA	0.88%	20	50	0.25	Present method

results obtained by the recommended procedure and ICP-AES have compared in Table 5. As it is seen, the results obtained by the proposed method and ICP-AES are in agreement with each other. Moreover, as it is expected, the Hg (II) concentration decreases as the distance from the electroplating plants increases.

CONCLUSIONS

The proposed SPE method possesses advantages such as easiness, and considerable selectivity in comparison with the previously reported procedures for isolation and determination of Hg^{2+} contents (Table 6). In summary, a selective and sensitive method for the determination of trace levels of Hg(II) based on magnetic nano-Fe_3O_4-DOP- DTA as a sorbent for the determination of the analytes in water samples. In addition, the preparation of magnetic nano-Fe_3O_4-DOP-DTA is relatively simple and rapid. However, the magnetic nano-Fe_3O_4-DOP- DTA sorbent has some drawbacks include lower reusability and stability, which can be repeated only 10 cycles [51-53]. This may make it difficult to put into practical use and should be a subject of further investigations.

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