

Perconcentration of Mercury (II) from Natural Water by Activated Charcol -loaded Schiff's Base 2-Propylpiperidine-1-Carbodithioate (PPCD) Phases

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Abstract: Activated Charcol phase loaded with 2-propylpiperidine-1-carbodithioate (PPCD) were synthesized based on chemical binding and physical adsorption approaches. The stability of a chemically modified PPCD especially in concentrated hydrochloric acid which was then used as a recycling and pre-concentration reagent for further uses of activated Charcol immobilized PPCD. The application of this activated Charcol for sorption of a series of metal ions was performed by using different controlling factors such as the pH of metal ion solution and the equilibration shaking time by the static technique. This difference was interpreted on the basis of selectivity incorporated in these sulfur containing activated Charcol phases. Hg (II) was found to exhibit the highest affinity towards extraction by these activated Charcol phases. The pronounced selectivity was also confirmed from the determined distribution coefficient (K_d) of all the metal ions, showing the highest value reported for mercury (II) to occur by activated Charcol immobilized PPCD phase. The potential applications of activated Charcol immobilized PPCD phase for selective extraction of mercury(II) to occur from aqueous solution were successfully accomplished as well as pre-concentration of low concentration of Hg(II) (40 pg ml^{-1}) from natural tap water with a pre-concentration factor of 200 for Hg(II) off-line analysis by cold vapor atomic absorption analysis.

Keywords: SPE (solid phase extraction), mercury (II), activated Charcol, 2-propylpiperidine-1-carbodithioate (PPCD)

INTRODUCTION

The direct determination of trace metals especially toxic metal ions such as mercury, tin lead and metalloids arsenic, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden *et al*, 1976). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest (Jones *et al*, 1983). This paper describes the applications of activated Charcol phase-impregnated 2-propylpiperidine-1-carbodithioate (PPCD) for selective extraction and solid phase pre-concentration of mercury (II) from aqueous and natural water samples.

Mercury has been considered as a human health hazard because it may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defects (IARC1993). 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 (Jin *et al*, 2003; Seiler *et al*, 1998). But it plays an important role in science and technology, and inevitably exists in the environment Seiler. The detection of mercury has long held the attention of the analytical community and, as such, a large number of protocols have arisen (Smith, 1963; Kantipuly *et al*, 1990;

Greenway *et al*, 1993; Manzoori *et al*, 1998). 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 (Pereira *et al*, 2003).

Recently, the solid-phase extraction (SPE) is being utilized for preconcentration of heavy metals due to its flexibility, economical and environmental-friendly, absence of emulsion, speed and simplicity, sampling in the field, safety and ease of automation(Thurman, Solid-Phase Extraction *et al*,1998; Mazlum Ardekany *et al*,2003, Mahmoud *et al*, 1997, Moghimi *et al*, 2006).But the selectivity associated with SPE using solid support such as active carbon (Koshima *et al*,1980), ionexchange resins (Swain *et al*, 2000), chelating fibers(Chang *et al*,2001; Moghimi, 2006; Yang *et al*, 2004) and chelating resins(Tewari *et al*,2000; Guo *et al*, Anal. Chim. Acta 2004; Guo *et al*, Talanta 2004) etc., is still to be improved for specific element. Nowadays, metal ion imprinted polymers (MIIP) have been investigated as highly selective sorbents for SPE in order to concentrate and clean up samples prior to analysis. One potential application that has recently attracted widespread interest is their use for clean up and enrichment of analytes

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present at low concentrations in complex matrices (Bae *et al.*, 1998; Daniel *et al.*, 2003; Daniel *et al.*, 2003; Rao *et al.*, 2004; Ensing *et al.*, 1999; Liu *et al.*, 2004).

The aim of this work was the development of a rapid, efficient and highly sensitive method for selective extraction and concentration of ultra trace amounts of Hg^{2+} ions from aqueous media using activated Charcol -loaded Schiff's base 2-propylpiperidine-1-carbodithioate (PPCD) phases and CV-AAS determination .

EXPERIMENTAL

Reagents and materials

Analytical grade nitrate salts of Hg, Mn, Fe and Cr lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II) and copper(II) of reagent grade and activated Charcol were of the highest purity. Ultra pure organic solvents were obtained from E. Merck, Darmstat, Germany, and High Purity deionized water was used throughout the experiments and 3-chloro propyl trimethoxysilane was received from Aldrich Chemical, USA. Organic solvents were dried according to conventional methods.

Apparatus. A Perkin-Elmer AA-6800 atomic absorption spectrometer in conjunction with a

Perkin-Elmer FIAS-400 flow injection system and an AS-90 autosampler were used in this study. The mercury was determined by flow injection cold vapor atomic absorption spectrometry (CV-AAS) modified from the published method (Mazlum *et al.*, 2003). A Perkin-Elmer mercury electrodeless discharge lamp operated at 180mA was used as the light source. The mercury absorbance was measured at 253.6 nm with the bandwidth 0.7 nm. The mercury compounds were reduced to metallic mercury with sodium tetrahydroborate and the mercury generator was operated with argon as carrier gas. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353). For all solutions double distilled water was used and the buffer solutions were prepared from 1.0M sodium acetate to which different volumes of 1.0M HCl; HNO_3 were mixed and the pH-value of the resulting solution was adjusted with the use of a pH- meter.

Preparation activated Charcol -loaded PPCD phases

Activation of surface activated Charcol was filtered, washed with toluene, ethanol and diethyl ether and dried in an oven at 70 °C for 6 h. An amount of 20.0 g of dry activated Charcol were added to 5.12 g (20 mmol) PPCD already dissolved in 400 ml dry and hot toluene in the presence of a few drops of pyridine and the reaction mixture was refluxed for 6 h. The resulting phase was filtered, washed with

toluene, ethanol and finally with water several times until the filtrate showed no characteristic colour of adsorbed PPCD. The phase was then dried in an oven at 60 °C for 7 h. activated Charcol physically adsorbed PPCD phase was prepared by reflux of 20.0 g of activated Charcol and 5.12 g PPCD in 400 ml toluene for 6 h. Phase was also washed and dried as mentioned above.

2.4. Stability studies

The stability of activated Charcol phases in different buffer solutions (pH 1–6) and concentrated hydrochloric and nitric acids was studied by batch equilibration. In this procedure, 500 mg of the phase was mixed with 50 ml of the selected solution in 100 ml measuring flask and automatically shaken for 5 h. The mixture was filtered, washed with 500 ml water and dried in an oven at 80 °C. Around 100 mg of the treated phase was added to 1.0 ml of 0.1M mercury (II) and 9.0 ml of 0.1M sodium acetate and the mixture was shaken for 30 min by an automatic shaker. The percentage of hydrolysis of PPCD from the surface of modified activated Charcol phases in different acidic solutions was calculated from the determined $\mu\text{mol g}^{-1}$ value of each treated phase.

Sorption studies

Determination of metal capacity values ($\mu\text{mol g}^{-1}$)

The determination of metal capacity of 13 metal ions, viz. Ba(II) Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Hg(II), Mg(II), Mn(II), Ni(II), Pb(II) and Zn(II) as a function of pH was studied by the static technique. Then 100 mg of the dry phase was added to a mixture of 1.0 ml of 0.1M metal ion and 9.0 ml of the buffer solution (pH 1–6 and 0.1M sodium acetate) in 50 ml measuring flask. The mixture was then automatically shaken for 30 min, filtered, washed with 50 ml water and the unbound metal ion was subjected to complexometric titration using the proper buffer and indicator solutions and/or atomic absorption analysis. The effect of shaking time on the percentage extraction of metal ions was also studied for only Hg(II) by the static technique. In this, 100 mg of the activated Charcol phase was added to 1.0 ml of 0.1M Hg(II) and 9.0 ml of 0.1M sodium acetate in 50 ml measuring flask and automatically shaken for the selected period of time (1, 5, 10, 20, 25, 30 and 35 min). The mixture was filtered, washed with 50 ml water and the free metal ion was determined as described above.

The effect of the pH

The pH of the sample solutions were adjusted to different values between 2-9 by addition of hydrochloric acid or a suitable buffer such as sodium acetate-acetic acid or sodium dihydrogen phosphate- disodium hydrogen phosphate, and then solutions passed through the disks.

Eventually, the metal ions were stripped by pure methanol or ethanol solutions followed by cold vapor atomic absorption spectrometry (CV-AAS) of the eluted mercury(II). Then, percentage recovery at various pH values was determined (Fig. 1). According to the results shown in Fig. 1 up to pH 2.5-7.5, 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 (PPCD) occurs and there is a weak tendency for retention between Hg(II) and (PPCD), whereas at higher values (pH>7.5), Hg(II) reacts with hydroxide ions to produce Hg(OH)₂. Therefore, sodium acetate-acetic acid buffer with pH=5 was used for the preconcentration step. Other solvents used for dissolving (PPCD) were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared and shown in Fig. 1. Mean while, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions and incompatibility with flame. Higher pH values (>7) were not tested because of the possibility of the hydrolysis of octadecyl silica in

Determination of the distribution coefficient

About 100 mg of the activated Charcol phase was mixed with 50 ml of the metal ion (1 mgml⁻¹) in a 100 ml measuring flask and shaken for 3 h by an automatic shaker. The mixture was filtered, washed with water and diluted with 2% nitric acid solution in order to fit in the linear dynamic range of each metal ion. A standard solution for each metal ion was also prepared in a similar way.

Percentage removal of mercury(II) from aqueous solutions

One liter of Hg(II) solution, containing 10, 50 and 100 ng ml⁻¹ was passed over a column (Mazlum *et al*, 2003) packed with 500 and 1000 mg each of activated Charcol. The flow rate was adjusted to 2.0 ml min⁻¹. The eluents were collected and 5ml was diluted with 20 ml of 2% nitric acid solution and subjected to cold vapor atomic absorption spectrometric analysis (CV-AAS).

RESULTS AND DISCUSSION

Stability studies

The stability of the newly synthesized activated Charcol phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in Section 3.2 revealed that the highest one corresponds to Hg(II), this ion was used to evaluate the stability measurements for the activated Charcol phase (Moghimi 2006). The results of this study proved that the activated

Charcol -chemically immobilized PPCD phase is more resistant than the chemically adsorbed analog especially in 1.0, 5.0 and 10.0M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively. However, the use of nitric acid with different concentration values (1.0, 5.0, 10.0 M) was found to change the color of activated Charcol phases from dark brown into reddish brown which is interpreted on the basis of chemical changes of the organic PPCD modifier via oxidation. In addition, stability of phases was also confirmed from the interaction with 10.0M hydrochloric acid for more than 1 week. This test proved a reasonable stability of activated Charcol phase compared to non-treated silica gel phases judging from the color change of the two phases as well as the metal capacity values determination of Hg(II) and comparison of these with those of the original non-treated activated Charcol phases. 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 polymeric matrix (Mahmoud 1997). Finally, the Charcol phase -loaded PPCD phases were also found to be stable over a range of 1 year during the course of this work.

covery of mercury added to 1000mL of different water samples (containing 0.1M acetate at pH= 5.5-6.0).

Sample	Hg ²⁺ added (µg)	Hg ²⁺ determined (ng mL ⁻¹)
Tap water	0.0	1.10(0.9) ^a
	10.0	11.12(1.3)
Snow water	0.0	NAPD ^b 10.53(1.9)
	10.0	
Rain water	0.0	NAPD 10.72(0.9)
	10.0	
Sea Water	0.0	11.56(1.7)
	10.0	21.96(1.6)

Values in parentheses are RSDs based on five individual replicate analysis
^b No adsorption, passes through disk

Percentage removal of Hg (II) from aqueous solution

In this study, we attempted to evaluate the percentage recovery of Hg(II) with different spiked concentrations, namely 10, 50 and 100 ng ml⁻¹ from 1 l of 0.1M NaOAc solution by the application of two different amounts (500 and 1000 mg) of activated Charcol -loaded PPCD phase packing. The results of the percentage removal of Hg(II) from aqueous solutions are presented in Table 1 which clearly demonstrate the suitability and validity of activated Charcol immobilized PPCD phase for removal and extraction of Hg(II). In addition, the effect of packing amount of silica gel

phase is also evident in Table 1, where the near completion of Hg(II) removal was accomplished by the use of 1000 mg phase. To assess the applicability of the method to real samples, it was applied to the extraction and determination of mercury from different water samples. Tap water(Tehran, taken after 10 min operation of the

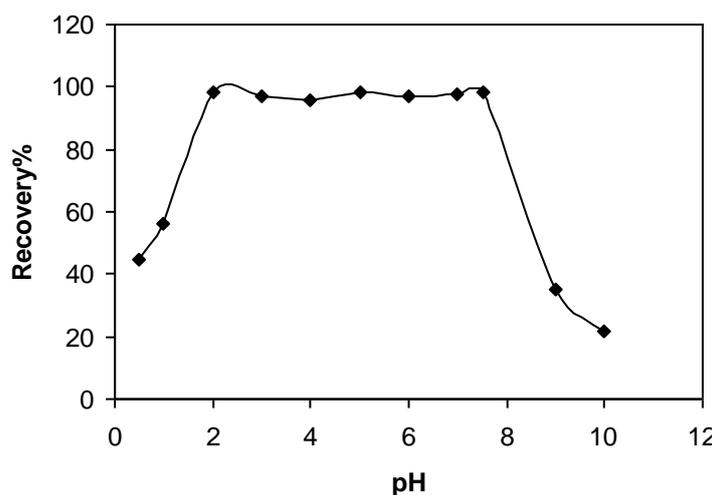
tap),rain water(Tehran, 23january, 2010), Snow water (Saveh , 8 February, 2010)and Sea water(taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed(Table 2). As can be seen from Table 2 the added mercury ions can be quantitatively recovered from the water samples used.

Table 1 .Percentage removal of Hg (II) from aqueous solutions by activated Charcol -loaded PPCD phase ^a

Hg(II) spiked (ng ml ⁻¹)	Phase (mg)	Percentage removal
10	500	94±1.5
50	500	96±3
100	500	94±6
10	1000	99±5
50	1000	98±2
100	1000	98±3

^a Values are based on triplicate analysis.

Fig. 1. Influence of sample pH and dissolving solvent of PPCD on the percentage recovery of Hg (II).



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