

Removal and recovery of mercury(II) from hazardous wastes using 1-(2-thiazolylazo)-2-naphthol functionalized activated carbon as solid phase extractant

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Abstract

As a part of removal of toxic heavy metals from hazardous wastes, solid phase extraction (SPE) of mercury(II) at trace and ultra trace levels was studied using 1-(2-thiazolylazo)-2-naphthol (TAN) functionalized activated carbon (AC). The SPE material removes traces of mercury(II) quantitatively in the pH range 6.0 ± 0.2 . Other parameters that influence quantitative recovery of mercury(II), viz. percent concentration of TAN in AC, amount of TAN-AC, preconcentration time and volume of aqueous phase were varied and optimized. The possible means of removal of Hg(II) from other metal ions that are likely to be present in the wastes of the chloroalkali industry is discussed. The potential of TAN-functionalized AC SPE material for decontaminating mercury from the brine sludge and cell house effluent of a chloralkali plant has been evaluated.

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1. Introduction

Mercury is highly toxic and cumulative poison. Mercury and its compounds especially methyl mercury is a neurotoxin and causes blockages of the enzyme binding sites and interferes in protein synthesis. Moreover, inorganic mercury, especially soluble mercury species, can be transformed into methyl mercury by the action of microorganisms under aerobic conditions. The safe limits for inorganic Hg(II) in drinking water and industrial waste water are 1.0 and 0.05 $\mu\text{g/ml}$, respectively. Hence, the contamination of Hg from brine sludge and effluents of chloralkali industry is more important compared to wastes from other industries such as paper and pulp, manufacture of vinyl chlorides, paints, pesticides, fungicides and cinnabar processing. In In-

dia, although the industries producing cast alkali have been switched over to more environmentally friendly membrane-based processes still 50% of chloralkali industries are based on mercury cell process. Hence, the removal and recovery of mercury from these hazardous wastes assumes increasing importance.

Conventional mercury treatment techniques include sulphate or hydrazine precipitation [1,2] ion-exchange, cementation [3,4], liquid-liquid extraction (LLE) [5,6] and solid phase extraction (SPE) via carbon adsorption [7]. SPE has several advantages [8–11] over other separation techniques in view of: (i) trace and major concentrations of mercury present in hazardous samples can be removed with equal ease; (ii) higher enrichment factors; (iii) reusability of the adsorbent; (iv) absence of emulsion; (v) minimal costs due to low consumption of reagents; (vi) ease of automation; (vii) environmental friendly; and (viii) safety with respect to hazardous samples. Accordingly, several solid phase

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Table 1
Summary of SPE preconcentration procedures developed for mercury since 1990

S. no.	Reagent	pH	Linear range ($\mu\text{g}/\text{ml}^{-1}$)	Detection limit (ng l^{-1})	Application	Reference
1	HMDC mixed with polyurethane foam	–	–	–	Na salts	[12]
2	Cysteine immobilized controlled pore glass	–	–	–	–	[13]
3	Biomass/seaweed immobilized in silica gel	5.5	–	–	–	[14]
4	Dithiocarbamate resin	–	–	0.28	–	[15]
5	Foam-PAP sorbent ($\mu\text{g}/\text{g}$)	–	–	0.1	–	[16]
6	Zr-loaded activated charcoal	–	–	–	–	[17]
7	Dithizone anchored PVP	–	–	–	–	[18]
8	Dithiocarbamate-loaded polyurethane foam	0.5–5.0	–	120/300	–	[19]
9	Crosslinked chitosan	4–10	30–40	12	Waters	[20]
10	Methylthiosalicylate functionalized silica gel	–	5–1000	–	Sea water and Biological samples	[21]
11	Dithizone immobilized on surfactant-loaded alumina	–	–	–	River and tap water	[22]
12	Dithizone-loaded silica gel	–	–	20	Tap water	[23]
13	6-Mercaptopurine-loaded polystyrene DVB (8%) (ng/ml)	5.5–6.0	Upto 19	20	Environmental samples	[24]
14	Dibenzodiazathia-18-crown-6-dione modified C_{18} silica membrane disc	–	–	3	–	[25]

extractants have been employed for enrichment of traces of mercury from dilute solutions. The salient features of these procedures reported in literature since 1990 are summarized in Table 1. However, very few SPE procedures were described for removal/recovery of mercury from real hazardous waste samples.

Activated carbon (AC) was used: (i) for enrichment of mercury(II), based on treatment with stannous chloride and liberated Hg vapour was carried by a stream of air or argon for subsequent determination by atomic absorption spectrometry (AAS) [26]; and (ii) collection of Hg by volatilization and trapping in gold trap of an AAS [27]. Nagatsuka and Taniyazaki [28] described an enrichment of Hg(II) over a pH range of 6.0–8.0 in the presence of pyrrolidine carbodithioate onto spectrographic carbon powder. Rao and Preetha [11] have reviewed various solid phase preconcentrative separation procedures of inorganics using naphthols as reagents. Hafez et al. [29] described the preparation of 1-(2-pyridylazo)-2-naphthol (PAN) functionalized chloromethylated polystyrene and has been used for preconcentration of ng/ml of Hg(II) from natural waters and subsequent determination by cold vapour atomic absorption spectrometry. PAN and 1-nitroso-2-naphthol functionalized neutral polymeric resins such as Amberlite XAD-4 and XAD-7 have been used for preconcentration of several toxic heavy metals including Hg(II) [30]. This procedure has not been applied to any real samples. Further, to our knowledge, there are no reports wherein 1-(2-thiazolylazo)-2-naphthol (TAN) functionalized SPEs were described for preconcentrative separation of Hg(II).

This paper reports the use of solid phase extractant 1-(2-thiazolylazo)-2-naphthol functionalized activated carbon for the removal and recovery of Hg(II) from brine sludge and cell house effluents of a chloralkali industry M/s Travancore Cochin Chemicals Limited, Cochin, India.

2. Materials and methods

Activated carbon, 1-(2-thiazolylazo)-2-naphthol was obtained from Aldrich, Milwaukee, WI, USA. All other chemicals used were of Analytical Reagent grade. A Hitachi-220 double beam spectrophotometer was used for estimation of Hg(II). LI-120 digital pH meter (ELICO, India) was used for pH measurements.

2.1. Preparation of TAN-functionalized AC

0.20 g of TAN was dissolved in minimum amount of acetone and was poured as a fine stream into 500 ml of water containing 10 g of AC with constant stirring at room temperature. The resulting solution was stirred for 1 h and was allowed to settle for 5 min. Then, it was filtered through a filter paper placed in a Buchner funnel by suction, washed with water and dried in an oven at 80 °C for several hours and then stored in a desiccator.

2.2. Solid phase extraction studies and analysis procedures

0.2 g of TAN-functionalized AC was added to 1.0 l of aqueous solution containing 5 μg of Hg(II) whose pH was adjusted to 6.0 ± 0.20 after adding 10 ml of 1.0 mol/l of ammonium acetate. This solution was stirred for 10 min at a stirring rate of ~ 1400 rpm and the Hg(II) adsorbed on TAN-functionalized AC was eluted with 2×10 ml of 1.0 mol/l HNO_3 . Hg(II) concentration in the eluent was determined spectrophotometrically using Iodide-Rhodamine 6G procedure [31]. A double beam microprocessor controlled Hitachi-220 spectrophotometer was used for measuring the absorbances. Metal ions such as Mg(II), Ca(II) and Ba(II) were determined through standard volumetric procedures [32].

Table 2
Effect of time of stirring on percent recovery of Hg(II)

Time (min)	Recovery of Hg(II) (%)
10	9.1
60	19.3
120	20.5
240	25.0

Hg(II) = 5 $\mu\text{g/l}$, AC = 0.2 g.

3. Results and discussion

3.1. Studies with activated carbon

The effect of time of stirring on the removal of 5 μg of Hg(II) present in 1 litre (at pH ~ 6.0) by activated carbon is shown in Table 2. The percent recovery was found to be $\sim 25\%$ even after stirring for 240 min. The removal of Hg(II) at a stirring time of 10 min as a function of carbon dosage by AC is shown in Fig. 1. It is clear that a minimum carbon dosage of 200 mg of AC was enough for maximum removal of Hg(II) when its concentration was maintained at 2 mg/l.

3.2. Studies with TAN modified AC

The SPE of 5 μg of Hg(II) present in 1.0 l of aqueous solution containing 10 ml of 1.0 mol/l ammonium acetate (pH 6.0 ± 0.2) onto 2% TAN-functionalized AC showed quantitative recovery. Various parameters that influence the recovery of Hg(II) at trace levels were studied. Table 3 shows the typical results obtained on the removal of Hg(II) from 1.0 l of sample solutions.

3.2.1. Effect of pH

The effect of pH on the recovery of 5 μg of Hg(II) present in 1.0 l of solution was studied. Mercury was quantitatively removed in the pH range 5.8–6.2 (see Table 3). The low recovery of Hg(II) in the pH range 5.0–5.5 is due to partial dissociation of Hg(II)–TAN complex due to relatively high acidity. Furthermore, the low recovery of Hg(II) at pHs >7.0 is due to the formation of mercuric hydroxide which again dissociate Hg(II)–TAN complex. Hence, in all subsequent work, the pH was adjusted to 6.0 ± 0.2 after the addition of 10 ml of 1.0 mol/l of ammonium acetate buffer.

3.2.2. Effect of TAN concentration in activated carbon

The concentration of TAN in AC was varied from 0.1 to 2.0%. The recovery of 5 μg of Hg(II) present in 1.0 l of solution was quantitative when the concentration of TAN in AC was greater than 2.0% (see Table 3). Hence, 2% TAN-functionalized AC was used in subsequent studies. Further, a minimum of 0.1 g of TAN-functionalized AC is required for quantitative removal of Hg(II).

3.2.3. Effect of time of stirring

The time of stirring was varied from 5 to 60 min during recovery of 5 μg of Hg(II) present in 1.0 l of solution by using TAN-functionalized AC. The results obtained are shown in Table 3 from which it is clear that a minimum of 10 min of stirring time was enough for quantitative removal of Hg(II) by TAN-functionalized AC. Ten minutes of stirring time was used in all subsequent experiments. Under these conditions, the recovery of Hg(II) using AC alone is $\sim 9.0\%$.

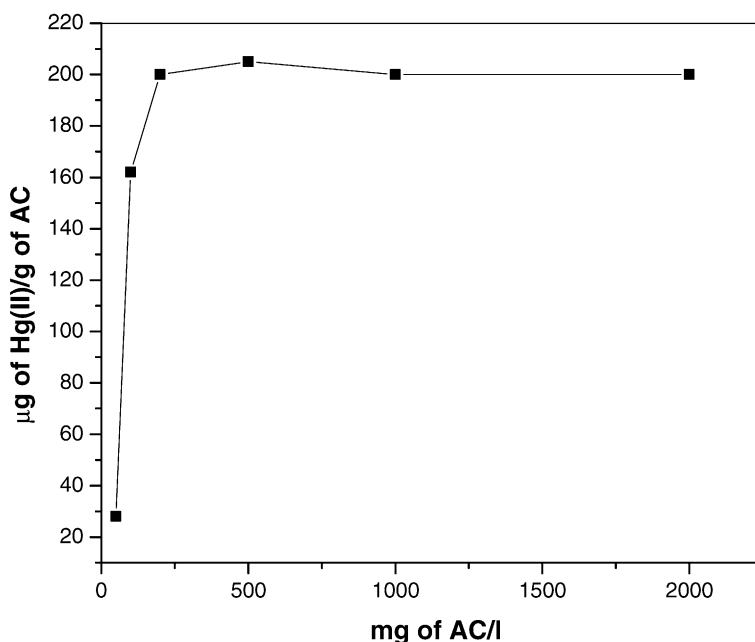


Fig. 1. Effect of carbon dosage on the removal of Hg(II) by AC (Hg(II) concentration = 2 mg/l; pH = 6.0 ± 0.2 ; stirring time = 10 min; stirring rate = 1400 rpm).

Table 3
Influence of various parameters on the recovery of mercury from dilute aqueous solutions

Parameter								
pH	5.0	5.5	5.8	6.5	6.2	7.5	8.0	9.5
Recovery (%)	5.8 ± 0.1	81.8 ± 0.2	>99.9	>99.9	>99.9	91.0 ± 0.2	15.0 ± 0.1	11.6 ± 0.1
TAN on AC (%)	0.1		1.0		2.0		5.0	
Recovery (%)	67.7 ± 0.1		89.0 ± 0.2		>99.9		>99.9	
Amount of TAN-functionalized AC (g)	0.05		0.1		0.2		0.5	
Recovery (%)	45.0 ± 0.1		>99.9		>99.9		>99.9	
Time of stirring (min)	5		10		30		60	
Recovery (%)	90.5 ± 0.2		>99.9		>99.9		>99.9	
Aqueous phase volume (ml)	25		50	100		250		1000
Recovery (%)	>99.9		>99.9	>99.9		>99.9		>99.9

Hg(II) = 5 µg, pH 6.0, 2% TAN-functionalized AC, 0.2 g of TAN-functionalized AC, 10 min preconcentration time, 1.0 l of Aqueous phase volume.

3.2.4. Effect of aqueous phase volume

The effect of aqueous phase volume on the recovery of 5 µg of Hg(II) with TAN-functionalized AC was studied in the range 25–1000 ml. As seen from Table 3, the results indicate the quantitative removal of Hg(II) upto 1.0 l of sample solution.

3.2.5. Adsorption capacity of TAN-functionalized AC

This experiment was carried out by taking a solution containing 0.5 mg of Hg(II) and 0.2 g of TAN-functionalized AC and 10 ml of 1.0 mol/l ammonium acetate buffer was added. The pH was adjusted to 6.0 ± 0.2 and was diluted to 25 ml in a 60 ml separating funnel. This solution was equilibrated for 30 min and filtered through a filter paper. The amount of Hg(II) left out in the filtrate was determined by I⁻-Rhodamine 6G procedure. The adsorption capacity of TAN-functionalized AC SPE material was found to be 2.24 mg/g of the adsorbent which is much higher when compared with the Quinoline-8-thiol functionalized naphthalene SPE (0.88 mg/g) [33].

3.2.6. Selectivity studies using TAN-functionalized AC SPE material

The solid phase extraction of Hg(II) in presence of different amounts of extraneous ions using 0.2 g of 2% TAN-functionalized AC was investigated and the results are shown in Table 4. It is clear from the table that none of the species that coexist with Hg(II) do not interfere. Thus, TAN-functionalized AC selectively separates Hg(II) when present

Table 4
Selectivity studies using TAN functionalized SPE material

S. no.	Interferents	Tolerance limit
1	Na, K, Mg(II), Ca(II) and Ba(II)	0.02 (mol/l)
2	Co(II), Ni(II), Mn(II), Cu(II), Zn(II), Cd(II), Pb(II), Al(III), V(V), As(V) and Cr(VI)	10 (mg/l)

Hg(II) = 5 µg/l, 0.2 g of 2% TAN-functionalized AC, stirring time = 10 min.

together with several alkali, alkaline earth, transition and heavy metal ions.

3.2.7. Recovery of mercury from brine sludge

The developed solid phase extraction procedure for extraction of Hg(II) using TAN-functionalized AC was applied for the removal and recovery of Hg(II) from the brine sludge collected from M/s Travancore Cochin Chemicals Limited. One gram of brine sludge sample was dissolved in 25 ml of 1:1 HNO₃ and heated until it dissolves. The resulting solution was diluted to 100 ml with deionized water. Fifty millilitres of this solution was taken, pH of this solution was adjusted to 6.0 ± 0.2 and 0.2 g of 2% TAN-functionalized AC was added. The resulting solution was stirred for 10 min and the Hg(II) adsorbed on TAN-functionalized AC was eluted with 2 × 10 ml of 1.0 mol/l HNO₃. Suitable aliquots of this eluent was taken and recovery of Hg(II) using TAN-functionalized AC SPE was determined by I⁻-Rhodamine 6G procedure. The recovery of Hg(II) by the developed preconcentration procedure was compared with the liquid-liquid extraction-cold vapour atomic absorption spectrometer (LLE-CVAAS) values (see Table 5). The recovery was found to be >99.8% indicating the quantitative removal of Hg(II) from brine sludge sample using the developed SPE procedure.

3.2.8. Recovery of Hg(II) from cell house effluent

Suitable aliquots of cell house effluent collected from M/s Travancore Cochin Chemicals Limited were taken and the pH was adjusted to 6.0 ± 0.2. The preconcentration, elution and determination by I⁻-Rhodamine 6G procedure were carried out as described in Section 2. The recoveries were found to be >99.8% using both SPE-spectrophotometry and liquid-liquid extraction-cold vapour atomic absorption spectrometric procedures (see Table 5). The Hg(II) concentration in cell house effluent was found to be ~1.60 mg/l.

This investigation reveals that >99.8% Hg(II) can be decontaminated from brine sludge/cell house effluent and quantitatively recovered by elution with 2 × 10 ml of 1.0 mol/l of HNO₃. Further, the SPE material can be reused for removal or recovery of Hg(II) from brine sludge/cell house effluent.

Table 5
Recovery of Hg(II) from brine sludge and cell house effluents of chloralkali industry*

S. no.	Description of sample	Hg(II) added	Hg(II) recovered**		Recovery (%)
			Present method (SPE–spectrophotometry)	LLE–CVAAS***	
1	Brine sludge ($\mu\text{g/g}$)	–	128.0 ± 1.0	128.0 ± 1.0	–
		60.0	188.0 ± 2.0		100
		120.0	250.0 ± 3.0		101
2	Cell house effluent (mg/l)	–	1.63 ± 0.01	1.60 ± 0.01	–
		0.80	2.42 ± 0.02		99
		1.60	3.23 ± 0.03		100

* Collected from M/s Travancore Cochin Chemicals Limited, Cochin, India.

** Average of three trials.

*** Liquid–liquid extraction–cold vapour atomic absorption spectrometry.

4. Conclusions

This study clearly demonstrates the usefulness of TAN-functionalized AC solid phase extractant for selective extraction of Hg(II) from Mg(II), Ca(II) and Ba(II) and several transition and heavy metal ions from dilute aqueous solutions. The removal of Hg(II) was made possible by chemically reacting with solid TAN-functionalized AC. Furthermore, the results clearly demonstrate the usefulness of TAN-functionalized AC for selective removal and recovery of mercury from hazardous materials like brine sludge and cell house effluents of chloralkali industry.

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References

- [1] E.R. Krishnan, P.W. Utrecht, A.N. Patkar, J.S. Davis, S.G. Pour, M.E. Foerst, Recovery of Metals from Sludges and Wastewaters, Noyes Data, Park Ridge, NJ, 1993.
- [2] W. Brooke-Devlin, Mercury and arsenic wastes removal, in: Recovery, Treatment and Disposal, US Environmental Protection Agency, Noyes Data, Park, Ridge, NJ, 1992.
- [3] J.M. Grau, J.M. Bisang, J. Chem. Technol. Biotechnol. 62 (1995) 153.
- [4] D.E. Beck, W.D. Bostick, K. Bowser, D.H. Bunch, R.L. Fellows, P.E. Osborne, G.F. Sellers, Presented at the Ninth Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, 1995.
- [5] K.K. Mitsui Cyanamid, Jpn. Patent Appl. 193,846 (1985).
- [6] Y. Baba, K. Inoue, K. Yoshizuka, Y. Ritzu, T. Masato, Jpn. Kokai, Kogyo, Koho, JP 04,164,817 (1992).
- [7] M. Grayson, Kirk–Othmer Encyclopedia of Chemical Technology, vol. 15, third ed., New York, 1981, p. 143.
- [8] A. Junker-Buchheit, J. Witzzenbacher, J. Chromatogr. A 737 (1996) 67.
- [9] K. Pyrzynska, M. Trozanowicz, Crit. Rev. Anal. Chem. 29 (1999) 313.
- [10] J. Mary Gladis, C.R. Preetha, T. Prasada Rao, Met. News 20 (2002) 14.
- [11] T. Prasada Rao, C.R. Preetha, Sep. Purif. Rev. 32 (2003) 1.
- [12] A. Alexandrova, S. Arpadjan, Analyst 118 (1993) 1309.
- [13] H.A.M. Elmahadi, G.M. Greenway, J. Anal. At. Spectrom. 8 (1993) 1011.
- [14] G.J. Ramelow, L. Liu, C. Himel, D. Fralick, Y. Zhao, C. Tong, Int. J. Environ. Anal. Chem. 53 (1993) 219.
- [15] H. Emteborg, D.C. Baxter, M. Sharp, W. Frech, Analyst 120 (1995) 69.
- [16] A. Alexandrova, S. Arpodjan, Anal. Chim. Acta 307 (1995) 71.
- [17] S. Peraniemi, M. Ahlgren, Anal. Chim. Acta 302 (1995) 89.
- [18] R. Shah, S. Devi, React. Funct. Polym. 31 (1996) 1.
- [19] S. Arpodjan, L. Vuchkova, E. Kostadinova, Analyst 122 (1997) 243.
- [20] M.L. Wang, G.Q. Huange, S.H. Qian, J.S. Jiang, Y.T. Van, Y.K. Chan, Fresenius J. Anal. Chem. 358 (1997) 856.
- [21] P.C. Rudner, J.M.C. Pavon, F.S. Rojas, A.G. Deforres, J. Anal. At. Spectrom. 13 (1998) 1167.
- [22] J.L. Manzoori, M.H. Sorouraddin, A.M.H. Shabani, J. Anal. At. Spectrom. 13 (1998) 305.
- [23] M.E. Mahmoud, M.M. Osman, M.E. Amar, Anal. Chim. Acta 415 (2000) 33.
- [24] B.C. Monda, D. Das, A.K. Das, Anal. Chim. Acta 450 (2001) 223.
- [25] M. Shamsipur, A. Ghiagvand, A. Sharghi, Int. J. Environ. Anal. Chem. 82 (2002) 23.
- [26] M. Bouyanne, J. Svie, I.A. Voinovitch, Analysis 7 (1979) 62.
- [27] H. Koshima, H. Onishi, Talanta 27 (1980) 795.
- [28] S. Nagatsuka, Y. Taniyazaki, Radioisotopes 27 (1978) 379.
- [29] M.A.H. Hafez, I.M.M. Kanawaz, M.A. Akl, R.R. Lashein, Talanta 53 (2001) 749.
- [30] N. Malcick, O. Oktar, M.E. Ozcer, P. Cagler, L. Bushloy, A. Vaughan, B. Kuswadi, R. Narayanaswamy, Sens. Actuators B 53 (1998) 211.
- [31] T.V. Ramakrishna, G. Aravamudan, M. Vijayakumar, Anal. Chim. Acta 84 (1976) 369.
- [32] A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, The ELBS & Longmans Green & Co. Limited, 1962.
- [33] R. Mathew, A.M. Starvin, T. Prasada Rao, Ind. J. Chem. 43 A (2004) 569.