

Removal and preconcentration of inorganic and methyl mercury from aqueous media using a sorbent prepared from the plant *Coriandrum sativum*

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Abstract

A sorbent prepared from the plant *Coriandrum sativum*, commonly known as coriander or Chinese parsley, was observed to remove inorganic (Hg^{2+}) and methyl mercury (CH_3Hg^+) from aqueous solutions with good efficiency. Batch experiments were carried out to determine the pH dependency in the range 1–10 and the time profiles of sorption for both the species. Removal of both the forms of mercury from spiked ground water samples was found to be efficient and not influenced by other ions. Column experiments with silica-immobilized coriander demonstrated that the sorbent is capable of removing considerable amounts of both forms of mercury from water. The sorption behaviour indicates the major role of carboxylic acid groups in binding the mercury. The studies suggest that the sorbent can be used for the decontamination of inorganic and methyl mercury from contaminated waters.

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1. Introduction

Mercury finds widespread usage in chloro-alkali plants, dentistry, science, military operations and in units manufacturing organo-mercurial compounds [1]. Effluents from these industries and subsequent use of other products constitute an important source of mercury in the environment. Exposure to methyl-mercury can cause central nervous system disorders, chromosomal aberrations, intellectual deterioration, cerebral palsy and even death [2]. The disastrous consequences of mercury bio-accumulation in aquatic ecosystems have been known since the Minamata incident and hence there is a need to eliminate or considerably reduce its concentration from effluents before discharge to nature. Mercury is considered by the Environmental Protection Agency (EPA) as a highly dangerous element because of its accumulative and persistent

character in the environment and biota [3]. Many reviews on the transport and fate of mercury in the environment can be found in the literature [4].

A number of chemical treatment methods employing plant and other biomaterials have been used for the removal of mercury from aqueous waste solutions [5]. Some of the various sorbents that have been used are coal-fly ash [6], peat moss [7], coffee grounds [8], chemically modified cotton [9], barks of trees [10], bicarbonate treated peanut hull [11], waste rubber [12] and bagasse pith [13]. Despite the fact that a variety of treatment methods are available, these methods are not equally effective for the removal of both inorganic and organic forms of mercury. Hence it is necessary to investigate removal approaches that efficiently and simultaneously remove both inorganic and organic mercury from aqueous solutions.

Recently Omura [14] has reported, in a totally different context, that the herb coriander removes mercury from neural tissue and connective tissues. In the present work we have

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investigated the ability of a sorbent prepared from coriander – a cheap and commonly available edible plant – for removal of mercury from aqueous solutions as a function of pH, rate of sorption. Column operations with this sorbent were carried out after immobilization on a silica matrix.

2. Experimental

2.1. Instrumentation

Mercury was analyzed by cold vapour atomic absorption spectrometry (CV-AAS) using a mercury analyzer (Model MA 5800E, Electronics Corporation of India Ltd., Hyderabad, India). To reduce the mercurial species to elemental mercury, 10% SnCl₂ or 2% NaBH₄ was added. SnCl₂ cannot reduce methyl mercury – whereas NaBH₄ can reduce both Hg²⁺ and CH₃Hg⁺ – to elemental mercury, albeit with different efficiencies. The sorbent bound mercury was desorbed using hydrochloric acid solutions and tested by reducing with SnCl₂ and/or NaBH₄ followed by analysis of mercury by CV-AAS.

2.2. Reagents

All the chemicals were of analytical reagent grade. Stannous chloride (SnCl₂) (10%, m/v) was prepared by dissolving the appropriate amount of SnCl₂ (E-Merck, India) in HCl and diluting to volume with high purity water. Then 2% (m/v) sodium tetrahydroborate (NaBH₄) (Merck, Darmstadt, Germany) was prepared by dissolving the solid in 2% m/v NaOH solution. The reducing agents were prepared fresh daily. About 10% HCl was used as carrier.

An inorganic mercury stock standard solution (1 mg ml⁻¹) was prepared using AR grade mercuric chloride. Methyl mercury standard was prepared by dissolving an accurately weighed amount of methyl mercury chloride in a minimum amount of acetone. This was made up to volume using water. Both stock standards were kept at 4 °C in a refrigerator and protected from light. Working mercury standards were prepared fresh just before use by appropriate dilution of the stock standard solutions.

2.3. Sorbent preparation

The sorbent employed in this study, *Coriandrum sativum*, is available extensively and cultivated as annual herb in India. The plant is commonly called coriander. Rajasthan, Andhrapradesh and Tamilnadu are the major coriander producing states in India. Both the bold round type (*C. sativum* var. *Vulgare*) and the small seeded type (*C. sativum* var. *Microcarpum*) are under cultivation [15]. India is a notable consumer of coriander as an edible plant for enhancing the flavour of cooking.

A large quantity of the coriander plants in the stage of floral initiation was obtained, washed thoroughly with wa-

ter to remove all the adhering soil particles. The whole plant (roots, stem, leaves) was cut into small pieces and dried at 40 °C in the conventional heating oven, ground in a planetary ball mill (Fritz, Germany) and sieved to collect 200–400 mesh size particles. A second sorbent was prepared by taking only the seeds of coriander and grinding them and collecting 200–400 mesh size particles.

2.4. Batch sorption studies

Batch sorption was performed at room temperature for the sorption of both inorganic and methyl mercury to optimize various parameters such as effect of pH (from 1 to 10), contact time (from 5 to 60 min), effect of other foreign ions. In these experiments, 250 mg of the sorbent was shaken with 20 ml of mercury solution containing 0.5 mg absolute amount of mercury, either in the form of mercury(II) chloride or methyl mercury(I) chloride. A mechanical shaker was used for shaking the mixture. The pH of solutions was adjusted to the desired value by dilute solutions of HCl or NaOH. At the end of the desired contact time contents were filtered through a Whatman filter paper and analyzed for residual mercury in the solution. pH of the solution mixture was recorded initially and again at the end of the experiment using a digital pH meter. The data shown in the present work are average values from three separate experiments.

2.4.1. Capacity studies of inorganic and methyl mercury by the sorbent

The total binding capacity of the sorbent for both the species of mercury was studied separately in a batch method. In these studies after 45 min sorption, the sorbent was re-suspended in 20 ml of fresh mercury solution and this cycle was repeated until the saturation of the sorbent was achieved, i.e. no change in the concentration of mercury in the initial and supernatant solution. The supernatants were analyzed for residual mercury and the total mercury sorbed on the sorbent was estimated.

2.4.2. Microwave digestion of sorbent for determination of retained mercury

The quantity of mercury sorbed was also verified by digesting the sorbent in a closed microwave digestion vessel of Parr bomb (nitric acid and hydrogen peroxide) using a domestic microwave oven (3 min at 650 W), followed by analysis for total mercury by CV-AAS. Appropriate blanks prepared similarly were also analyzed.

2.5. Column studies

A continuous process employing a packed bed of substrate is often considered to be more efficient and economical to operate than a batch process. Thus the sorbent was immobilized onto a silica matrix, which was used for column studies.

2.5.1. Immobilization of coriander on sodium silicate

The method for immobilization of material within a polysilicate matrix was similar to that reported by Huel-Yang and Rayson [16] as well as by Gardea-Torresdey et al. [17]. An amount of 75 ml of 5% H₂SO₄ was mixed with sufficient 6% sodium silicate (Na₂SiO₃) solution to raise the pH to 2.0. An amount of 5 g of sorbent was added to the silica solution and stirred for 15 min. The pH was then raised slowly by the addition of 6% sodium silicate to reach pH 7.0. The polymer gel was washed with water thoroughly until the addition of barium chloride (BaCl₂) resulted in no white precipitate due to the presence of sulphate. The polymer gel with immobilized coriander was dried overnight at 45–50 °C and ground by mortar and pestle and sieved to get 50–100 mesh size.

2.5.2. Column preparation

Column was prepared using a glass column (25 × 1.0 cm i.d.) with a stopcock. Cotton wool was inserted at the bottom and at the top of the sorbent. About 1 g of immobilized coriander was suspended in distilled water for about 30 min and then transferred to the column. The height of the resin bed was about 3 cm. Inorganic/methyl mercury solutions containing 25 mg/l of mercury in desired form at pH 6.0 was allowed to pass through the column at a flow rate of 2 ml/min.

3. Results and discussion

3.1. Batch experiments

3.1.1. Effect of pH on the uptake of inorganic and methyl mercury

Experimental results showing the removal of both inorganic and organic mercury species by the sorbent as a function of pH in the range of 1–10 are presented in Fig. 1. It has been observed that the sorption of both inorganic and methyl

mercury reached a maximum (>95%) around a pH of 4 and remained constant till a pH of 10. A perusal of literature on mercury speciation shows that the dominant species at pH > 3 are Hg²⁺, HgCl⁺, Hg(OH)⁺, Hg(OH)₂, HgCl₂ [12]. Hence the removal of the mercury from aqueous solutions was determined at various pH conditions and the extent of mercury removal was determined after digestion of the sorbent. The results are shown in Table 1a and b for inorganic mercury and methyl mercury, respectively. These results indicate an efficient removal of mercury from the aqueous solutions over the studied pH range of 4–10 irrespective of the chemical form in which it was present in the solution.

The final pH of the mercury solutions was observed to change (Fig. 2) with sorption of the mercury ions by the sorbent. The final pH of the solution after sorption was found to lie between pH 3.5 and 5.5 when the initial pH of the aqueous solution was varied from 1 to 10. In all subsequent experiments a pH of 6.0 was used, as this is much closer to natural waters.

3.1.2. Effect of contact time

The sorption of inorganic and organic mercury by the sorbent against time was studied. The percentage of sorption was determined at different time intervals ranging from 5 to 60 min. From the initial concentration and the concentration measured after various intervals of time, the percentage of mercury sorbed was calculated. The results of the above experiments are presented in Fig. 3.

These studies clearly indicate that the binding of both species of mercury is rapid and more than 65% is taken up in the first 10 min. The sorption of CH₃Hg⁺ is more rapid than that of inorganic mercury; about 80% was removed from solution at the end of 10 min. The percentage inorganic mercury removal reached >95% by the end of a contact period of 45 min, whereas methyl mercury removal reached its maximum value within a contact period of 30 min. Further increase

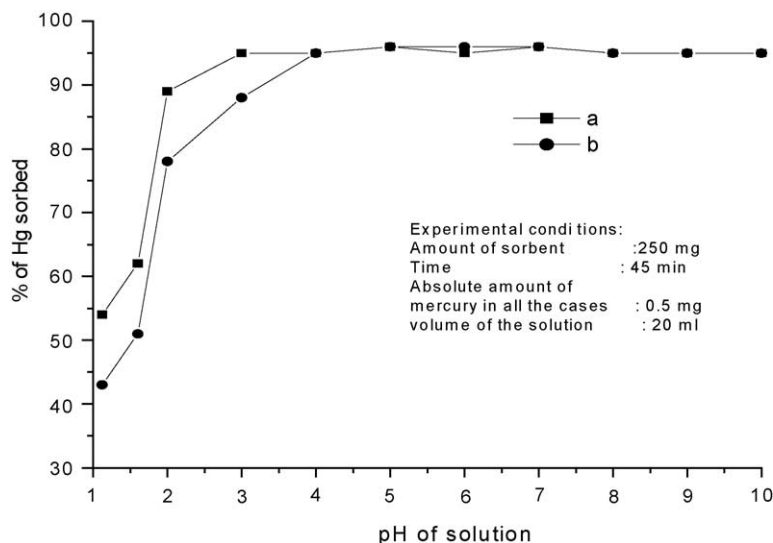


Fig. 1. Effect of pH on the sorption of (a) Hg²⁺ and (b) CH₃Hg⁺.

Table 1

(a) Recovery of inorganic mercury after sorption from aqueous solutions of different pH values

pH of the solution	Hg(II) added (μg)	Mercury found ^{a,b} (μg)		Recovery (%)
		Solid phase	Liquid phase	
2.0	500	437	55	98.4
4.0	500	483	10	98.6
6.0	500	488	8	99.2
8.0	500	485	9	98.8

(b) Recovery of methyl mercury after sorption from aqueous solutions of different pH values

pH of the solution	Methyl mercury added (μg)	Mercury found ^{a,b} (μg)		Recovery (%)
		Solid phase	Liquid phase	
2.0	500	392	101	98.6
4.0	500	488	11	99.8
6.0	500	491	12	100.6
8.0	500	482	10	98.4

Volume of the solution = 20 ml, weight of the sorbent = 250 mg, equilibration time = 45 min.

^a Average of three determinations.^b Determined after microwave digestion.

in contact period to 60 min had no significant effect. Therefore, a contact time of 45 min was used for all subsequent experiments.

Sorption studies were carried out with sorbents prepared using different parts of the coriander plant (stem, root, leaves). The results indicated that the sorbent prepared from the stem showed higher sorption than sorbents prepared from the roots and leaves.

3.1.3. Uptake efficiency studies of inorganic and methyl mercury

The capacities of the sorbent for inorganic and methyl mercury (in terms of absolute amount of mercury) were found to be ~ 24 and ~ 7 mg/g of sorbent, respectively, from the above studies. The capacities were confirmed by determination of mercury bound to the sorbent after subjecting it to closed mi-

crowave digestion. The lower capacity for methyl mercury and the more rapid desorption of CH_3Hg^+ ions (discussed later) might indicate the bulkier group's inability to diffuse inside the sorbent and absorption may be essentially on the surface of the sorbent. The different rates of sorption for inorganic and organic mercury, their different capacities and difference in the pH dependence of sorption also may indicate that more than one mechanism may be responsible for the sorption of these species by the coriander.

3.1.4. Desorption studies

Desorption of the mercurial species sorbed by coriander was investigated as a function of concentration of HCl by mechanical shaking. An amount of 250 mg of the sorbent on which previously 0.5 mg of absolute amount of mercury (inorganic/methyl mercury) sorbed was taken in a 10 ml of

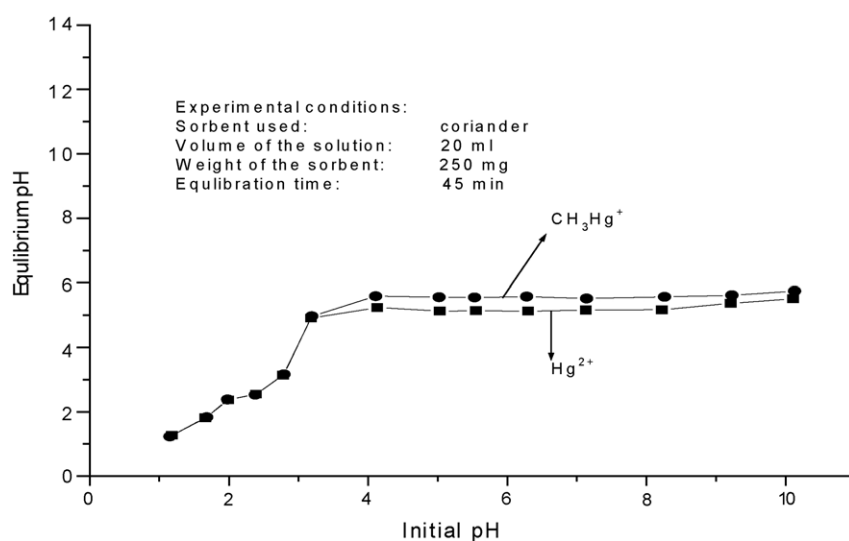


Fig. 2. Effect of pH after equilibration in the presence of inorganic and methyl mercury.

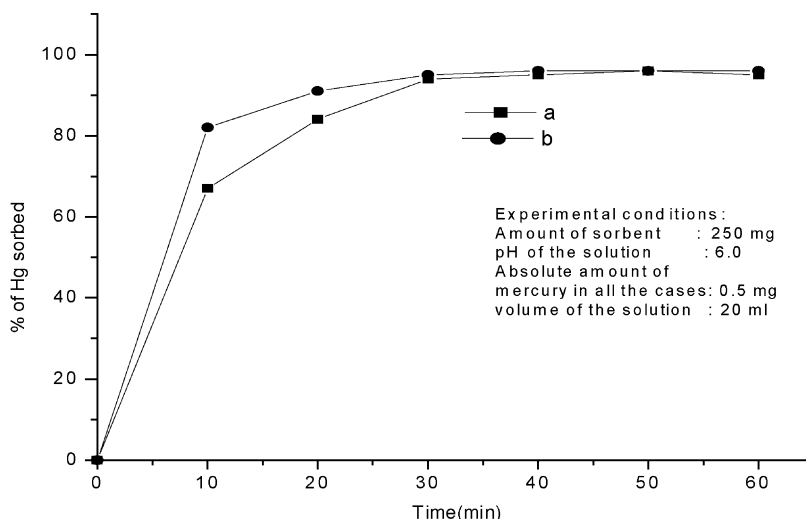


Fig. 3. Time dependence of sorption of (a) Hg^{2+} and (b) CH_3Hg^+ by coriander.

HCl solution in the concentration range of 1–6 M. The mercury content in the filtered supernatant was determined. From the concentration in the supernatant the desorbed amount of mercury was calculated.

The results in Fig. 4 show that the extent of desorption of inorganic mercury when carried out by using mechanical shaker. More than 95% desorption of organic mercury occurred at an HCl concentration of 1 M. The complete desorption (>95%) in the case of Hg^{2+} could be achieved only with 6 M HCl. This could be due to formation of HgCl_4^{2-} .

The observations that methyl mercury is desorbed at lower concentration of acid than the Hg^{2+} are consistent with those reported by Rio-Segade et al. [18], even though they had desorbed the mercurial species from mussel tissue. Similar desorption characteristics were also exhibited by another sorbent prepared from the soil fungus, *Aspergillus niger* and tested by us [19] for its mercurial species sorption capacity. Thus, it appears that in general methyl mercury ion is more loosely held by the sorbents.

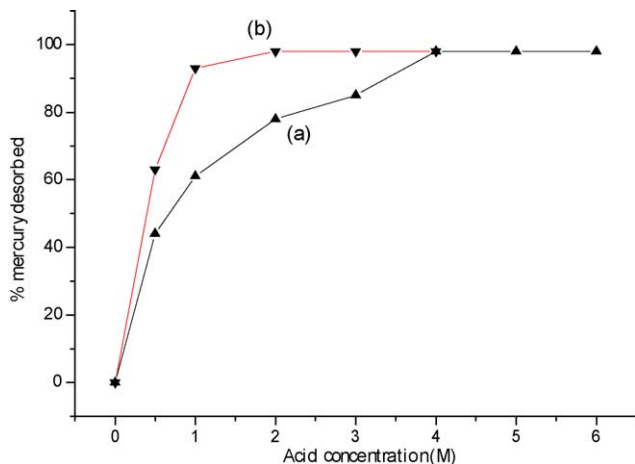


Fig. 4. Desorption of mercurial species with HCl (a) Hg^{2+} and (b) CH_3Hg^+ .

3.1.5. Effect of other ions

In natural wastewaters, toxic metallic species rarely exist singly and coexist with various other metal ions. Hence the presence of those metals gives rise to interactive effects that could influence the removal of the desired contaminant. Hence inorganic and methyl mercury were spiked into a sample of ground water and their removal was investigated with the sorbent. Experiments were carried out to study the uptake efficiency of mercury in the presence of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Cu^{2+} , Cl^- and SO_4^{2-} . The pH of the solutions was adjusted to ~ 6.0 . The volume of the solution (20 ml) and weight of the sorbent (250 mg) were kept constant. These experiments showed that the sorption of mercury from aqueous solutions was not affected by the presence of above-mentioned ions.

3.1.6. Functional groups responsible for sorption

Perusal of literature also indicates that the metal ion sorption on both, specific and non-specific sorbents has been known to be pH dependent [20]. The pH of the solution affects the solubility and the form in which a metal is present in the solution and the ionization of functional groups on the surface of the sorbent [21–22]. As seen in Fig. 1 the sorption of mercury initially increased with pH and a plateau occurred pH 4 onwards. This pH dependent trend implies that the mechanism of mercury binding may be through the deprotonation of functional groups, similar to another sorbent investigated by us, for sorption of mercury, prepared from the soil fungus, *A. niger* [18]. It was shown in that study by esterification and deesterification of the sorbent that carboxylic acid groups played a major role in the binding of the mercurial species. The similarities in the sorption characteristics and the pH profiles of the sorption and desorption in the present sorbent prepared from coriander indicate that the carboxylic acid groups play an important role in the binding of mercury.

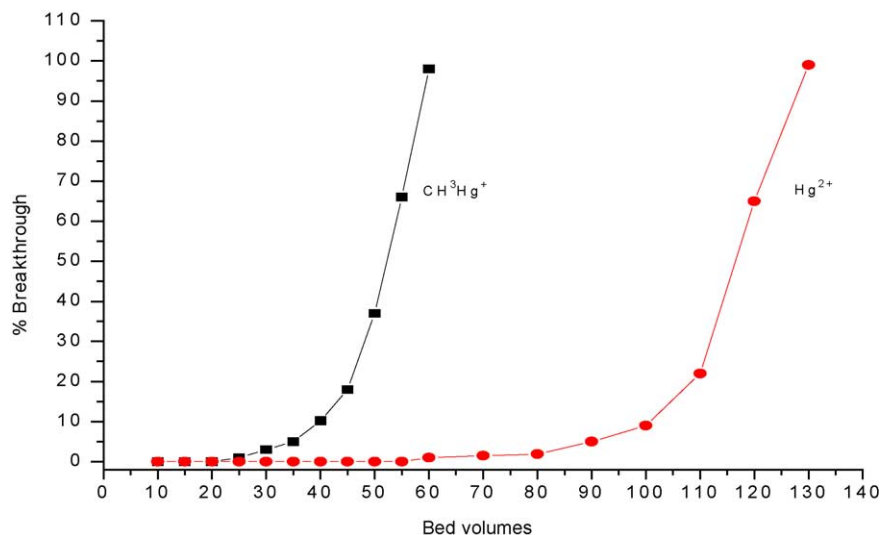


Fig. 5. Percentage breakthrough in the effluent after being passed through a column of immobilized coriander 25 ppm solution was passed at a flow rate of 2 ml/min one bed volume equals to the volume of silica immobilized coriander (3 ml).

4. Column studies

4.1. Adsorption capacity of immobilized coriander using breakthrough curves

A feed solution containing 25 µg/ml of inorganic/methyl mercury was passed separately through a column at an optimized constant flow rate of 2 ml/min. The pH of the feed solution was maintained at ~6.0. Samples were collected from the column periodically and assayed for residual mercury. Breakthrough curves for inorganic/methyl mercury were obtained by plotting the percentage breakthrough $[(C/C_0) \times 100]$ against the number of bed volumes, where C_0 and C are the concentrations of mercury in the initial solution and the effluent, respectively.

As seen from Fig. 5, methyl mercury concentration in the effluent was close to the background level up to about 30 bed volumes. After 30 bed volumes, a decrease in the binding of methyl mercury was observed and the column reached the saturation after 40 bed volumes of the solution had been passed.

In the case of inorganic mercury even after passing 80 bed volumes, the residual concentration in the effluent was undetectable. The percentage breakthrough was still below 10% even after 95 bed volumes had been passed through the column. The column reached saturation after 110 bed volumes on passing the solution with 25 µg/ml of inorganic mercury. These results suggest that immobilized coriander also exhibits very high affinity for inorganic/methyl mercury. The maximum amount of adsorption capacity achieved was 55 mg/g for inorganic and 17 mg/g for methyl mercury.

4.2. Elution curves

Elution studies were carried out with different acid concentrations of HCl at a flow rate of 2 ml/min, to desorb the

mercury. Samples were collected at different intervals and the residual mercury content was determined. It was found that more than 95% of inorganic mercury could be desorbed with only 10 ml (about three bed volumes) of 4 M HCl where as quantitative desorption of methyl mercury was achieved with 10 ml of 0.5 M HCl. Fig. 6 shows the effect of passing 4 M HCl and 0.5 M HCl separately through the column of immobilized coriander on which inorganic and methyl mercury were sorbed.

4.3. Application to natural water samples

A synthetic water sample having Na⁺ (30 mg/l), K⁺ (8 mg/l), Mg²⁺ (40 mg/l), Ca²⁺ (110 mg/l), Fe³⁺ (0.4 mg/l),

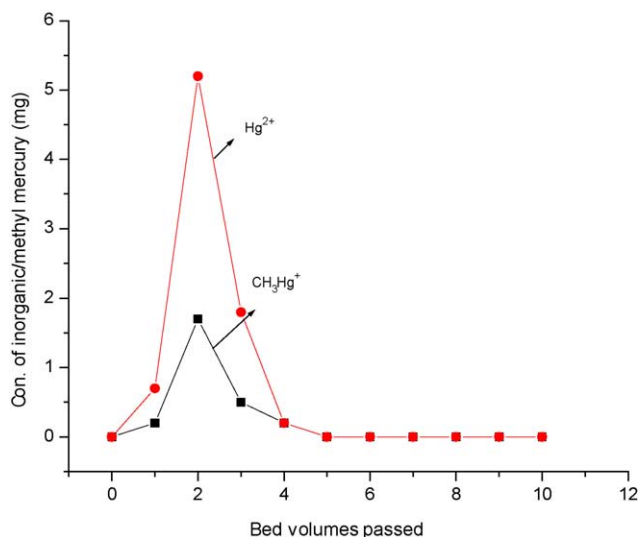


Fig. 6. Recovery of inorganic mercury with 4 M HCl and methyl mercury with 0.5 M HCl from the column of immobilized coriander flow rate of 2 ml/min was used.

Table 2
Analysis of synthetic water

Species	Added (ng)	Found (ng)	Recovery (%)
Hg ²⁺	250	246 ± 18	98.4
	500	501 ± 34	100.2
CH ₃ Hg ⁺	250	242 ± 12	96.8
	500	485 ± 18	97

Table 3
Determination of mercury in water samples

Mercury (ng l ⁻¹)			
Sample	Added	Found	Recovery
Ground water ^a	0	547.5 ± 6.3	101
	500	1055.2 ± 7.6	
Tap water	0	123.2 ± 5.8	96
	500	617.8 ± 4.7	

Volume of sample passed = 1000 ml.

^a Collected from a bore well adjacent to a battery manufacturing factory, Hyderabad, India.

Cu²⁺ (0.12 mg/l), Cl⁻ (248 mg/l), SO₄²⁻ (158 mg/l) was spiked with inorganic mercury(II) and methyl mercury and analyzed by the developed column method. Potassium persulfate was used for converting methyl mercury into inorganic mercury prior to its analysis. The results (Table 2) show good recoveries.

The procedure was also applied to a ground water sample (from a bore well which is located about 15 m away from the waste lagoon) collected near a battery manufacturing unit in Hyderabad, India, and tap water for their mercury levels. The reliability of the method was checked by recovery experiments, which yielded quantitative results. These are shown in Table 3. It may be seen from the results that the immobilized coriander can be used for pre-concentration of mercury present at ultra trace levels in natural waters.

5. Conclusion

The sorbent *C. sativum* was found to sorb mercury from aqueous solutions with good efficiency in both batch and column (immobilized) conditions. The degree of removal was found to be greater than 95% in pH range of 4–10. The optimum contact time was observed to be about 45 min for the batch studies. Maximum absorption occurred at a pH of ~6 with capacities for Hg²⁺ and CH₃Hg⁺ of ~24 and ~7 mg/g of dry sorbent, respectively. These investigations show that carboxylic groups might be mainly responsible for the sorption of the mercurials. Column studies showed that the capacity of coriander immobilized was ~55 and ~17 mg/g for inorganic (Hg²⁺ species) and CH₃Hg⁺, respectively. Coriander appears

an attractive material which could have the potential for use in decontaminating mercury.

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