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REMOVAL OF MERCURY BY 1-NAPHTHYLTHIOCARBAMIDE DOPED XEROGEL USING RADIOTRACER TECHNIQUE

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ABSTRACT

1-Naphthylthiocarbamide (ANTU) doped xerogel was prepared and investigated for removal of mercury ions from aqueous media. Physicochemical parameters such as effect of pH, equilibration time, and adsorption isotherm on the removal of mercury were evaluated to optimize the conditions to utilize the data on a large scale. It was observed that uptake and retention of mercury ions inside the pores take place by the formation of a complex with the entrapped reagent molecules. The data show that a xerogel doped with 0.2 mmol ANTU/g of sorbent can remove 0.096 mmol Hg. The probable composition of the mercury complex has been deduced and a removal mechanism is suggested. The regeneration

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and reuse of doped gel for the removal of targeted metal has been discussed.

INTRODUCTION

Mercury is considered as nonessential ions present in biological systems having no known biological function in living systems.[1] Nonetheless, in high concentration, it will be toxic to biological systems. Mercury poisoning results in severe nausea, vomiting, abdominal pain, and kidney damage. The extremely low possible limit Hg ions in water is 0.001 mg/L (WHO 1972) and the significant release of Hg and other heavy metal ions into water bodies through industries, sewage sludge, and agriculture pesticides has been alarming to environmental scientists prompting them to search for an efficient removal system from aqueous wastes. Literature survey reveals that a variety of synthetic solid sorbents such as metal oxides, ion exchangers, chelating resins, and polyurethane foam[2–6] have been used for separation preconcentration of heavy metals. Most of these sorbents are found to be expensive, time consuming, less selective, difficult in availability, and demand advance technology for manufacturing and some times their nondurable or highly poisonous nature does not allow their practical use for removal of metal ions from waters or decontamination of industrial or radioactive effluents.

The development of organically doped sol–gels having some unique properties such as physical rigidity, high abrasion resistivity, negligible swelling in both aqueous and organic solutions, chemical inertness due to low interaction with analytes and slower poisoning by irreversible side reactions, high biodegradation, photochemical and thermal stability, excellent optical transparency, and intrinsic fluorescence, etc., opened new doors of research.

Sol–gel silica doped with organic reagents has been used for the development of a variety of sensors[7,8] and their use for different applications is expanding every day. In this article, we tried to work out the feasibility of sol–gel doped with 1-naphthylthiocarbamide (ANTU) for removal of mercury.

EXPERIMENTAL

Reagents

The chemicals such as tetraethoxysilane, ethanol, ANTU, and ammonium fluoride have been used without further purification. All other chemicals were of A.R. grade. Double distilled water was used in all experimental work. ^{203}Hg

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radiotracer was prepared by neutron irradiation of pure metal oxide in the PARR-1 research reactor of this Institute mainly through (n, gamma) reaction.

Equipment

The radiochemical purity of the radiotracers was checked by gamma spectrometry with a 30 cm Ge (Li) detector in conjunction with a Nuclear Data model ND-4410 computerized analyzer system. The gamma activity was counted with a Nuclear Chicago single-channel analyzer, model 872, coupled with a $7.5 \times 7.5\,cm^2$ NaI (TI) well-type scintillation detector.

Preparation of 1-Naphthylthiocarbamide Doped Xerogel

The experiments were carried out using doped sol–gel glasses prepared as: 10.0 mL of tetraethoxysilane, 10.0 mL of double distilled water, and 25 mL ethanol solution of a reagent in the presence of 10^{-2} mol/L ammonium fluoride as a catalyst were mixed, allowed to gel for three days, and dried in an oven to constant weight. After drying, the glasses were crushed and sieved. The sieved glasses were thoroughly washed by shaking with distilled water to remove the unbound reagent and then soaked in proper buffer solution to allow the leachable reagent to leach out before the sorbent was used for removal of metals. About 0.04 g of ANTU was doped per gram of sorbent. Plain xerogel without reagent was also prepared according to the above procedure.

Procedure for Removal of Mercury Ions from Solution by Sorbent

The adsorption isotherms were determined by the batch technique at room temperature (25 ± 1°C). In all the experiments, to study the removal of mercury by sol–gel, a proper quantity of tracer alone or both the tracer and carrier were added to 5 mL aqueous solution of required pH in 30 mL glass vials and were shaken for 2 min. After shaking, 1 mL was taken out for estimating the initial concentration of mercury. The remaining solution was allowed to equilibrate for 30 min with proper amount of sorbent. After equilibration, the vials were centrifuged and the supernatant aqueous phase was analyzed for Hg^{203} by a scintillation counter. The following equation was used to compute the amount of mercury removed by the adsorbent:

$$\text{Amount of mercury removed} = (C_i - C_f)\frac{V}{W}$$

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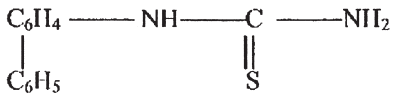
where C_i is the initial concentration of metal ion in solution, C_f the final concentration of metal ion in solution at equilibrium with the solid phase, V the volume of solution, and W is the mass of xerogel.

The values quoted are the average of at least triplicate measurements.

RESULTS AND DISCUSSION

1-Naphthylthiocarbamide as a Reagent

1-Naphthylthiocarbamide is the organic derivative of urea. Its structure formula is



It was selected for this study based on the following reasons.

(i) It carries a thio group, which belongs to soft base group and has a strong affinity for soft acid Hg ions.
(ii) It has functional groups =S, —N—, and $—NH_2$ for ion exchange and/or complexation.
(iii) It has been used for extraction of mercury.[9]
(iv) Its molecule can be securely entrapped inside the pores of xerogel.
(v) It has been found very selective, stable, and easily available.

Mechanism for Removal of Mercury by Sorbent

The removal of mercury by the xerogel modified with ANTU may be contributed by the two processes mentioned below.

(1) The removal of mercury by the plain sol–gel silica without being doped with the reagent, i.e., ion exchange of mercury with silinol groups (—SiOH)— and/or adsorption of mercury by —SiO— on the surface of silica.
(2) The removal of mercury by the entrapped reagent, i.e., ion exchange and/or complexation of mercury with ANTU entrapped in the xerogel. Our data show that the removal of mercury by plain xerogel

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is negligible, therefore, in the present study the probability that the removal follows the second process is very high.

Effect of pH on the Removal of Mercury by ANTU Doped Xerogel

The removal of mercury by plain and ANTU doped xerogel was studied at pH range 1–7. The pH of solution in each vial was maintained by using appropriate buffer solutions: pH 1–2 (potassium chloride plus hydrogen chloride), pH 3–6 (acetic acid plus sodium acetate), pH 7.0 (boric acid plus sodium hydroxide) and the results for removal of mercury by using these buffer solutions are shown in Fig. 1. The removal increases with an increase in pH from 1 to 6 and attains its maximum value at pH 6. The observed pH dependence of mercury removal can be explained by taking the following points into account:

(1) the acid base equilibrium of ANTU,
(2) the surface charge of sol–gel silica,
(3) the availability of free mercury ions in the solution.

The removal increases with an increase in pH due to the following.

(i) Deprotonation of the nitrogen and sulfur atoms of —NH—, —N—, and =S groups.
(ii) The availability of both nitrogen and S atoms for co-ordination at neutral pH where as, at lower pH, only the sulfur atom is available for coordination.

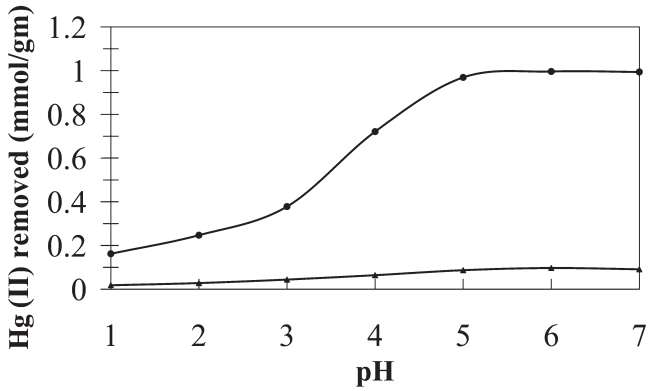

Figure 1. Removal of mercury at equilibrium by xerogel as a function of pH. (▲) Blank xerogel, (●) doped xerogel.

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(iii) At lower pH, the functional groups —NH— and —N— are protonated and thus bearing positively charged surface sites, which will effectively hinder the uptake of positively charged Hg ions.

This increase is partially balanced by the counter decrease in the availability of free mercury ions at high pH due to more hydrolysis at high pH, and thus the removal by the sorbent. The measurements were carried out at pH < 7 in order to avoid the precipitation of mercury hydroxides and to prevent the activation of —SiOH— group, which becomes active at higher pH.

Kinetics of Mercury Removal by Xerogel

The influence of agitation time on the sorption of mercury was examined from 1 to 30 min at pH 6.0 and the results are shown in Fig. 2. The sorption increases with an increase in time and reaches its maximum value within 10 min. The fast attainment of equilibration reflects strong affinity of the reagent for the metal and low energy requirement for the metal to make a bond with the complexing reagent. The slow removal may be explained from the hindrance faced by mercury metal ions by the interconnected three-dimensional net work of pores and channels and occupy the very tight remaining sites at the entrapped reagent molecules.

Isotherm for Removal of Mercury by Xerogel

The removal of mercury by ANTU doped xerogel was studied at pH 6.0. The experimental data are shown in Fig. 3. The data for the removal of mercury

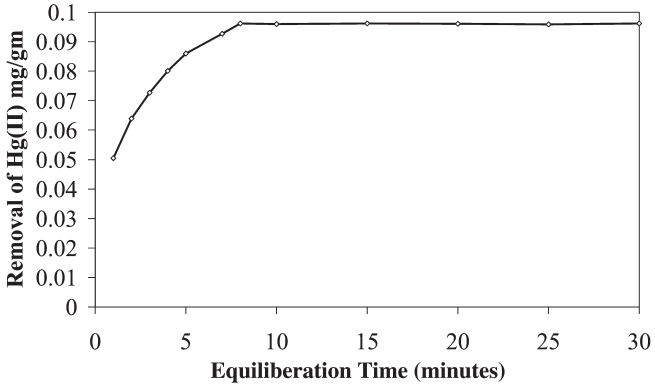

Figure 2. Effect of equilibrium time on the removal of Hg(II) at pH 6.0.

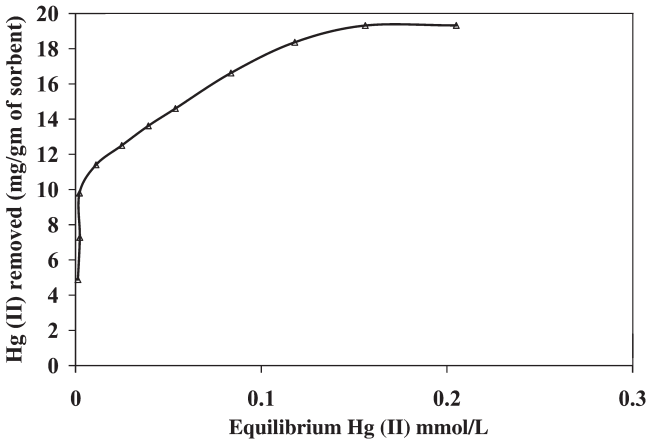

Figure 3. Effect of concentration of Hg(II) in solution on the removal of Hg(II) at pH 6.0.

by ANTU doped xerogel show that the removal increases sharply at low concentrations but slowly at higher concentrations, and eventually attains its maximum value, which represents a saturation of the sol–gel by mercury ions.

The maximum capacities of the plain and ANTU doped xerogel for removal of mercury were 0.4 mg and 19.32 mg/g, respectively. The greater capacity of the ANTU xerogel clearly indicates that the entrapped ANTU plays a major role in the removal of mercury while the role of plain silica gel is very limited. Moreover, our data show that the sorbent loaded with 0.04 g ANTU/g removes 0.0193 g Hg or approximately 0.096 mmol Hg. If we suppose that the mercury removal is only due to entrapped ANTU, then the approximate ratio of the metal to reagent is very close to 1:2. It should be noted that not all the entrapped reagent molecules would be accessible to mercury ions as some of them may be entrapped inside the very tight or even closed pores or in the pores deep inside the center of the particles of xerogel.

Recovery of Mercury and Regeneration of Sorbent

A fast quantitative desorption of metal ions is essential for a high efficiency of the sorbent. About 0.1 *N* HNO_3 was used to study the recovery of mercury from the sorbent and regeneration of sorbent. The sorbent loaded with a known amount of mercury was washed with a pH 6 solution. The washings were discarded after analyzing for mercury. After washing, this loaded sorbent was

shaken with 10 mL 0.1 *N* HNO_3 solution in two steps and the concentration of released mercury was determined. After mercury was completely recovered from the sorbent, the sorbent was regenerated by washing with enough distilled water and soaking in pH 6 buffer solution. This regenerated sorbent was used again for the recovery of mercury.

The cycle of removal and recovery/regeneration was repeated four times for one batch of sorbent. The removal capacity of regenerated sorbent was found very close to the freshly prepared sorbent. This clearly shows that the xerogel sorbent can be regenerated and reused repeatedly at least four times.

CONCLUSIONS

As seen from the above data, the ANTU doped sol–gel having functional groups with both nitrogen and sulfur atoms can be used for the removal of Hg(II) ions. The proposed material possesses the following main features:

(a) high rate of attainment of equilibrium,
(b) high stability towards temperature and medium,
(c) easy regeneration and complete recovery of sorbed metal ions,
(d) these features determine the value of ANTU doped sol–gel for concentrating and removing mercury ions and thus it looks very promising in the determination and abatement of pollution caused by heavy metals particularly mercury.

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