

Mercury Ion Removal Using a Packed-Bed Column with Granular Aminated Chitosan

JEON, CHOONG*

Department of Environmental & Applied Chemical Engineering, Kangnung National University, Kangnung Daehangno 120, Kangnung, Kangwon-do 210-702, Korea

Received: July 15, 2004

Accepted: December 4, 2004

Abstract This study deals with the removal of mercury species using a packed-bed column with spherical aminated chitosan material. These adsorbents revealed a high adsorption capacity for mercury species. Experiments with feed solutions of 10 ppm Hg dissolved in distilled water showed an excellent removal with a sharp increase of the filter effluent concentration after a total throughput of 900 bed volumes of feed water. Up to 95% desorption was reached by using 3 bed volumes of 0.01 N EDTA solution. EDTA could be recovered by means of sulfuric acid with about 75% efficiency. Almost the same results were obtained in repeated sorption and desorption experiments at identical conditions. The experiments demonstrated that the sorbents possessed practically no sorption capacity for alkaline earth ions (Ca^{2+} and Mg^{2+}). Their influence on the sorption of mercury was negligible. In experiments with spiked tap water of the Karlsruhe Research Centre and a feed mercury concentration of 0.01 mg/l, the breakthrough of Hg was observed only after a total throughput of about 6,000 bed volumes of feed water.

Key words: Biosorption, chitosan, mercury, packed-bed column, EDTA, desorption

Among the heavy metals, mercury and most of its compounds are well known as being poisonous [11]. Methyl mercury is extremely toxic for humans as it attacks the central nervous system and causes irreversible damage. Heavy metal-bearing industrial wastewaters are usually treated by means of chemical precipitation. However, these processes involve the production of a toxic sludge, which has to be post-treated before being environmentally safe for disposal [2]. Further methods for elimination of

heavy metals are presented by sorption methods. Among this group of processes, sorption onto biosorbents shows some advantages, compared to standard ion-exchange, adsorption, electrode deposition, and membrane processes. These advantages include cheap cost of materials, easiness of operation, and selectivity over alkaline and alkaline earth metals [8, 10]. Recently, many biopolymers have been known to strongly bind metals. Their application as biosorbents for the recovery of valuable metals or the removal of toxic metal contaminants has been studied by a large number of authors. Among them, many studies have especially been carried out on the application of chitosan, which possesses amine and hydroxyl groups for elimination and separation of heavy metals. Yang and Zall [12] reported that chitosan chelates five to six times greater amounts of metals than chitin due to the free amine groups exposed during deacetylation. Heisen and Rorrer [4] suggested N-acylation as a means of increasing porosity. They N-acylated chitosan, cast it into beads, and then cross-linked the beads with glutaric dialdehyde in order to overcome solubility. N-acylation improved the uptake capacity for Cd over nonacylated beads from 169 to 216 mg/g. Chitosan is especially well known as an excellent biosorbent for mercury ion removal because of its amine groups. Even though chitosan is highly sorptive in its natural state, its uptake capacity should be increased more in order to compete with commercial ion-exchange resin. Therefore, our research has been concentrated on increasing its uptake capacity for mercury ions, and aminated chitosan beads showed a higher uptake capacity over mercury ions than that of natural chitosan in batch experiments [5].

However, like other sorbents, biosorbent materials would be applied in packed beds, which is the most common technical solution in water and wastewater treatment [1]. As a consequence, the aim of this study was to investigate the efficiency of mercury removal and recovery using a

*Corresponding author
Phone: 82-33-640-2405; Fax: 82-33-640-2410;
E-mail: chch1229@hotmail.com

packed-bed column with aminated chitosan material. The studies also included the regeneration of the column material and the recovery of both the heavy metal and the regenerant.

METHODS

Biosorbent Preparation

Experiments for mercury ion removal from synthetic wastewater were carried out using spherical aminated chitosan material, which were prepared according to the methods described earlier [5]. For the experiments, the material was first pretreated with hydrochloric acid and sodium hydroxide to remove impurities. After extensive rinsing with distilled water, the beads were applied for the experiments.

Column Operation

The column experiments were carried out in a laboratory-scale installation, which is schematically shown in Fig. 1. The adsorbent material was stored in a column with an inner diameter of 2.0 cm and a bed height of 20 cm. From the stock of feed solution, raw water was first pumped into an intermediate buffer vessel with reflux of the excess flow. From this vessel, the feed was conducted across the packed bed using a peristaltic precision pump. For most of the experiments, upstream throughput was selected. The throughput was in downstream direction only at comparatively large volume flows. Effluent samples were automatically taken from the filter. The feed water (either distilled or tap water) was spiked with mercury nitrate solution. For the experiments with distilled water, the feed concentration amounted to 10 mg/l Hg, in the experiment with tap water to 0.01 mg/l Hg. A 0.01 N EDTA solution was used for desorption/regeneration. The effect of alkaline earth metals

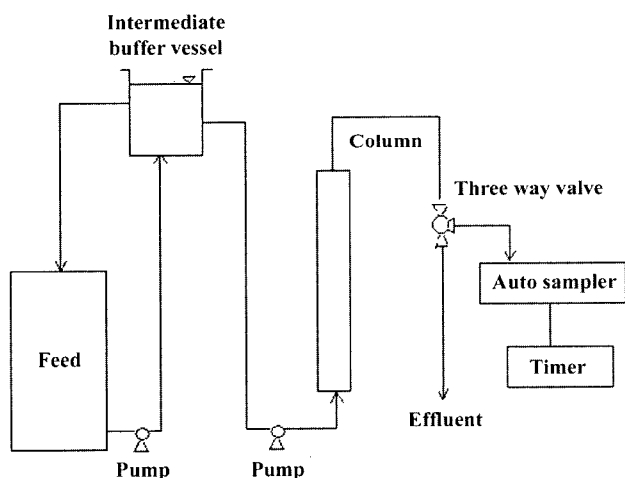


Fig. 1. Schematic diagram of the laboratory-scale installation (up-flow direction).

Table 1. Concentrations of main components of tap water at the Karlsruhe Research Centre [3].

Element	Concentration (mg/l)
Calcium	98.1
Magnesium	12.6
Sodium	18.9
Chloride	35.6
Nitrate	4.5
Sulfate	76.1
DOC	0.5–1.5

on the mercury sorption capacity was investigated by adding the respective salts in different concentrations. The spiked tap water of the Karlsruhe Research Centre had a background salt content with different chlorides, sulfates, and hydrogen carbonates of calcium, magnesium, and sodium. Table 1 shows the concentration of the main components [3].

The concentration of metal ions in feed and effluent samples was measured by means of an atomic absorption device (Perkin-Elmer 1100 B).

RESULTS AND DISCUSSION

Breakthrough Curve for Mercury

Figure 2 shows the effect of flow rate on breakthrough curve of the column packed with aminated chitosan bead. As shown in this figure, the breakthrough point, which is generally defined as 5% of the feed concentration, was reached after total throughputs of around 800 bed volumes (20 BV/h) and 900 bed volumes (10 BV/h), except for a few samples. Before the breakthrough point, the concentrations

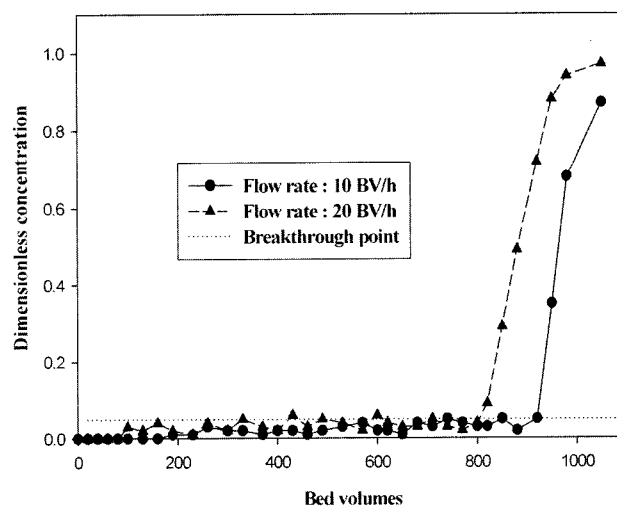


Fig. 2. Effect of flow rate on breakthrough curve of mercury ions (Bed volume=60 ml; Influent concentration=10 mg/l).

of a few samples were below the limit of measurement by AAS. The result shows an excellent sorption, but with some influence of the contact time or the rate of filtration. It has been reported in the literature that the breakthrough of mercury in a packed-bed column with thiourea-based coordinating resins with a similar sorption capacity of 2.0 mmol/g dry mass occurred after around 450 bed volumes [15]. Although the two materials have a similar adsorption capacity, there is a considerable difference in the performance. Biosorbent with lower affinity to metal ions cannot effectively remove heavy metal species from aqueous solutions, even if a great sorption capacity might be assumed because of the structure [7]. In the case of aminated chitosan bead, the breakthrough curves increased sharply, indicating the good affinity for mercury species.

Recovery of Mercury Ion Using EDTA Solution

As shown in Fig. 3, the Hg^{2+} ions bound to the aminated chitosan material was readily released and quantitatively recovered by means of a few bed volumes of 0.01 N EDTA solution, whose efficiency had previously been determined in batch experiments as the optimum concentration. To achieve a desorption efficiency of above 95%, about 3 bed volumes of solution were required regardless of the flow rate.

The maximum concentration factor, defined as the ratio of effluent and influent concentration, differed depending on the flow rate. In the case of a low flow rate, the value amounted to about 770 and was much bigger than that of high flow rate. Because the contact time decreases with increasing flow rate [13], the elution of mercury becomes more effective at low flow rates, resulting in a narrower and higher concentration peak in the effluent. The high

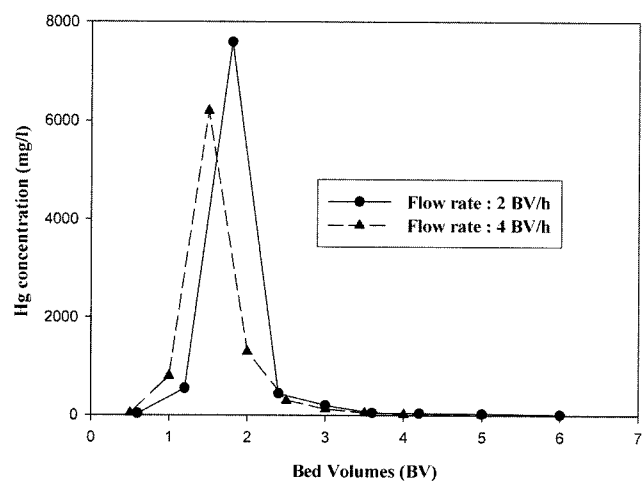


Fig. 3. Effect of flow rate on desorption of mercury ions using 0.01 N EDTA solution (Amount of pre-loading with mercury=9.240 mg/l).

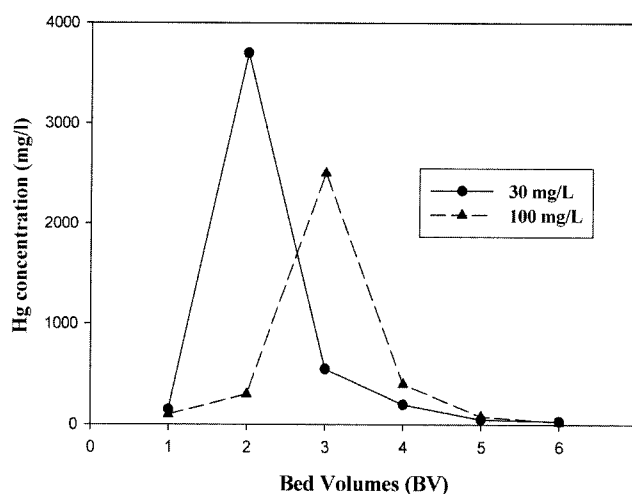


Fig. 4. Development of desorption at different initial mercury ion concentrations (Bed volume=60 ml; Flow rate=2 BV/h).

concentration factor reduces the volume of the highly concentrated mercury solution.

EDTA is a very strong desorbent, but it is an expensive chemical. Therefore, the reuse of EDTA containing mercury at different concentrations was carried out. For this investigation, mercury nitrate was added to a 0.01 N EDTA solution. The development of elution at two different initial mercury concentrations is plotted in Fig. 4. In both cases, the elution of mercury was complete and required about 4 BV of EDTA solution. However, the desorption efficiency and the maximum concentration factor were decreased as the concentration of mercury ion increased. In comparison with an Hg-free EDTA solution, the decrease of elution efficiency amounted to about 50% with 30 mg/l of initial mercury concentration and 35% with 100 mg/l of initial mercury concentration.

To improve the applicability of EDTA and to solve the problem of toxicity of the mercury-EDTA complexes in the elution effluents, the splitting of the complexes as a post-treatment might offer a solution: EDTA-metal complexes can be separated as solid EDTA and metal chloride/sulfate, respectively, by means of hydrochloric acid or sulfuric acid. For this investigation, both acids were applied to split the mercury-EDTA complexes. Addition of sulfuric acid led to a gradual precipitation of EDTA at a pH value of 2.1. After precipitation was completed, the solid EDTA was washed several times and dried. The yield of EDTA obtained from this treatment was about 95%. In order to investigate the efficiency of reused EDTA, another desorption experiment was carried out. As shown in Fig. 5, about 4 bed volumes of EDTA solution were again required by which about 75% of the mercury adsorbed was eluted. The maximum Hg concentration in the effluent was about 5,500 mg/l. The result shows the possibility to reuse recovered EDTA.

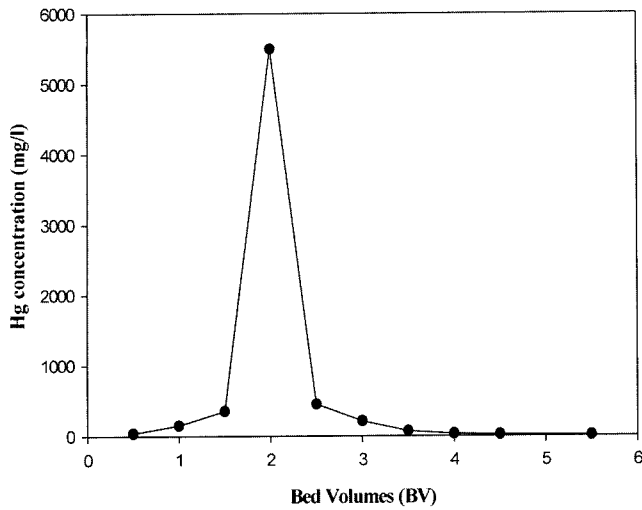


Fig. 5. Development of desorption of mercury species using recovered EDTA (Bed volume=60 ml; Flow rate=2 BV/h).

Regeneration of Aminated Chitosan Bead

The results of the repeated sorption/desorption processes are listed in Table 2, which gives the breakthrough bed volumes of the subsequent experiments. As the figures indicate, approximately the same lengths of the operation cycles were obtained. This also means that the aminated chitosan bead was not deteriorated by EDTA solution. Therefore, an economic application of such adsorbents seems reasonable.

Effect of Alkaline Metal Ions on Mercury Removal

It has been known that biosorbents very selectively adsorb heavy metals [11]. To confirm this selectivity, experiments with calcium and magnesium-bearing raw waters were carried out. As shown in Fig. 6, the alkaline earth ions showed an immediate breakthrough at very relatively small volumes of throughput, while the breakthrough point of mercury did not change and occurred at around 800 bed volumes. This supports the assumption that the sorption of mercury was practically not affected by the alkaline earth ions. This result is in agreement with data from literature that show that the presence of alkaline earth ions at concentrations of 100 ppm did not significantly decrease the rate and capacity of sorption of cadmium [6]. As a consequence, it can be expected that aminated chitosan material can

Table 2. Breakthrough throughputs from repeated adsorption and desorption experiments.

Cycle number	Bed volumes
1	865
2	840
3	790
4	820

Flow rate: 2 BV/h; Bed volume=60 ml; Influent concentration: 10 mg/l; Breakthrough point: 0.5 mg/l.

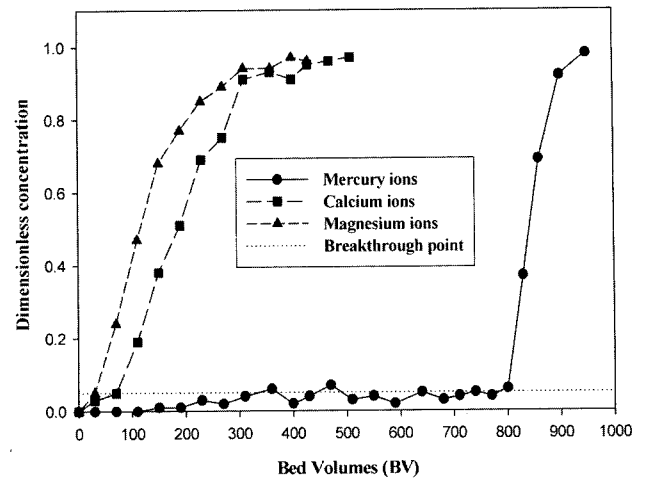


Fig. 6. Breakthrough performance of calcium and magnesium ions and their effect on the breakthrough of mercury (Bed volume=60 ml; Flow rate=10 BV/h; Influent concentration of mixed metal solution=0.05 mol/l).

replace commercially available ion exchangers that do not show the same kind of selectivity for heavy metals.

Mercury Removal from Spiked Tap Water

Figure 7 shows results of an experiment in which the aminated chitosan material was contacted with Hg-spiked tap water. Unlike in the preceding experiments, the feed concentration was in the range of 8.0–9.0 µg/l. According to the drinking water standards, the breakthrough point for mercury ions was assumed to be 1 µg/l. As shown in this figure, this breakthrough point was exceeded after about 6,000 bed volumes. Because of the strongly decreased feed concentration, a much larger total volume of water can be

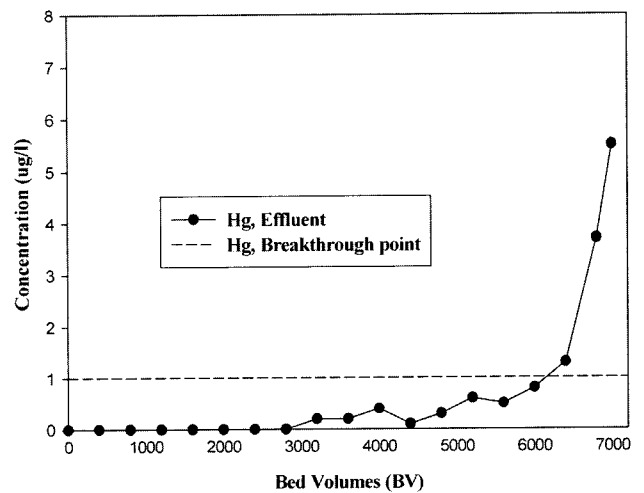


Fig. 7. Development of mercury elimination from spiked tap water of the Karlsruhe Research Centre (Bed volume=60 ml; Flow rate=20 BV/h; Influent concentration= 8.0–9.0 µg/l).

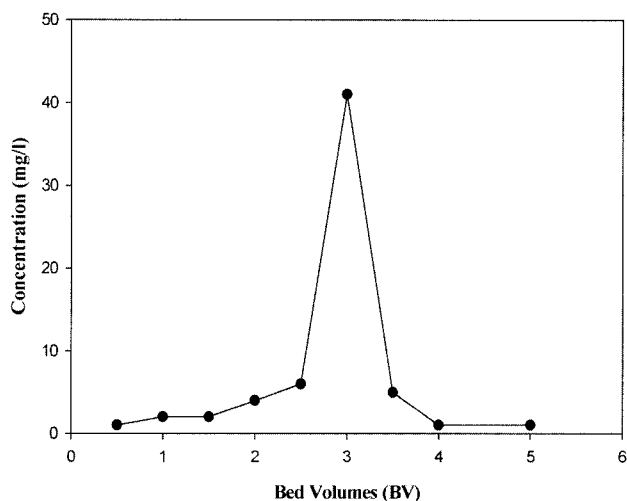


Fig. 8. Development of desorption of mercury ions using 0.01 N EDTA (Source water: Spiked tap water at the Karlsruhe Research Centre; Amount of pre-loading with mercury ions=65 mg/l; Flow rate=2 BV/h).

treated. Corresponding to the equilibrium of sorption, the metal uptake capacity (i.e., amount of metal per unit mass of biosorbent) decreases. Similar phenomena have also been reported by Zulfadhly *et al.* [14], who investigated the effect of feed concentration on the breakthrough performance of lead ions. The decrease is also in agreement with results of Zhao *et al.* [13], who used a chitosan-based exchanger. Because of the length of the concentration profile in a column, the length of the column can have some influence on the sorption and improve the efficiency [9].

Figure 8 shows the development of desorption of mercury, which is quantitatively displaced from the aminated chitosan material by means of about 4 bed volumes of 0.01 N EDTA. Elution efficiency amounted to about 95%. The maximum concentration factor for mercury reached the values of about 4,200. These results demonstrate the efficiency of the elimination process for natural waters.

The potential of aminated chitosan material as a biosorbent for mercury removal has been demonstrated by means of packed-bed column tests. The material revealed an efficient elimination with a steep increase of effluent concentration after rather large throughputs. Mercury species (Hg^{2+}) adsorbed by the material was readily eluted and recovered quantitatively from the column by 4 bed volumes of a 0.01 N EDTA solution. Used EDTA could be recovered after precipitation by means of sulfuric acid. The recovered EDTA could elute mercury with an efficiency of about 75%. Mercury sorption was practically independent from the background alkaline earth cations. Results obtained with distilled water could be confirmed by experiments in which a spiked natural water was applied.

Acknowledgment

This study was supported by a research fund provided by Forschungszentrum Karlsruhe, Germany.

REFERENCES

1. Bolto, B. A. and L. Pawlowski. 1987. *Wastewater Treatment by Ion-exchange*, pp. 195–202. E.&F.N. SPON, New York.
2. Brooks, C. S. 1991. *Metal Recovery from Industrial Waters*. Lewis publishers, Chelsea, MI.
3. Hoell, W. H., C. Bartosch, X. Zhao, and S. He. 2002. Elimination of trace heavy metals from drinking water by means of weakly basic anion exchangers. *J. Water Supply: Research and Technology-AQUA* **51(3)**: 165–172.
4. Heisen, T. Y. and G. L. Rorrer. 1995. Effects of acylation and crosslinking on the material properties and cadmium ion adsorption capacity of porous chitosan beads. *Separ. Sci. Technol.* **30(12)**: 2455–2475.
5. Jeon, C. and W. H. Hoell. 2003. Chemical modification of chitosan and equilibrium study for mercury ion removal. *Water Res.* **37**: 4770–4780.
6. Jha, I. N., L. Iyengar, and A. V. S. Rao. 1988. Removal of cadmium using chitosan. *J. Environ. Eng.* **114**: 962–974.
7. Kim, Y. H. 1996. Heavy metal removal using chemically modified marine brown alga, *Undaria pinnatifida*. Ph.D Thesis, Seoul National University.
8. Pradhan, S., S. Sarita, C. R. Lal, and L. P. Dorothy. 1998. Evaluation of metal biosorption efficiency of laboratory grown microcystis under various environmental conditions. *J. Microbiol. Biotechnol.* **8**: 53–60.
9. Pradip, P. K. and M. M. Sharma. 1991. Recovery of heterocyclic amines from dilute aqueous solution waste streams. *Ind. Eng. Chem. Res.* **30**: 1880–1886.
10. Remmers, P. and K. D. Vorlop. 1992. Production of highly elastic polyvinyl alcohol biocatalyst beads and their use for continuous denitrification, pp. 939–942. In: *Proceedings of the De CHEMA Biotechnology Conferences*, Vol. 5, VCH, Weinheim.
11. Volesky, B. 1990. *Biosorption of Heavy Metals*, pp. 11–12. CRC Press, Inc.
12. Yang, T. C. and R. R. Zall. 1984. Absorption of metals by natural polymers generated from seafood processing waters. *Ind. Eng. Chem. Prod. Res. Dev.* **23**: 168–172.
13. Zhao, X., W. H. Hoell, and G. Yun. 2002. Elimination of cadmium trace contaminations from drinking water. *Water Res.* **36**: 851–858.
14. Zulfadhly, Z., M. D. Mashitah, and S. Bhatia. 2001. Heavy metals removal in fixed-bed column by the macro fungus *Pycnoporus sanguineus*. *Environ. Poll.* **112**: 463–470.
15. Zuo, G. and M. Muhammed. 1995. Selective binding of mercury to thiourea-based coordinating resins. *React. Polym.* **27**: 187–198.