

Dry-column Vacuum Chromatographic Removal of Hg²⁺ from Wastewater Based on an Acridino-crown Ether-modified Spherical Silica Gel Adsorbent

Panna Vezse¹, János Attila Kalóczkai¹, Dániel Ster¹, László Bezúr², Ádám Golcs^{1*}, Péter Huszthy¹, Tünde Tóth^{1,3}

¹ Department of Organic Chemistry and Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary

² Department of Inorganic and Analytical Chemistry, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary

³ Institute for Energy Security and Environmental Safety, Centre for Energy Research, Konkoly-Thege Miklós út 29–33., H-1121 Budapest, Hungary

* Corresponding author, e-mail: golcs.adam@edu.bme.hu

Received: 19 November 2022, Accepted: 28 March 2023, Published online: 09 May 2023

Abstract

Dry-column vacuum chromatographic technique is introduced for remediation of wastewater for the first time. A previously prepared chemically modified silica gel containing covalently immobilized Hg²⁺-selective acridino-crown ether selector molecules was used as an adsorbent. Removal of Hg²⁺ from highly contaminated river water was carried out to study practical applicability. Adsorption capacity, preconcentration factor, pH-sensitivity and selectivity in separation were determined. The adsorbent proved to be outstanding in selectivity, only Ag⁺ and Cu²⁺ interfered among 29 cations, was inert toward organic contaminants, exhibited regenerability and pH-independency between 3.0 ≤ pH ≤ 7.0. The proposed method showed a moderate efficiency in both adsorption (32 mg Hg²⁺ / 1 g adsorbent) and preconcentration (preconcentration factor of 100). A maximum 10 L of wastewater / 1 g adsorbent ratio is recommended as an upper limit for applicability. The described method showed a unique robustness and simplicity compared to conventional ion-chromatographic methods and an improved selectivity over physical interaction- or simple functional group-based adsorptions.

Keywords

mercury, wastewater, remediation, chromatography, molecular recognition

1 Introduction

Heavy metal contamination belongs to the biggest concerns regarding environmental issues, due to the destructive effects to human- and wildlife [1]. Mercury is one of the most toxic elements. It originates from both natural and anthropogenic sources, e.g., agriculture, fossil fuel combustion, light, heavy and pharmaceutical industries [2]. The global emission of mercury reaches at least 7 kt/year [3]. In aquatic environment, the greatest threat is caused by dissolved Hg²⁺ since microorganisms convert many forms of mercury to methyl mercury, which can enter the food chain [4]. Due to the high binding affinity to free sulfhydryl groups, mercury can damage the structure of proteins and disturb the membrane potential causing serious cardiovascular, neurotic and renal disorders [5, 6].

Monitoring and restricting environmental contamination are strongly required to avoid the highly toxic impacts of mercury. Natural sources typically cause only a low mercury content in surface waters (e.g., the maximum concentration of mercury was measured as 1.0 ng·L⁻¹, 3.2 ng·L⁻¹ and 2.78 ng·L⁻¹ in the Great Lakes [7], in Lake Baikal [8] or in 29 European streams [9], respectively). Attributed to anthropological activities, mercury concentrations in surface waters are usually orders of magnitude higher (e.g., the mean concentration of mercury was determined as 1.4 μg·L⁻¹, 0.12 μg·L⁻¹ and 0.74 μg·L⁻¹ in Caspian Sea [10], in Yellow River [11] or in Sarno River [12], respectively) and can even reach a level of 2.6 mg·L⁻¹ in highly contaminated areas [13].

Numerous methods have been developed for removing Hg^{2+} , including chemical precipitation, bio-remediation, ion exchange, solvent extraction, membrane separation and adsorption. These methods show several drawbacks compared to adsorption, e.g., the use of hazardous chemicals, adverse reusability, tendency for secondary pollution, large quantities of solvent, weak selectivity, mechanically adverse materials or complicated operation [14–19].

Recent research activities still focus on new remediation techniques, because besides their high efficiency in recovering mercury, robustness, selectivity, scalability or regenerability are among the areas, which need to be improved [20–29].

The combination of physical (porous structural materials with large surface areas) and chemical (organic binding sites) adsorption is expected to result in both the highest removal efficiency and adsorption capacity in practice [14]. Recently, chemically modified porous nanomaterials, – i.e., covalent organic frameworks, porous organic polymers, porous metal oxides, metal organic frameworks, mesoporous organosilicas and modified graphene oxides – are considered as promising classes of adsorptive materials because of their high surface area and strong host-guest interactions [30, 31]. However, they generally show a high acid-sensitivity, which is clearly a disadvantage as the removal of Hg^{2+} is especially difficult in acidic medium [16, 32].

On the other hand, the most frequently used adsorbents, – i.e., carbon-based materials, silicas, post-modified polymers – typically suffer from a reduced selectivity as besides the physical interactions polar functional group-driven coordination is primarily responsible for adsorption [33]. The surface of the adsorbents is often functionalized with amine, carbonyl, carboxyl, phenol, quinone, lactone and especially with sulfonic acid, sulphur or thiol units [15, 30, 31, 34]. The proper ionization forms of these polar units are prone to bind Hg^{2+} mainly by their lone pairs (soft-soft metal-ligand / electrophile-nucleophile interaction). Thus, these separation techniques typically show a strong pH-dependence [34, 35]. Moreover, contaminants and competitive agents also tend to have a high affinity to the functionalized, charged surfaces [36].

Selectivity can be improved by applying widely used adsorbents supported by covalently immobilized host molecules, e.g., crown ethers [37]. Since these synthetic receptors are able to recognize and form inclusion complexes with a targeted species, the probability for binding a competitor or a contaminant is also decreased.

In our research group, Kertész et al. successfully bounded an acridino-18-crown-6 ether to spherical silica

gel and this adsorbent was preliminary studied in separation of metal ions [38]. We report herein the practical application-oriented studies of this adsorbent using it as a stationary phase in a dry-column vacuum chromatographic process to remove Hg^{2+} from wastewater. This is the first time that this technique is used for heavy metal remediation. Furthermore, this method applied previously for purification in organic synthesis [39, 40] was firstly introduced as a scalable, less complicated and more environmentally friendly (less amounts of solvent and adsorbent are required) alternative to the conventional liquid chromatography in metal ion separation.

2 Experimental

2.1 Materials and apparatus

Functionalization of the silica gel adsorbent was carried out based on a reported procedure [38]. Spherical silica gel [PharmPrep® 60 CC (40–63 μm), Merck] (12.0 g) and 12-[3-(triethoxysilyl)propyl]-6,9,15,18-tetraoxa-12,25-diazatetracyclo[21.3.1.0^{5,26}.0^{19,24}]heptaco-1(26),2,4,19,21,23(27),24-heptaene (1.18 g, 2.05 mmol) [38] in dry and pure toluene (125 mL) were stirred at reflux temperature under Ar atmosphere for 2 days. The reaction mixture was cooled down to 20 °C and the modified silica gel was filtered off and washed with toluene (60 mL), dichloromethane containing 1% triethylamine (60 mL), methanol (60 mL), aqueous methanol (67 V/V%, 60 mL) and methanol (60 mL), respectively. Then the functionalized silica gel adsorbent was dried at 65 °C for 1 day. Untreated silica gel as a blank sample was consequently dried. The elemental analysis of this blank sample provided the following results C: 0.31; H: 1.25; N: 0.00, while that of the modified silica gel gave C: 4.86; H: 1.67; N: 0.46. According to these measurements, each gram of the functionalized adsorbent contains 0.16 mmol (by C%), 0.14 mmol (by H%), and 0.16 mmol (by N%) of the acridino-crown ether selector molecule.

Studies were carried out by using a special glass column with a sidearm for vacuum (Fig. 1).

Vacuum was provided with a water aspirator and was kept at 20.0 ± 2.0 mbar which resulted in a volumetric flow rate of 15.0 ± 3.0 mL \cdot min⁻¹. The column of 21.5 mm inner diameter was filled with 14.0 g of dry adsorbent, which resulted in well-compacted bed height of 70.0 mm (part B of Fig. 1). There was a porous glass filter with a pore size of 5–15 μm at the bottom of the column (part C of Fig. 1).

The samples were collected from river Danube (Budapest, Hungary GPS coordinates: 47°29'06.5"N 19°03'11.8"E, 12/10/2021. 8⁰⁰) and filtered with a porous

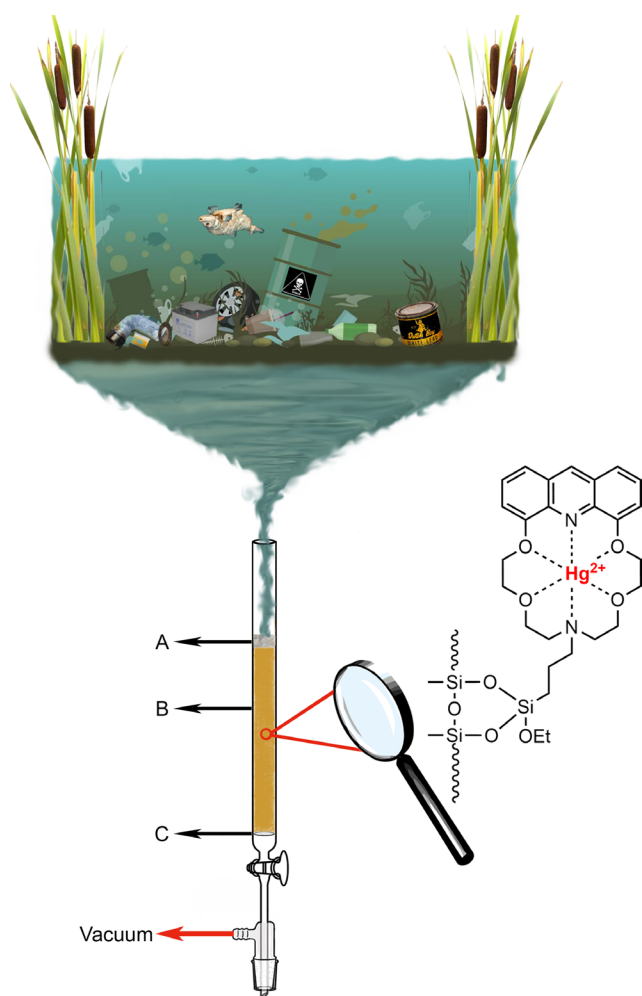


Fig. 1 The applied vacuum chromatographic column (A: sand layer, B: adsorbent, C: glass filter)

glass filter with a pore size of 5–15 μm . Detailed information regarding the composition of the river water samples can be found in the Supplement. The pH of the river water was originally 7.8, which was adjusted to 3.0 by using nitric acid to avoid the precipitation of the metal ions. The pretreated samples were spiked with $\text{Hg}(\text{NO}_3)_2$ to gain simulated wastewater for separation studies.

2.2 Studies on removal of Hg^{2+}

The adsorbent was suspended in acetone and this suspension was poured into the column. The column was tapped gently to compress the stationary phase and to remove voids, then the solvent was sucked from the column. This method resulted in a more compacted adsorbent bed compared to dry filling. A splashguard was applied to avoid the bumping of the dried adsorbent. For this purpose, a 2 cm high inert and fine-grained sand layer (porous size: 100–300 μm , see part A of Fig. 1) was used on the top of the adsorbent and the wastewater was directed onto this. Moreover, this layer provided a homogenous distribution of the wastewater

before contacting the adsorbent. As a final step, the bed was pressed down carefully while applying full suction.

The stationary phase was tested for voids and channels by eluting acetone, while applying suction. During this procedure, the surface of the adsorbent bed was kept covered with the solvent for 5 min. Then the addition of the solvent was interrupted and the column was sucked dry. The flow rate was constant, no channels and voids occurred and an adsorbent bed of uniform consistency was obtained.

During the experiments, the fractions of the sample were poured onto the sand layer protecting the surface of the adsorbent. The volume of the fractions varied with the desired resolution of the results. When a fraction was sucked through the column, the vacuum was discontinued and the fraction was segregated. After eluting the final portion of the wastewater sample the column was regenerated by using aqueous solution of nitric acid (10 V/V%) and distilled water subsequently as reported in Section 3.3.

2.3 Analytical measurements

The composition of multielement samples was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Sample solutions were measured in simultaneous, multielement mode by a Labtest Plasmalab ICP-spectrometer (Labtest Equipment Company, USA) with a 40-channel Paschen-Runge vacuum polychromator with photomultiplier detectors. Additional information on instrumentation and measurement settings can be found in the Supplement.

Concentration of Hg^{2+} was determined by cold vapor mercury method (CV-Hg-AAS) in the cases of samples with $c(\text{Hg}^{2+}) < 10$ ppm. The mixed, micro reactor type cold vapor instrument with a 7 cm long gas cuvette was attached to a Unicam SP-9 atomic absorption spectrometer (Pye Unicam Ltd., UK) combined with PC data station. Sample volume of 3.00 mL and an SnCl_2 reduction agent was used. The calibration covered the range of 0.01–10 ppm for Hg^{2+} .

3 Results and discussion

3.1 Removal of Hg^{2+}

Natural water samples were collected from river Danube and artificially contaminated with Hg^{2+} to gain wastewater samples for studies on the efficiency of the modified silica gel adsorbent in removing Hg^{2+} . An unusually high concentration of Hg^{2+} had to be applied to be able to determine the maximum adsorption capacity. The ionic composition of the simulated wastewater sample can be found in the Supplement. As the selective retention is directly caused by forming reversible inclusion complexes with crown

ethers (1:1) when flowing through the stationary phase, the theoretical adsorption capacity was calculated based on the amount of the immobilized host molecule [38]. The total adsorption capacity of the adsorbent was calculated to be 32 mg Hg²⁺/ 1 g adsorbent (Hg²⁺ was present as nitrate salt in the samples since nitric acid was used for pH-adjustments.).

During the study, 100 mL-portions of wastewater were subsequently poured on the column and sucked through the adsorbent layer under vacuum. The relative adsorption capacity related to the theoretically calculated maximum effectiveness for the retention of Hg²⁺ was recorded as a function of the eluted volume. The results are reported in Fig. 2.

Acidic conditions adversely affect the complexation of the immobilized host molecules [41] since the complexing ligands become partially protonated. Thus, the capacity values determined at pH = 3.0 can be considered as pessimistic estimates of the maximum available real binding capacity of the adsorbent. However, it can be seen, that the real adsorption capacity almost reached the theoretical maximum. It follows, that the pH of the wastewater has only a negligible influence on the removal of Hg²⁺ in a broad pH-range of 3.0-7.0, which means an outstanding pH-independency and robustness in practical applicability. Based on the observed adsorption capacity, 1 g of the adsorbent is able to totally remove Hg²⁺ from 10 L of extremely contaminated wastewater [13].

3.2 Selectivity in separation

Since river waters contain many cations from natural sources, the analysis of the eluted fractions also provides opportunity for studying the selectivity in ion-separation. The changes in the ion concentration of each fraction during the separation process can be seen in Fig. 3 in the cases of only those ions, which concentration changed significantly upon passing through the adsorbent.

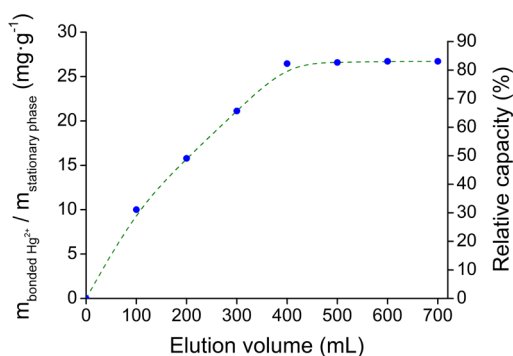


Fig. 2 Removal of Hg²⁺ from contaminated river water with an extremely high Hg²⁺-content of above 600 ppm (pH was adjusted to 3.0 with nitric acid)

The diagrams show, that in addition to Hg²⁺, the binding of Sn²⁺, K⁺, Fe²⁺, Al³⁺ and Cr³⁺ also took place. In the cases of the other 24 investigated cations (see Supplement), no significant retention was observed as the immobilized host molecules did not coordinate them. The relatively high concentration of Sn²⁺ in the wastewater can be attributed to spiking the river water with Hg²⁺, which simultaneously caused an additional contamination with Sn²⁺ due to its copresence (Fig. 3 (b)). The initial concentrations of the other ions can be considered typical for the natural source. Binding the competing ions was significant only in the initial state covering the elution of the first 400 mL of the sample. In this state, the total amount of the competing ions occupied approximately 10-12% of the binding capacity. It also means, that the difference between the theoretically calculated maximum capacity of the adsorbent and its determined real value is caused by the weak coordination of the competing ions. After the fourth fraction, all of the competing ions were eluted from the adsorbent because of the highly reversible complexation of the immobilized host molecules. Obviously, the affinity toward other ions was not as high as in the case of Hg²⁺. Among cations, only an untypically large concentration of Ag⁺ or Cu²⁺ can limit the applicability according to preliminary studies on the selectivity of the applied host molecule [38].

3.3 Regeneration of the stationary phase

Since the crown ether immobilized to the silica gel form a highly reversible complex with Hg²⁺ ($\log K_{\text{complex}} \approx 2$, [38]), a large amount of water can also induce the decomplexation of the ligands. It is clearly an adverse property for removing the contaminants, but an advantage from the aspect of regeneration and reusability. From the latter point of view, regenerability was firstly studied by using distilled water as an eluent after reaching the total occupation of the adsorbent during a previous Hg²⁺-recovery procedure. Results are shown in Fig. 4.

Based on the measurements, the almost complete regeneration of the adsorbent totally saturated with Hg²⁺ required the use of 15 L distilled water. Naturally, the leaching of complexed Hg²⁺ from the adsorbent would take place later in the case of eluting wastewater or other solutions of high ionic strength as well as in the case of a partial utilization of the full adsorption capacity. Thus, it is an especially pessimistic estimation for the possibility of leaching during the elution.

When slightly contaminated river water with a Hg²⁺-content of 0.4 ppm passed through a column containing the regenerated adsorbent (0.0% relative saturation), no

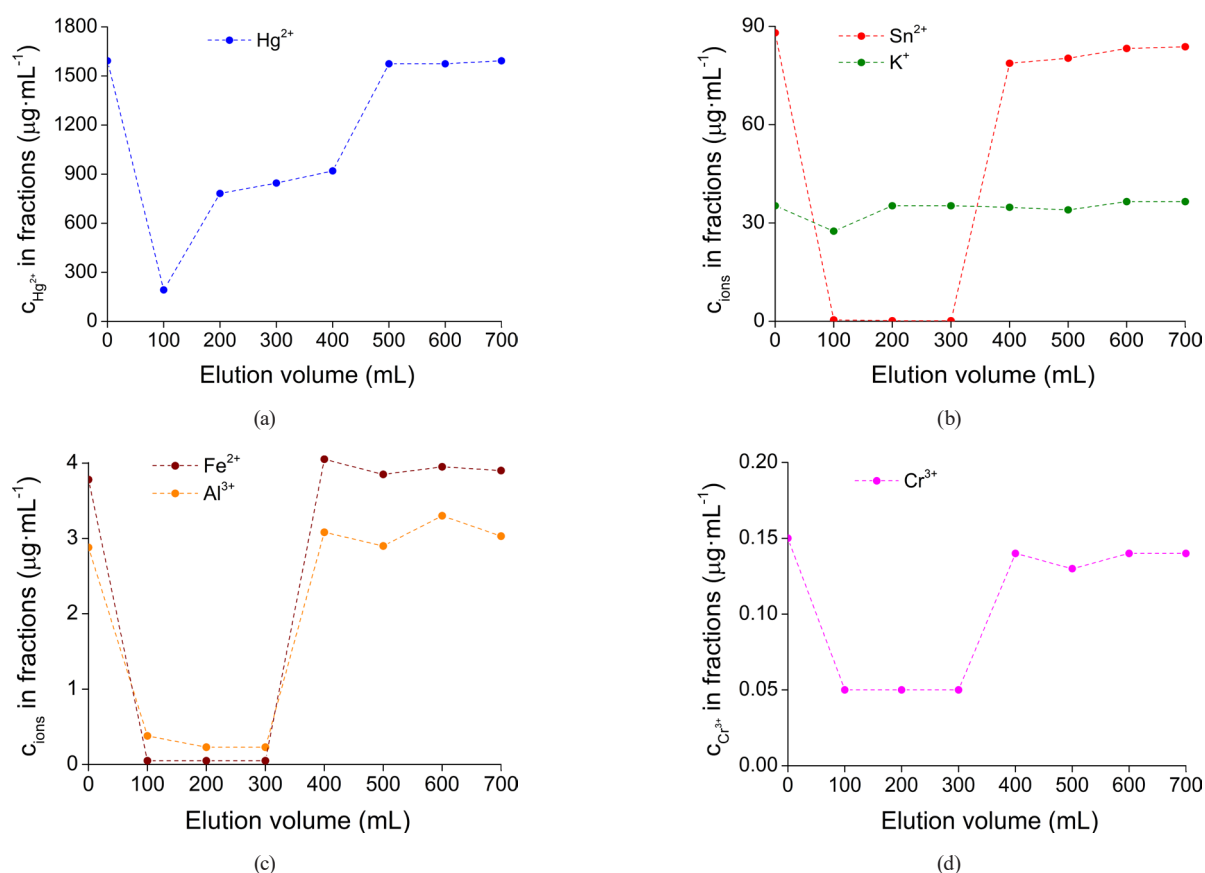


Fig. 3 Changes in the concentration of the remediated wastewater-fractions in the cases of potential competing ions (The competing ions come from a natural source except Sn^{2+} , which increased concentration in the samples is attributed to spiking with Hg^{2+} . The pH of the initial wastewater was adjusted to 3.0 using nitric acid.); (a) Changes in Hg^{2+} -content during remediation; (b) Changes in Sn^{2+} - and K^{+} -content during remediation; (c) Changes in Fe^{2+} - and Al^{3+} -content during remediation; (d) Changes in Cr^{3+} -content during remediation

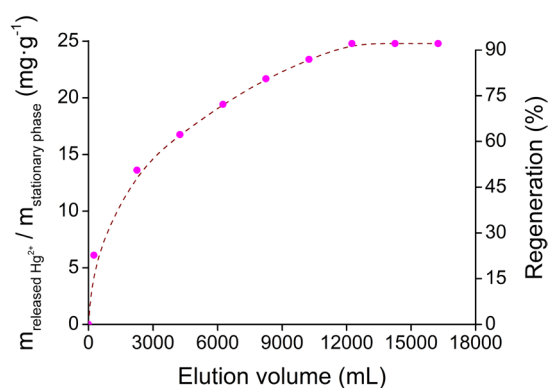


Fig. 4 The release of Hg^{2+} from a fully saturated adsorbent using distilled water as an eluent

significant decomplexation of Hg^{2+} was observed up to 10 L of elution volume / 1 g adsorbent (12.5% relative saturation). Additional information can be found in the Supplement. It indicates, that the removal of Hg^{2+} can be effectively performed unless applying the adsorbent highly saturated with Hg^{2+} . On the other hand, the highly reversible complexing ability of the immobilized ligand designates an upper limit in applicability for removal of Hg^{2+} . It means, that effective retention of Hg^{2+} can be maintained until reaching the critical

ratio of 10 L wastewater / 1 g adsorbent when the ionic strength is below $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ (typical for surface waters).

Studies on reusability were reported in the Supplement. It was found, that subsequent Hg^{2+} -removal processes can be performed with similar efficiency. The binding capacity of the adsorbent did not show a decreasing trend.

For rapid and simple regeneration, 100 mL of 10 V/V% aqueous solution of nitric acid was successfully used. It proved to be suitable for the complete removal of Hg^{2+} from the adsorbent. Consequently, the preconcentration factor was 100. After regeneration, the residues of acid need to be washed off using a three-fold excess of distilled water.

3.4 Comparison with other methods

The studied spherical silica gel-based stationary phase showed a unique robustness among chemically modified adsorbents as an unprecedented pH-independent working range of 3.0–7.0 was obtained coupled with an exceptional regenerability and selectivity in separation.

The high selectivity of the studied stationary phase to other adsorbents is related to the formation of special-type

coordinating interactions for retaining Hg^{2+} . The immobilized supramolecular inclusion ligand greatly surpasses conventional chemically polarized material-surfaces in selective coordination of cations due to its structural specificity and ability for molecular recognition. The majority of adsorbents functionalized with polar groups [15, 30, 31, 34, 37] can coordinate any soft electrophilic cations besides Hg^{2+} as well as organic compounds, which have an electrophilic character. Therefore, the exposure of these adsorbents to both competing ions and organic contaminants is greatly increased, which inevitably decreases the selectivity in separation [33, 36, 37].

For similar reasons, the studied adsorbent overcomes the conventional ones (typically exploiting polarity-based interactions) by its large range of pH-independency since all of the molecular centers of the immobilized ligand responsible for coordination cannot be directly disabled by protonation. Thus, it is needless to adjust the pH precisely unless unusual conditions are present, which carries an exceptional simplicity comparing to other procedures for removal of Hg^{2+} [16, 32, 34, 35].

The insensitivity to hard conditions, especially to acids during both application and regeneration renders a further contribution to the robustness of the procedure. Moreover, plugging and fouling of the column can be easily eliminated. While solid contaminants tend to trap on the top of the small-pore-size adsorbent layer, organic contaminants adhering to the stationary phase can be easily washed off with apolar organic solvents. (Acetone is recommended as it can be removed by eluting water.) The presence of organic contaminants (investigated by using a mixture of amino acids, see Supplement) did not influence the separation.

Compared to other adsorbents [14–16, 31, 37, 42], an adsorption capacity of a medium value was obtained due to the few binding sites, which value appreciates in the light of the improved selectivity.

The preconcentration factor was determined as 100, which can be regarded moderately high among chemically modified adsorbents [37].

4 Conclusions

The novelty of the present work lies on the introduction of dry-column vacuum chromatography in wastewater-remediation for the first time. It provides a faster,

less complicated (no continuous flow system and efforts against column-drying) and more environmentally friendly (less eluent, adsorbent and preparation) alternative to functionalized stationary phase-based conventional liquid chromatography.

The studied adsorbent is especially suitable for preconcentration and for the removal of Hg^{2+} from previously preconcentrated samples or highly contaminated wastewaters. The reversible complexing property of the immobilized ligand resulted in an outstanding regenerability and gave a maximum permissible ratio of 10 L wastewater to 1 g adsorbent as a recommended upper limit for applicability considering both binding capacity and limitations from the decomplexation of bonded Hg^{2+} .

It can be concluded, that the competitiveness of acridino-crown ether-modified silica gel compared to other adsorbents was demonstrated by its several advantages (wide range of pH-independency, robustness, regenerability, selectivity) in practice. Based on the present results, the application of dry-column vacuum-chromatographic method can establish a novel direction in heavy metal separation and in remediation of highly contaminated wastewaters.

Sections in the Supplement

Further information can be found in the Supplement regarding the following topics:

1. Additional information on instrumentation and measurement settings regarding the ICP-OES method.
2. Ionic composition of the river- and untreated wastewater samples.
3. Removing Hg^{2+} from slightly contaminated wastewater using a regenerated adsorbent.
4. Studies on reusability.
5. Studies on the possible limitations caused by organic contaminants.

Acknowledgement

Special thanks to Ferenc Viczián for manufacturing the chromatographic equipment. The authors express their thanks to Dr. Júlia Kertész and to Dr. Attila Kormos for their preliminary work on the applied stationary phase. The financial support of the National Research, Development and Innovation Office (grant number: K128473) is gratefully acknowledged.

References

- [1] Nagajyoti, P. C., Lee, K. D., Sreekanth, T. V. M. "Heavy metals, occurrence and toxicity for plants: A review", *Environmental Chemistry Letters*, 8(3), pp. 199–216, 2010.
<https://doi.org/10.1007/s10311-010-0297-8>
- [2] Gworek, B., Dmuchowski, W., Baczevska, A. H., Brągoszewska, P., Bemowska-Kałabun, O., Wrzosek-Jakubowska, J. "Air contamination by mercury, emissions and transformations - A review", *Water, Air, and Soil Pollution*, 228(4), 123, 2017.
<https://doi.org/10.1007/s11270-017-3311-y>
- [3] Gworek, B., Dmuchowski, W., Baczevska-Dąbrowska, A. H. "Mercury in the terrestrial environment: A review", *Environmental Sciences Europe*, 32(1), 128, 2020.
<https://doi.org/10.1186/s12302-020-00401-x>
- [4] Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., Beeregowda, K. N. "Toxicity, mechanism and health effects of some heavy metals", *Interdisciplinary Toxicology*, 7(2), pp. 60–72, 2014.
<https://doi.org/10.2478/intox-2014-0009>
- [5] Hernández-Esquível, L., Zazueta, C., Buelna-Chontal, M., Hernández-Reséndiz, S., Pavón, N., Chávez, E. "Protective behavior of tamoxifen against Hg²⁺-induced toxicity on kidney mitochondria: In vitro and in vivo experiments", *The Journal of Steroid Biochemistry and Molecular Biology*, 127(3–5), pp. 345–350, 2011.
<https://doi.org/10.1016/j.jsbmb.2011.07.004>
- [6] Zhang, Y., Song, Z., Huang, S., Zhang, P., Peng, Y., Wu, P., Gu, J., Dutkiewicz, S., Zhang, H., Wu, S., Wang, F., Chen, L., Wang, S., Li, P. "Global health effects of future atmospheric mercury emissions", *Nature Communications*, 12(1), 3035, 2021.
<https://doi.org/10.1038/s41467-021-23391-7>
- [7] Wiener, J. G., Evers, D. C., Gay, D. A., Morrison, H. A., Williams, K. A. "Mercury contamination in the Laurentian Great Lakes region: Introduction and overview", *Environmental Pollution*, 161, pp. 243–251, 2012.
<https://doi.org/10.1016/j.envpol.2011.08.051>
- [8] Roberts, S., Adams, J. K., Mackay, A. W., Swann, G. E. A., McGowan, S., Rose, N. L., Panizzo, V., Yang, H., Vologina, E., Sturm, M., Shchetnikov, A. A. "Mercury loading within the Selenga River basin and Lake Baikal, Siberia", *Environmental Pollution*, 259, 113814, 2020.
<https://doi.org/10.1016/j.envpol.2019.113814>
- [9] Bravo, A. G., Kothawala, D. N., Attermeyer, K., Tessier, E., Bodmer, P., Ledesma, J., Audet, J., Casas-Ruiz, J. P., Catalán, N., Cauvy-Fraunié, S., Colls, M., ..., Amouroux, D. "The interplay between total mercury, methylmercury and dissolved organic matter in fluvial systems: A latitudinal study across Europe", *Water Research*, 144, pp. 172–182, 2018.
<https://doi.org/10.1016/j.watres.2018.06.064>
- [10] Abadi, M., Zamani, A., Parizanganeh, A., Khosravi, Y., Badiee, H. "Heavy metals and arsenic content in water along the southern Caspian coasts in Iran", *Environmental Science and Pollution Research*, 25(24), pp. 23725–23735, 2018.
<https://doi.org/10.1007/s11356-018-2455-7>
- [11] Li, Z.-H., Li, Z.-P., Tang, X., Hou, W.-H., Li, P. "Distribution and risk assessment of toxic pollutants in surface water of the lower Yellow River, China", *Water*, 13(11), 1582, 2021.
<https://doi.org/10.3390/w13111582>
- [12] Montuori, P., Lama, P., Aurino, S., Naviglio, D., Triassi, M. "Metals loads into the Mediterranean Sea: estimate of Sarno River inputs and ecological risk", *Ecotoxicology*, 22(2), pp. 295–307, 2013.
<https://doi.org/10.1007/s10646-012-1026-9>
- [13] Obasi, P. N., Akudinobi, B. B. "Potential health risk and levels of heavy metals in water resources of lead-zinc mining communities of Abakaliki, southeast Nigeria", *Applied Water Science*, 10(7), 184, 2020.
<https://doi.org/10.1007/s13201-020-01233-z>
- [14] Xia, M., Chen, Z., Li, Y., Li, C., Ahmad, N. M., Cheema, W. A., Zhu, S. "Removal of Hg(II) in aqueous solutions through physical and chemical adsorption principles", *RSC Advances*, 9(36), pp. 20941–20953, 2019.
<https://doi.org/10.1039/C9RA01924C>
- [15] Al-Yaari, M., Saleh, T. A., Saber, O. "Removal of mercury from polluted water by a novel composite of polymer carbon nanofiber: kinetic, isotherm, and thermodynamic studies", *RSC Advances*, 11(1), pp. 380–389, 2021.
<https://doi.org/10.1039/D0RA08882J>
- [16] Hua, K., Xu, X., Luo, Z., Fang, D., Bao, R., Yi, J. "Effective removal of mercury ions in aqueous solutions: A review", *Current Nanoscience*, 16(3), pp. 363–375, 2020.
<https://doi.org/10.2174/1573413715666190112110659>
- [17] Al-Ghouti, M. A., Da'ana, D., Abu-Dieyeh, M., Khraisheh, M. "Adsorptive removal of mercury from water by adsorbents derived from date pits", *Scientific Reports*, 9(1), 15327, 2019.
<https://doi.org/10.1038/s41598-019-51594-y>
- [18] Atwood D. A., Zaman M. K. "Mercury Removal from Water", In: Atwood D. A. (ed.) *Recent Developments in Mercury Science*, Springer, 2006, pp. 163–182. ISBN 978-3-540-31254-3
https://doi.org/10.1007/430_013
- [19] Pohl, A. "Removal of heavy metal ions from water and wastewaters by sulfur-containing precipitation agents", *Water, Air, & Soil Pollution*, 231(10), 503, 2020.
<https://doi.org/10.1007/s11270-020-04863-w>
- [20] Wang, L., Hou, D., Cao, Y., Ok, Y. S., Tack, F. M. G., Rinklebe, J., O'Connor, D. "Remediation of mercury contaminated soil, water, and air: A review of emerging materials and innovative technologies", *Environment International*, 134, 105281, 2020.
<https://doi.org/10.1016/j.envint.2019.105281>
- [21] Yang, Z., Gu, Y., Yuan, B., Tian, Y., Shang, J., Tsang, D. C. W., Liu M., Gan, L., Mao, S., Li, L. "Thio-groups decorated covalent triazine frameworks for selective mercury removal", *Journal of Hazardous Materials*, 403, 123702, 2021.
<https://doi.org/10.1016/j.jhazmat.2020.123702>
- [22] Wang, L., Wang, M., Li, Z., Gong, Y. "Enhanced removal of trace mercury from surface water using a novel Mg₂Al layered double hydroxide supported iron sulfide composite", *Chemical Engineering Journal*, 393, 124635, 2020.
<https://doi.org/10.1016/j.cej.2020.124635>
- [23] Zhu, Y., Peng, S., Lu, P., Chen, T., Yang, Y. "Mercury removal from aqueous solutions using modified pyrite: A column experiment", *Minerals*, 10(1), 43, 2020.
<https://doi.org/10.3390/min10010043>

- [24] Yap, P. L., Tung, T. T., Kabiri, S., Matulick, N., Tran, D. N. H., Losic, D. "Polyamine-modified reduced graphene oxide: A new and cost-effective adsorbent for efficient removal of mercury in waters", *Separation and Purification Technology*, 238, 116441, 2020.
<https://doi.org/10.1016/j.seppur.2019.116441>
- [25] Kim, H. K., Nguyen, P. T., Kim, M. I., Kim, B. C. "Aptamer-functionalized and silver-coated polydopamine-copper hybrid nanoflower adsorbent embedded with magnetic nanoparticles for efficient mercury removal", *Chemosphere*, 288, 132584, 2022.
<https://doi.org/10.1016/j.chemosphere.2021.132584>
- [26] Bakry, A. M., Awad, F. S., Bobb, J. A., Ibrahim, A. A., El-Shall, M. S. "Melamine-based functionalized graphene oxide and zirconium phosphate for high performance removal of mercury and lead ions from water", *RSC Advances*, 10(62), pp. 37883–37897, 2020.
<https://doi.org/10.1039/D0RA07546A>
- [27] Han, D. S., Solayman, K. M. D., Shon, H. K., Abdel-Wahab, A. "Pyrite (FeS₂)-supported ultrafiltration system for removal of mercury (II) from water", *Emergent Materials*, 4(5), pp. 1441–1453, 2021.
<https://doi.org/10.1007/s42247-021-00282-7>
- [28] Afshari, M., Dinari, M., Zargoosh, K., Moradi, H. "Novel triazine-based covalent organic framework as a superadsorbent for the removal of mercury(II) from aqueous solutions", *Industrial & Engineering Chemistry Research*, 59(19), pp. 9116–9126, 2020.
<https://doi.org/10.1021/acs.iecr.0c00953>
- [29] Dai, D., Yang, J., Wang, Y., Yang, Y.-W. "Recent progress in functional materials for selective detection and removal of mercury(II) ions", *Advanced Functional Materials*, 31(1), 2006168, 2021.
<https://doi.org/10.1002/adfm.202006168>
- [30] Chowdhury, A., Das, S. K., Mondal, S., Ruidas, S., Chakraborty, D., Chatterjee, S., Bhunia, M. K., Chandra, D., Hara, M., Bhaumik, A. "Sulfur-containing nitrogen-rich robust hierarchically porous organic polymer for adsorptive removal of mercury: Experimental and theoretical insights", *Environmental Science: Nano*, 8(9), pp. 2641–2649, 2021.
<https://doi.org/10.1039/D1EN00448D>
- [31] Mario, E. D. A., Liu, C., Ezugwu, C. I., Mao, S., Jia, F., Song, S. "Molybdenum disulfide/montmorillonite composite as a highly efficient adsorbent for mercury removal from wastewater", *Applied Clay Science*, 184, 105370, 2020.
<https://doi.org/10.1016/j.clay.2019.105370>
- [32] Wang, L., Xu, H., Qiu, Y., Liu, X., Huang, W., Yan, N., Qu, Z. "Utilization of Ag nanoparticles anchored in covalent organic frameworks for mercury removal from acidic waste water", *Journal of Hazardous Materials*, 389, 121824, 2020.
<https://doi.org/10.1016/j.jhazmat.2019.121824>
- [33] Abdallah, M. A. M., Mahmoud, M. E., Osman, M. M., Ahmed, S. B. "New biosorbent in removing some metals from industrial wastewater in El Mex Bay, Egypt", *Applied Water Science*, 7(4), pp. 1931–1942, 2017.
<https://doi.org/10.1007/s13201-015-0371-2>
- [34] Khulbe, K. C., Matsuura, T. "Removal of heavy metals and pollutants by membrane adsorption techniques", *Applied Water Science*, 8(1), 19, 2018.
<https://doi.org/10.1007/s13201-018-0661-6>
- [35] Chiarle, S., Ratto, M., Rovatti, M. "Mercury removal from water by ion exchange resins adsorption", *Water Research*, 34(11), pp. 2971–2978, 2000.
[https://doi.org/10.1016/S0043-1354\(00\)00044-0](https://doi.org/10.1016/S0043-1354(00)00044-0)
- [36] Baimenov, A. Z., Berillo, D. A., Moustakas, K., Inglezakis, V. J. "Efficient removal of mercury (II) from water by use of cryogels and comparison to commercial adsorbents under environmentally relevant conditions", *Journal of Hazardous Materials*, 399, 123056, 2020.
<https://doi.org/10.1016/j.jhazmat.2020.123056>
- [37] Kara, D., Fisher, A. "Modified silica gels and their use for the preconcentration of trace elements", *Separation & Purification Reviews*, 41(4), pp. 267–317, 2012.
<https://doi.org/10.1080/15422119.2011.608765>
- [38] Kertész, J., Huszthy, P., Kormos, A., Bezúr, L. "Synthesis of silica gel-bound acridino-18-crown-6 ether and preliminary studies on its metal ion selectivity", *Tetrahedron*, 67(29), pp. 5206–5212, 2011.
<https://doi.org/10.1016/j.tet.2011.05.050>
- [39] Pedersen, D. S., Rosenbohm, C. "Dry column vacuum chromatography", *Synthesis*, 2001(16), pp. 2431–2434, 2001.
<https://doi.org/10.1055/s-2001-18722>
- [40] Shusterman, A. J., McDougal, P. G., Glasfeld, A. "Dry-column flash chromatography", *Journal of Chemical Education*, 74(10), 1222, 1997.
<https://doi.org/10.1021/ed074p1222>
- [41] Gócs, Á., Vezse, P., Ádám, B. Á., Huszthy, P., Tóth, T. "Comparison in practical applications of crown ether sensor molecules containing an acridone or an acridine unit – a study on protonation and complex formation", *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, 101(1), pp. 63–75, 2021.
<https://doi.org/10.1007/s10847-021-01086-2>
- [42] Albatrni, H., Qiblawey, H., El-Naas, M. H. "Comparative study between adsorption and membrane technologies for the removal of mercury", *Separation and Purification Technology*, 257, 117833, 2021.
<https://doi.org/10.1016/j.seppur.2020.117833>