

Article



Arsenic(V) Removal from Water by Resin Impregnated with Cyclodextrin Ligand

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Abstract: More rigorous environmental rules on hazardous metals release require the implementation of diverse methods to remove them from contaminated streams. The adsorption process is the most attractive method for removal of toxic metal ions from different aqueous solutions. In the present study, batch and fixed bed column experiments were carried out to investigate the performance of permethylated β -cyclodextrin impregnated resin for the removal of As(V) ions from aqueous solutions. Sorption of As(V) ions was performed in groups under a variety of pH and metal concentrations. It was noted that removal efficiency was the highest (98%) at pH 6.0, and at an initial As(V) concentration equal to 0.1 mg/L. Sorption model use for experimental data indicates that the removal mechanism of As(V) by the permethylated β -cyclodextrin impregnated resin was the physical sorption. The adsorption capacity of the cyclodextrin ligand immobilized onto Amberlite XAD-4 resin was 19 mg/g. In addition, the impregnated resin was regenerable, thus was able to be used over and over.

Keywords: cyclodextrin; impregnated resin; arsenic(V)



Heavy metal and metalloid presence in the environment, due to their toxicity, is harmful, and mitigating this problem is now of great importance. Contamination of water by toxic metal ions has gradually increased over recent years due to overpopulation, insufficient hazardous waste storage, and industrial activity. Arsenic is one of the toxic metals of environmental concern due to occupational or domestic exposure, and is listed in the US Agency for Toxic Substances and Disease Registry's (ATSDR) "Top 20 Hazardous Substances" in cooperation with United States Environmental Protection Agency (US EPA) [1].

Arsenic can filter into aquatic environments naturally, for example dissolution of minerals by weathering, microbial activity, and complexation with natural organic materials. However, anthropogenic activities, including industrial mining and metallurgical activity, fossil fuel combustion, arsenic pesticide usage, herbicides, and crop desiccants, can lead to arsenic contamination in soils and surface water [2,3].

Arsenic occurs in the following oxidation states: -3, 0, +3 and +5; however, arsenite (As(III) and arsenate (As(V)) are most commonly met in water [4,5]. As(V) is the predominant species present under oxidizing conditions, and exists in the form of oxyanions of arsenic acid (H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻, and AsO₄³⁻), while As(III) exists in the form arsenious acid (H₃AsO₃, H₂AsO₃⁻, and HAsO₃²⁻) under mildly reducing conditions [6]. Arsenic's toxic effects are well-documented [7,8]. It can cause harmful effects to humans health, such as dermal abnormalities, problems with the bloodstream, neurological symptoms, diabetes, respiratory complications, and issues with the liver and kidneys [9,10]. In



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Poland, the permissible contents of arsenic in groundwater and wastewater in the light of applicable legal requirements are 0.01 and 0.1 mg/L, respectively [11].

The separation of toxic metals from water is vital for public health. Chemical precipitation, extraction, ion exchange, membrane separation, and sorption are techniques that have been developed to eliminate heavy metals from different aqueous waste streams at varying concentrations [12–14]. Sorption processes act in eliminating toxic metals from water as they are highly efficient in a great variety of metal ion concentrations, as well as being easily manipulable; it is also worth noting the selectivity and quickness of these methods [15,16]. Choosing the correct adsorbent is imperative for achieving full recovery of metal ions [15]. Common adsorbents include activated carbon, alumina, silica, and ferric oxide, which tend to have high metal adsorption capacity. However, they are high-priced and hard to separate from water after use [16]. Alternatively, agricultural by-products, although easily available and inexpensive, do not satisfactorily decontaminate aqueous waste streams with respect to their operational costs, as well as generally poor stability and binding capacity. As a result, beneficial adsorbents to effectively remove metal ions from aqueous streams must be developed [17].

Cyclodextrin (CDs) use has revealed a growing importance in the production of new cheap adsorbents for eliminating contaminants from natural water and wastewater [18]. CDs are cyclic oligosaccharides made of D-glucose units attached by R-1,4-glucosidic bonds, occurring naturally from starch through degradation with the enzyme cyclodextrin glucanosyltransferase (CGTase). There are many types of CDs that exist, but only three are commonly found in nature: α , β , and γ -CD, with six, seven, and eight membered sugar-ring molecules, respectively [19,20].

CDs have many polar primary and secondary hydroxyl groups, which form hydrogen bonds or can easily be functionalized further. Furthermore, they have hydrophobic cavities and can therefore form host-guest assemblies [21] from varying interaction forms (van der Waals force, hydrophobic interaction, electrostatic affinity, dipole-dipole interaction, and hydrogen bonding) [22]. CDs in their native state are soluble in water [23]. Prior to use, therefore, CDs must be rendered immobile on an unsolvable matrix via chemical or physical interaction, or cross-linked with various cross-linkers, resulting in the obtainment of unsolvable CD-based polymer materials [24]. Cova et al. 2018 [25], Sikder et al. 2018 [26] and Cova at al. 2021 [18] recently published reviews of the advance in creating CD-based materials, including polymers, hydrogels, and nanocomposites, employed as sorbents for eliminating toxic compounds from water and wastewater. Different methods have been used to modify CDs to form derivatives with high linking for chosen contaminants in aqueous solutions. Modification depends, for example, on β -CD bonding directly by crosslinking with a coupling agent, or covalent binding of β -CD molecules to a pre-existing insoluble matrix, including polysaccharides such as chitosan and alginates, nanofibers, textiles, silica beads, and zeolites. These materials have high adsorption capacity and are efficient in eliminating water contaminants present at trace concentrations, and show quite high rapidity.

Modifying Amberlite XAD-4 with CD ligands could also result in the functionalized resin's high capacity and selectivity. The extractant is kept in an inert polymer's micropores with no chemical bonds to the polymer matrix, and the immobilized extractant's properties are responsible for adsorptive properties of novel resin [27]. The functionalized Amberlite XAD-4 resin due to its macroreticular structure, and a high surface area, good selectivity, thermal and mechanical stability, easy regeneration, and good reproducibility offers promising solution to the sorption technology [14,27].

The aim of this study is to determine the As(V) elimination efficiency from water using permethylated β -cyclodextrin immobilized onto Amberlite XAD-4 resin under various conditions of treatment system and evaluation of removal mechanism through various equilibrium sorption models.

2. Materials and Methods

2.1. Reagents

Inorganic analytical grade chemicals were purchased from POCh (Gliwice, Poland). Synthetic arsenic solutions were prepared using arsenate(V) sodium (Na₂HAsO₄·7H₂O). Amberlite XAD-4 resin (polystyrene divinyl benzene type, 20–60 mesh, surface area of 750 m²/g and a pore size of 100 Å) and all organic reagent grades chemicals were obtained from Merck (Darmstadt, Germany).

2.2. Preparation of Permethylated β -Cyclodextrin (β -CD)

 β -CD (1.135 g; 0.001 mol) was dissolved in dry DMF (120 mL) and cooled to 0 °C. Sodium hydride (1 g) (60% in mineral oil) was carefully integrated, and the mixture was agitated at this temperature for 1 h, then at room temperature for 1 h. The reaction mixture was then cooled to 0 °C, and methyl iodide (3.17 mL; 50.94 mmol) was added drop by drop. The reaction mixture was stirred at 0 °C for 1 h, and then left to warm gradually to room temperature. After 24 h of stirring, the mixture was cooled to 0 °C and methanol (25 mL) was integrated. The mixture was transferred into icy water and extracted with chloroform or dichloromethane (5 × 80 mL). The organic layer was rinsed with 3% sodium thiosulfate and deionized water, dried over Na₂SO₄, and the solvent was evaporated. The residue can be purified by column chromatography on silica eluting with ethyl acetate containing 0.1% methanol [28] to produce permethylated β -CD (ligand 1) as a white solid.

The procedure of preparation of permethylated β-CD was shown in Figure 1. ¹H NMR (600 MHz, CDCl₃): δ 5.13 (d, J = 3.6 Hz, 7H, H-1), 3.87–3.78 (m, 14H, H-3,H-5), 3.65 (s, 21H, 7CH₃, CH₃O-3), 3.64–3.56 (m, 14H, H-6a, H-6b), 3.51 (s, 21H, 7CH₃, CH₃O-2), 3.63–3.49 (m, 7H, H-4), 3.39 (s, 21H, 7CH₃, CH₃O-6), 3.21–3.17 (m, 7H, H-2). ¹³C NMR (150 MHz, CDCl₃): δ 98.96, 82.05, 81.75, 80.30, 71.40, 70.92, 61.45, 58.96, 58.51. ESI (+)-MS *m*/*z*: calcd for C₆₃H₁₁₂O₃₅Na 1451.69, found 1451.64.

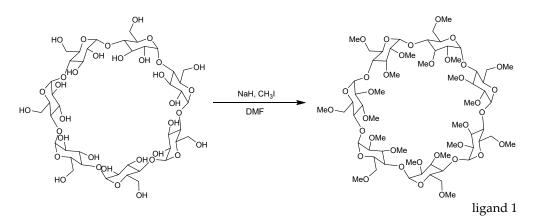


Figure 1. Methylation of β-CD.

2.3. Preparation of Impregnated Resin

A 2 g portion of dry Amberlite XAD-4 was placed in 20 mL of dichloromethane containing ligand 1 (1.0×10^{-4} mol) and stirred for 24 h. A sintered glass filter was used to separate the resin, which was rinsed with water to remove the solvent. The gravimetric assay was applied to determine the amount of the ligand immobilized onto Amberlite XAD-4 resin [14]. The maximum value of ligand 1 saturation reached 1.0×10^{-5} mol/g. The scanning electron microscope (VEGA 3, TESCAN, Brno, Czech Republic) images before and after immobilization of permethylated β -CD onto Amberlite XAD-4 resin (Figure 2) indicates the change in surface area of the "raw" and the impregnated resin, indicating the presence of the ligand 1 onto resin.

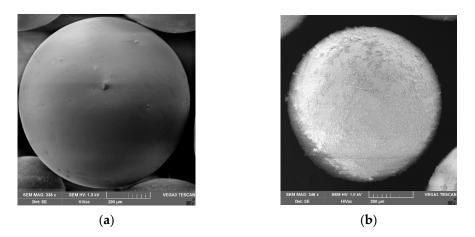


Figure 2. Scanning electron microscopic study of the surface morphology of the "raw" (**a**) and impregnated (**b**) Amberlite XAD-4 resin.

2.4. Batch Sorption Procedures

Batch experiments were carried out by putting of 0.1 g of impregnated resin into glass bottles and adding of 100 mL of arsenic solution at a 0.1 mg/L (up to 1 mg/L in the case of concentration change) for pH range = 3–9. Arsenic(V) solutions were prepared by dissolving Na₂HAsO₄·7H₂O in deionized water to the desired concentration and used without further purification. The pH of As(V) solution was adjusted within the range 3–7 (before contact with the adsorbent) with 0.1 M HCl or NaOH. The mixture was shaken at room temperature for 60 minutes, the adsorbent was filtered off, and arsenic concentration in aqueous phase was measured by Inductively Coupled Plasma Mass Spectrometry (ICP MS) (Elan 6000, PerkinElmer, Waltham, Massachusetts, United States).

The effectiveness of arsenic removal (%) and metal uptake (mg of metal ion/g of the permethylated β -CD) were determined as the following:

% removal =
$$((C_0 - C_e) \times 100)/C_0$$
 (1)

$$q_e = ((C_0 - C_e) \times V)/m \tag{2}$$

where q_e is adsorption capacity at equilibrium (mg/g), C_0 and C_e are the initial and the final As(V) concentration (mg/L), respectively, *V* is the volume of solution (L), and *m* is the sorbent weight (g) in dry form

No notable adsorption capacity of Amberlite XAD-4 resin was observed in the blank experiments when ligand 1 was non attending.

The reported values correlated with the average of three replicates, and the observed standard deviation was less than 2%.

The Langmuir, Freundlich, and Temkin adsorption models, as well as the van't Hoff equation, were applied to interpret data obtained for the sorption of As(V) ions onto the impregnated resin.

2.4.1. Langmuir Model

The Langmuir isotherm is a generally used model for adsorption on a completely homogenous surface where adsorbed molecules show little interplay [14]. The model assumes uniform adsorption energies onto the surface and maximum adsorption controlling by the monolayer's saturation level.

Langmuir model can be represented by the following linear equation [29]:

$$\frac{C_e}{q_e} = \frac{1}{k V_m} + \frac{C_e}{V_m} \tag{3}$$

where q_e represents the mass of adsorbed metal per unit of resin (mg/g), V_m is the monolayer capacity, k is the equilibrium constant, and C_e is the equilibrium concentration of the solution (mg/L). The Langmuir plot was used to determine k and V_m .

2.4.2. Freundlich Model

The Freundlich model is considered the earliest empirical equation and is consistent with exponential spreading of active centers, which is characteristic of heterogeneous surfaces [14]. The Freundlich equation (linear form) is [30]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where K_f and n represent adsorption capacity and favor, respectively. The magnitude of the n indicates the favorability of adsorption [31].

2.4.3. Temkin Model

The Temkin model reveals that a decrease in the heat of adsorption is linear, and adsorption is defined by an uniform distribution of binding energies. The Temkin isotherm is represented by the following equation [27]:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \text{ or } q_e = B_1 \ln K_T + B_1 \ln C_e$$
 (5)

where K_T is the equilibrium binding constant (L/mg), *b* refers to heat of adsorption (kJ/mol), *R* is the gas constant (8.314 × 10⁻³ kJ/(K·mol) and *T* is the absolute temperature (K).

2.4.4. Van't Hoff Equation

The van't Hoff equation relates the change in the equilibrium constant of the adsorption, to the change in temperature, given the changes in enthalpy (ΔH) and entropy (ΔS) of the process [32]. The van't Hoff equation (linear form) is [32]:

$$\ln k = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{6}$$

The values of ΔH and ΔS were calculated from the slope and intercept of the linear plot of ln *k* versus 1/T.

2.5. Column Experiment Design

A flow-through column test (using Millipore column, Tygon tubing, and peristaltic pump Manostat Carter) was used to investigate the effectiveness of ligand 1 immobilized onto Amberlite XAD-4 resin for the removal of arsenic ions from water. The 1.0 g of impregnated resin was placed in a Millipore column (length 250 mm, internal diameter 10 mm). The column was subsequently saturated by the upward flow of distilled water. The water was displaced with the upward flow of the synthetic arsenic solution (at concentration of 1.0 mg/L) once saturation was achieved at a constant flow rate of 4.0 mL/min. A spur at the top of the column was used to collect effluents into covered glass collection vessels and analyze them to determine the arsenic concentration by Inductively Coupled Plasma Mass Spectrometry (ICP MS) (Elan 6000, PerkinElmer Waltham, Massachusetts, United States). Effluents were taken until the value of proportion of effluent concentration (*c*) to initial concentration (c_0) was 1.

The moment of breakthrough emergence and the profile of the breakthrough curve are crucial features in determining the dynamic sorption capacity. The loading behavior of a sorbent in a fixed bed is generally expressed in terms of adsorbed metal concentration (c_{ad} = inlet metal concentration (c_0) – effluent metal concentration (c)) or normalized concentration defined as the ratio of effluent metal concentration to inlet metal concentration (c/c_0) as a function of time or volume of effluent for a given bed height. The area under

the breakthrough curve (*A*) is obtained by integrating the adsorbed concentration (c_{ad} ; mg/L) versus *t* (min). A graph of the breakthrough curve can be used to determine the total adsorbed metal quantity (maximum column capacity) [33].

Total adsorbed metal quantity (q_t ; mg) in the column for a given feed concentration and flow rate is calculated from the following equation:

$$q_t = (QA)/1000$$
 (7)

where Q is the flow rate (mL/min).

Equilibrium metal uptake (q_e) (or maximum adsorption capacity) in the column is defined by the total amount of metal sorbed (q_t) per gram of sorbent (m) after total flow time:

$$q_e = q_t / m \tag{8}$$

The breakthrough is generally defined as the point when the effluent concentration from the column is approximately 3–5% of the influent concentration [34].

The impregnated resin was washed with deionized water so that the As(V) ions which were not sorbed could be displaced. Arsenic(V) ions sorbed on the impregnated resin were subsequently eluted using 0.1 M NaOH.

3. Results and Discussion

3.1. Batch Sorption Procedures

3.1.1. Effect of pH

A crucial operational parameter in the sorption process is pH, as it determines the solubility of the metal ions, concentration of the counter ions on the sorbent's functional groups, and the extent of ionization of the sorbate during reaction [35].

As shown in Figure 3, the removal of As(V) using permethylated β -cyclodextrin impregnated resin depends notably on pH of water. The highest removal As(V) efficiency (more than 90%) was at pH ranges from 5 to 7. As(V) mainly exists then in the form of $H_2AsO_4^-$ or $HAsO_4^{2-}$ [36,37]. The As(V) removal efficiency decreased significantly at pH < 5, because of the high ionic mobility of $[H_3O]$ + in water as compared with most other ions [38]. Metal ions are able to be eliminated from water as they interact with the protonated or deprotonated hydroxyl groups of CDs, placed at both rims of the CD framework. For derivated CDs, the complexation mechanism can be more complicated. For instance, alkylated CDs can mostly bind via coordination bond from lone pair electron of oxygen, other forces such as van der Waals, dipole-dipole may together catch metal ions [18]. Under neutral conditions, the surface of the studied sorbent becomes more positively charged, causing adsorbent-adsorbate electrostatic attraction [39]. In turn, when the adsorbent was placed in an alkaline environment, its surface is net negatively charged. Considering arsenic's dominant form $(H_2AsO_4^{-})$, there will be electrostatic repulsion due to the adsorbent's negative surface charge at alkaline pH [40]. Therefore, the performance of the adsorbent for arsenic(V) ions was diminished in an alkaline medium.

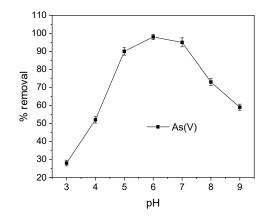


Figure 3. Effect of pH of water on percentage removal of As(V) ions using impregnated resin (at As(V) concentration of 0.1 mg/L).

3.1.2. Effect of Initial Arsenic(V) Concentration

The effect of initial concentration on uptake of As(V) ions by permethylated β -CD immobilized onto Amberlite XAD-4 resin is shown in Figure 4. The quantity of As(V) sorbed uniformly increased as metal concentration increased up to the value of 1.0 mg/L. The uptake of As(V) was 6.8 mg/g at a metal concentration of 0.1 mg/L, while at a concentration of 1 mg/L–19.0 mg/g. It was found that immobilized permethylated β -CD performs well in sorption of As(V) from water, a result of the larger surface area provided by the framework of Amberlite resin to the ligand for interaction with As(V) ions, along with inclusion complexation via macrocyclic ring [1,18]. Moreover, at initial concentration of 0.1 mg/L the highest As(V) removal efficiency (98%) was achieved; the arsenic concentration was then below the limit in drinking water (10 µg/L).

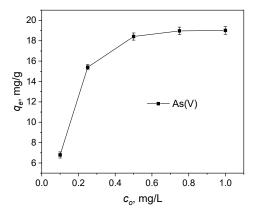


Figure 4. Effect of initial As(V) concentration on metal uptake by impregnated resin (for pH = 6).

3.1.3. Adsorption Isotherms

The Langmuir, Freundlich, and Temkin isotherms for a temperature of 293 K, and a van 't Hoff plot (in the range of temperature 293–313 K) are shown in Figure 5. All value constants determined from adsorption isotherms and van't Hoff plot are given in Table 1.

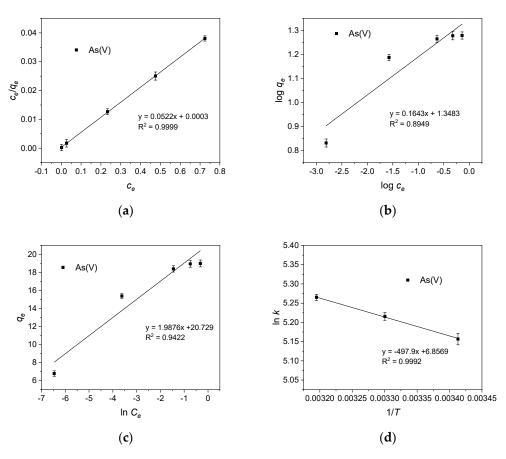


Figure 5. Application of Langmuir (**a**), Freundlich (**b**), Temkin (**c**) and van't Hoff (**d**) models to the experimental data.

Table 1. Isotherms and van't Hoff equation parameters calculated for As(V) ions adsorption onto resin impregnated with permethylated β -CD.

| Langmuir Isotherm Parameters | | Freundlich Isotherm Parameters | | | Temkin Isotherm Parameters | | | Van't Hoff Equation Parameters | | | |
|------------------------------|-------|--------------------------------|----------------|-----|----------------------------|----------------|-----|--------------------------------|------------|------------|----------------|
| V_m | k | R ² | K _f | п | R ² | K _T | b | R ² | ΔH | ΔS | R ² |
| 19.2 | 173.6 | 0.9999 | 22.3 | 6.1 | 0.8949 | 33860.4 | 1.2 | 0.9422 | 4.1 | 0.06 | 0.9992 |

As(V) ions' adsorption parameters onto impregnated resin are consistent with the Langmuir and van't Hoff models. R^2 values are considered a measure of the correspondence of experimental data to the isotherm model. These values for As(V) ions are very similar to 1. Therefore, the following order to fit isotherms is indicated by determination coefficients: Langmuir > van't Hoff > Temkin > Freundlich, for adsorption of As(V) ions onto impregnated resin. A Freundlich constant *n* value larger than 1 shows the beneficial character of adsorption [14].

The Temkin isotherm shows that (i) there is a linear decrease in adsorption heat of all the molecules in the layer with coverage due to adsorbent–adsorbate interactions, and that (ii) a uniform distribution of binding energies characterizes adsorption. Ion-exchange mechanisms typically have binding energies in the order of 8–16 kJ/mol, while physisorption processes are mentioned to have low adsorption energies [41]. Low *b* and Δ H values (1.2 and 4.1 kJ/mol, respectively) noted in the present study show minimal sorbate-adsorbent ionic interactions, indicating the physisorption of arsenic(V) ions. Moreover, the positive magnitude of Δ H indicates the endothermic character of As(V) adsorption process and the positive magnitude of Δ S suggests the affinity of the immobilized permethylated β -CD for arsenic, as well as increase of randomness at solid–solution boundary by way of metal ion uptake [42].

Many different adsorbents used to eliminate arsenic(V) ions from aqueous solutions have been demonstrated in the literature. A summary of the published adsorption capacity of different adsorbents for trace and low initial concentrations of arsenic(V) (up to 2 mg/L) is presented in Table 2, including the results from this work. As is shown in Table 2, the adsorption capacity of As(V) ions for permethylated β -CD impregnated Amberlite XAD-4 resin was, in most cases, higher than for different adsorbents reported in the literature.

Table 2. Comparison of equilibrium uptake capacity (q_e) of different adsorbents for As(V) ions.

| Adsorbent | Initial Concentration [mg/L] | pН | Adsorption Capacity [mg/g] | Reference |
|---|------------------------------|-----|----------------------------|------------|
| granular ferric oxide (GFO) | 0.01 | 7.5 | 0.57 | [43] |
| nano zero valent iron supported on activated carbon | 2.0 | 6.5 | 12.0 | [44] |
| ascorbic acid coated Fe ₃ O ₄ nanoparticles | 0.10 | 7.0 | 16.6 | [45] |
| nanoscale Fe-Mn binary oxides loaded on zeolite | 2.0 | 7.0 | 201.1 | [46] |
| multiwall carbon nanotubes zirconia nano hybrid | 0.1 | 6.0 | 5.0 | [47] |
| modified natural manganese oxide ore | 0.5 | 7.0 | 0.11 | [48] |
| bone char | 0.1 | 5.0 | 0.75 | [49] |
| permethylated β-CD immobilized onto resin | 1.0 | 6.0 | 19.0 | this study |

3.2. Column System

The breakthrough curve of As(V) adsorption is presented in Figure 6. It can be seen that breakthrough occurred after 30 minutes (feeding solution flow of 120 mL). The loading of column was achieved after 150 minutes (feeding solution flow of 600 mL). The calculated adsorption column capacity value for arsenic(V) was 19.1 mg As(V) per g of permethylated β -CD immobilized onto resin. This is a similar value to that obtained in batch experiment at the identical (1.0 mg/L) concentration of arsenic(V) solution.

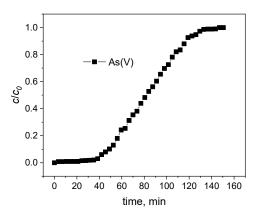


Figure 6. Breakthrough curve of As(V) adsorption by permethylated β -CD impregnated Amberlite XAD-4 resin.

A significant reduction of the overall cost of water treatment process would be achieved by an adsorbent with good adsorption capacity, as well as showing favorable regeneration properties. The successful regeneration of an adsorbent can therefore be considered an essential action for determining the applicability of an adsorbent in water remediation practice [50]. The results of regeneration studies indicated that 0.1 M NaOH solution is worthy for this operation in the case of immobilized CD ligand and can be applied as a regenerating factor. The desorption rate was high; when a volume of 60 mL of regeneration solution was passed through column, more than 95% of As(V) ions were desorbed.

The stability and potential reusability of the impregnated resin were also evaluated by monitoring the change in recoveries of As(V) ions through several sorption and desorption cycles, for initial As(V) concentration of 1.0 mg/L. The results of adsorption/desorption cycles using the column mode with permethylated β -CD impregnated resin are shown in Figure 7. It was found that, during five cycles, no noticeable change in sorption capacity of the resin occurred and comparable percentage values for the desorption of As(V) ions

were achieved. These results indicate that the permethylated β -CD impregnated Amberlite XAD-4 resin was stable and easily regenerable without any physical or chemical damage, thus could be re-used.

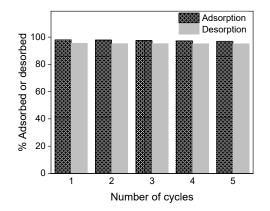


Figure 7. Adsorption/desorption cycles for removal of As(V) using permethylated β -CD impregnated resin.

4. Conclusions

The permethylated β -CD impregnated Amberlite XAD-4 resin has been found efficient for adsorption of As(V) ions from water.

It was reported that the removal of As(V) using the impregnated resin depends particularly on pH and initial metal ion concentration; the highest As(V) removal efficiency (98%) was achieved at pH 6.0 and an initial concentration of 0.1 mg/L. The arsenic concentration was below the limit in drinking water (10 μ g/L) then.

The adsorption parameters of As(V) ions onto impregnated resin were consistent with the Langmuir model. Moreover, using sorption models on the experimental results shows that the arsenate ion extraction mechanism onto permethylated β -CD impregnated resin was physisorption. The adsorption capacity, both in batch and column tests, was 19 mg As(V) per g of the CD ligand immobilized onto resin.

Thus, the novel adsorbent could help in extracting arsenic(V) at trace and low concentrations from the polluted water. Moreover, the permethylated β -CD impregnated Amberlite XAD-4 resin is regenerative and can be used several times.

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References

- 1. Zawierucha, I.; Kozlowski, C.; Malina, G. Immobilized materials for removal of toxic metal ions from surface/groundwaters and aqueous waste streams. *Environ. Sci. Proc. Impacts* **2016**, *18*, 429–444. [CrossRef] [PubMed]
- Hao, L.; Liu, M.; Wang, N.; Li, G. A critical review on arsenic removal from water using iron-based adsorbents. RSC Adv. 2018, 8, 39545–39560. [CrossRef]
- 3. Yao, R.; Yang, H. An overview of As(V) removal from water by adsorption technology. Ann. Musculoskelet. Med. 2020, 4, 015–020.

- 4. Tokoro, C.; Kadokura, M.; Kato, T. Mechanism of arsenate coprecipitation at the solid/liquid interface of ferrihydrite: A perspective review. *Adv. Powder Technol.* **2020**, *31*, 859–866. [CrossRef]
- Pous, N.; Casentini, B.; Rossetti, S.; Fazi, S.; Puig, S.; Aulenta, F. Anaerobic arsenite oxidation with an electrode serving as the sole electron acceptor: A novel approach to the bioremediation of arsenic-polluted groundwater. J. Hazard. Mater. 2015, 283, 617–622. [CrossRef] [PubMed]
- Altowayti, W.A.H.; Othman, N.; Shahir, S.; Alshalif, A.F.; Al Gheethi, A.A.; Towayti, A.L.F.A.H.; Saleh, Z.M.; Haris, S.A. Removal of arsenic from wastewater by using different technologies and adsorbents: A review. *Int. J. Environ. Sci. Technol.* 2021, 1–24. [CrossRef]
- Majzlan, J.; Plášil, J.; Škoda, R.; Gescher, J.; Kögler, F.; Rusznyak, A.; Küsel, K.; Neu, T.R.; Mangold, S.; Rothe, J. Arsenic-rich acid mine water with extreme arsenic concentration: Mineralogy, geochemistry, microbiology, and environmental implications. *Environ. Sci. Technol.* 2014, 48, 13685–13693. [CrossRef]
- Tardy, V.; Casiot, C.; Fernandez-Rojo, L.; Resongles, E.; Desoeuvre, A.; Joulian, C.; Battaglia-Brunet, F.; Héry, M. Temperature and nutrients as drivers of microbially mediated arsenic oxidation and removal from acid mine drainage. *Appl. Microbiol. Biotechnol.* 2018, 102, 2413–2424. [CrossRef]
- 9. Abdul, K.S.M.; Jayasinghe, S.S.; Chandana, E.P.S.; Jayasumana, C.; Silva, P.M.C.S.D. Arsenic and human health effects: A review. *Environ. Toxicol. Pharmacol.* **2015**, *40*, 828–846. [CrossRef]
- 10. Mandal, S.K.T. Arsenic round the world: A review. Talanta 2002, 58, 201–235. [CrossRef]
- Gajec, M.; Krol, A.; Kukulska-Zajac, E. Determination of metals in selected elements of the environment in the context of applicable legal regulations. *Nafta-Gaz* 2019, *5*, 283–292. [CrossRef]
- 12. Kavak, D.; Demir, M.; Başsayel, B.; Anagün, A.S. Factorial experimental design for optimizing the removal of lead ions from aqueous solutions by cation exchange resin. *Desalin. Water Treat.* **2013**, *51*, 1712–1719. [CrossRef]
- 13. Zawierucha, I.; Nowik-Zajac, A.; Kozlowski, C. Application of Cr(VI) transport across the polymer inclusion membrane with calixresorcin4arene derivative as ion carrier. *Sep. Sci. Technol.* **2020**, *55*, 2204–2210. [CrossRef]
- 14. Zawierucha, I.; Kozlowska, J.; Kozlowski, C.; Trochimczuk, A. Sorption of Pb(II), Cd(II) and Zn(II) performed with the use of carboxyphenylresorcinarene-impregnated Amberlite XAD-4 resin. *Desalin. Water Treat.* **2014**, *52*, 314–323. [CrossRef]
- Ghaedi, M.; Karami, B.; Ehsani, S.; Marahel, F.; Soylak, M. Preconcentration–separation of Co²⁺, Ni²⁺, Cu₂₊ and Cd²⁺ in real samples by solid phase extraction of a calix4resorcinarene modified Amberlite XAD-16 resin. *J. Hazard. Mater.* 2009, 172, 802–808. [CrossRef] [PubMed]
- 16. Mohan, S.; Gandhimathi, R. Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent. *J. Hazard. Mater.* **2009**, *169*, 351–359. [CrossRef]
- 17. Adhikari, B.B.; Kanemitsu, M.; Kawakita, H.; Jumina, O.K. Synthesis and application of a highly efficient polyvinylcalix4arene tetraacetic acid resin for adsorptive removal of lead from aqueous solutions. *Chem. Eng. J.* 2011, *172*, 341–353. [CrossRef]
- Cova, T.F.; Murtinho, D.; Aguado, R.; Pais, A.A.C.C.; Valente, A.J.M. Cyclodextrin Polymers and Cyclodextrin-Containing. Polysaccharides for Water Remediation. *Polysaccharides* 2021, 2, 16–38. [CrossRef]
- Łagiewka, J.; Girek, T.; Ciesielski, W. Cyclodextrins-Peptides/Proteins Conjugates: Synthesis, Properties and Applications. *Polymers* 2021, 13, 1759. [CrossRef]
- 20. Islam, M.S. Arsenic Removal by α , β and γ Cyclodextrin Polymers from Contaminated Water. *Hydrology* **2017**, *5*, 73–76. [CrossRef]
- Wang, Q.-Q. Supramolecular catalysis using organic macrocycles. In *Handbook of Macrocyclic Supramolecular Assembly*; Liu, Y., Chen, Y., Zhang, H.-Y., Eds.; Springer: Berlin/Heidelberg, Germany, 2019; pp. 1–47.
- 22. Raoov, M.; Mohamad, S.; Abas, M.R. Synthesis and Characterization of β-Cyclodextrin Functionalized Ionic Liquid Polymer as a Macroporous Material for the Removal of Phenols and As(V). *Int. J. Mol. Sci.* **2014**, *15*, 100–119. [CrossRef]
- Skorjanc, T.; Shetty, D.; Trabolsi, A. Pollutant removal with organic macrocycle-based covalent organic polymers and frameworks. Chem 2021, 7, 882–918. [CrossRef]
- Zhao, F. Cross-linked chitosan and β-cyclodextrin as functional adsorbents in water treatment. In *Advanced Water Treatment*. *Adsorption*, 1st ed.; Sillanpää, M., Ed.; Elsevier: Amsterdam, The Netherlands, 2020.
- Cova, T.F.G.G.; Murtinho, D.; Pais, A.A.C.C.; Valente, A.J.M. Cyclodextrin-based Materials for Removing Micropollutants From Wastewater. *Curr. Org. Chem.* 2018, 22, 2150–2181. [CrossRef]
- Sikder, T.; Jakariya, M.R.; Hosokawa, T.; Kurasaki, M.; Saito, T. Remediation of water pollution with native cyclodextrins and modified cyclodextrins: A comparative overview and perspectives, *Chem. Eng. J.* 2019, 355, 920–944. [CrossRef]
- 27. Zawierucha, I.; Kozlowski, C.; Malina, G. Removal of toxic metal ions from landfill leachate by complementary sorption and transport across polymer inclusion membranes. *Waste Manag.* **2013**, *33*, 2129–2136. [CrossRef]
- 28. Faiz, J.A.; Spencer, N.; Pikramenou, Z. Acetylenic cyclodextrins for multireceptor architectures: Cups with sticky ends for the formation of extension wires and junctions. *Org. Biomol. Chem.* **2005**, *3*, 1008–1012. [CrossRef]
- 29. Byambaa, E.; Seon, J.; Kim, T.-H.; Kim, S.D.; Ji, W.H.; Hwang, Y. Arsenic (V) Removal by an Adsorbent Material Derived from Acid Mine Drainage Sludge. *Appl. Sci.* 2021, *11*, 47. [CrossRef]
- 30. Foo, K.Y.; Hameed, B.H. Insights into the modeling of adsorption isotherm systems. Chem. Eng. J. 2010, 156, 2–10. [CrossRef]
- Agrawal, A.; Sahu, K.K.; Pandey, B.D. Systematic studies on adsorption of lead on sea nodule residues. *J. Colloid Interface Sci.* 2005, 281, 291–298. [CrossRef]

- 32. Yoshida, Y.; Shimada, T.; Ishida, T.; Takagi, S. Thermodynamic study of the adsorption of acridinium derivatives on the clay surface. *RSC Adv.* **2020**, *10*, 21360. [CrossRef]
- Zawierucha, I.; Nowik-Zajac, A. Evaluation of permeable sorption barriers for treating of heavy metals contaminated groundwater. Water Sci. Technol. 2019, 80, 448–457. [CrossRef]
- Chen, J.P.; Wang, X. Removing copper, zinc, and lead ion by granular activated carbon in pretreated fixed bed columns. Sep. Purif. Technol. 2000, 19, 157–167. [CrossRef]
- Goher, M.E.; Hassan, A.M.; Abdel-Moniem, I.A.; Fahmy, A.H.; Abdo, M.H.; El-sayed, S.M. Removal of aluminum, iron and manganese ions from industrial wastes using granular activated carbon and Amberlite IR-120 H. *Egypt. J. Aquat. Res.* 2015, 41, 155–164. [CrossRef]
- 36. Baskan, M.B.; Pala, A. A statistical experiment design approach for arsenic removal by coagulation process using aluminum sulfate. *Desalination* **2010**, 254, 42–48. [CrossRef]
- 37. Nicomel, N.R.; Leus, K.; Folens, K.; Van Der Voort, P.; Du Laing, G. Technologies for arsenic removal from water: Current status and future perspectives. *Int. J. Environ. Res. Public Health* **2016**, *13*, 62. [CrossRef]
- Sikder, M.T.; Kikuchi, T.; Suzuki, J.; Hosokawa, T.; Saito, T.; Kurasaki, M. Removal of Cadmium and Chromium Ions Using Modified α, β, and γ-Cyclodextrin Polymers. *Sep. Sci. Technol.* 2013, 48, 587–597. [CrossRef]
- Sikder, M.T.; Tanaka, S.; Saito, T.; Kurasaki, M. Application of zerovalent iron impregnated chitosan-caboxymethyl-β-cyclodextrin composite beads as arsenic sorbent. J. Environ. Chem. Eng. 2014, 2, 370–376. [CrossRef]
- Foroutan, R.; Mohammadi, R.; Adeleye, A.S.; Farjadfard, S.; Esvandi, Z.; Arfaeinia, H.; Sorial, G.A.; Ramavandi, B.; Sahebi, S. Efficient arsenic(V) removal from contaminated water using natural clay and clay composite adsorbents. *Environ. Sci. Pollut. Res.* 2019, 26, 29748–29762. [CrossRef]
- 41. Qureshi, I.; Memon, S.; Yilmaz, M. Estimation of chromium(VI) sorption efficiency of novel regenerable p-tert-butylcalix8areneoctamide impregnated Amberlite resin. *J. Hazard. Mater.* **2009**, *164*, 675–682. [CrossRef]
- 42. Danesh, N.; Ghorbani, M.; Marjani, A. Separation of copper ions by nanocomposites using adsorption process. *Sci. Rep.* **2021**, *11*, 1676. [CrossRef]
- Collivignarelli, M.C.; Canato, M.; Sorlini, S.; Crotti, B.M. Monitoring of a pilot GFO filter for removal of low-concentration arsenic in water. *Water Pract. Technol.* 2016, 11, 702–711.
- 44. Zhu, H.; Jia, Y.; Wua, X.; Wanga, H. Removal of arsenic from water by supported nano zero-valent iron on activated carbon. *J. Hazard. Mater.* **2009**, *172*, 1591–1596. [CrossRef]
- Feng, L.; Cao, M.; Ma, X.; Zhu, Y.; Hu, C. Superparamagnetic high-surface-area Fe₃O₄ nanoparticles as adsorbents for arsenic removal. J. Hazard. Mater. 2012, 217–218, 439–446. [CrossRef]
- 46. Kong, S.; Wang, Y.; Zhan, H.; Yuan, S.; Yu, M.; Liu, M. Adsorption/oxidation of arsenic in groundwater by nanoscale Fe-Mn binary oxides loaded on zeolite. *Water Environ. Res.* 2014, *86*, 147–155. [CrossRef]
- Natim, S.A.; Mitra, S. Adsorption of arsenic on multiwall carbon nanotube-zirconia nano hybrid for potential drinking water purification. J. Colloid Interface Sci. 2012, 375, 154–159. [CrossRef]
- Nguyen, T.T.Q.; Loganathan, P.; Nguyen, T.V.; Vigneswaran, S. Removing arsenic from water with an original and modified natural manganese oxide ore: Batch kinetic and equilibrium adsorption studies. *Environ. Sci. Pollut. Res.* 2020, 27, 5490–5502. [CrossRef]
- 49. Villela-Martinez, D.E.; Leyva-Ramos, R.; Aragon-Pina, A.; Navarro-Tovar, R. Arsenic elimination from water solutions by adsorption on bone char. effect of operating conditions and removal from actual drinking water. *Water Air Soil Pollut.* **2020**, 231, 201. [CrossRef]
- 50. Christoforidis, A.K.; Orfanidis, S.; Papageorgiou, S.K.; Lazaridou, A.N.; Favvas, E.P.; Mitropoulos, A.C. Study of Cu(II) removal by *Cystoseira crinitophylla* biomass in batch and continuous flow biosorption. *Chem. Eng. J.* **2015**, 277, 334–340. [CrossRef]