Hybrid Sorbents for Removal of Arsenic

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ABSTRACT

The paper analyzes data on the removal of arsenic by sorption methods using materials that have prospects for large-scale application in water treatment. These materials include transition metal oxides in the micro- and nano-dimensional form, including those in the composition of composite materials with inorganic matrices, or hybrid sorbents in the composition with polymer resins or natural biopolymers. Examples of the use of composite (hybrid) sorbents for the removal of arsenic from solutions with low concentrations (at the level of MPC) are given. The objective of this article was to sum the up-to-date information about the most important features of chitosan-containing and chitosan-carbon materials we developed in view their use in arsenic removal processes at low concentrations to concentrations that meet WHO requirements. The paper presents data on the sorption properties of Mo-containing activated carbon fibers and chitosan-carbon composite materials towards arsenic (V) when it is extracted from bidistilled and tap water under static and dynamic conditions. The factors of the different behavior of the sorbents depending on the form of a biopolymer deposited on the fiber and the stability of the sorbents during the sorption of arsenic are discussed.

Keywords: arsenic, sorption, composites, hybrid sorbents, carbon fiber, chitosan.

Introduction

Various technologies are used to solve numerous environmental problems. In particular, the following methods are used for the removal of toxic pollutants from water: oxidation/precipitation, coagulation, co-precipitation, sorption, ion exchange, and membrane technologies [1, 2, 3, 4]. Among them, sorption/adsorption is considered as a relatively simple, effective, and cost-efficient techniques for removing pollutants, it is also suitable for the use in rural areas. In addition, no sludge is formed when applying this technology.

Arsenic is known to be one of the most toxic chemical elements at very low concentrations [1, 5, 6, 7, 8]: it is one of the most well-known environmental pollutants. Arsenic affects the human body at very low concentrations, so that the World Health Organization (WHO) recommended reducing the maximum permissible concentration (MPC) of As in drinking water down to 10 μg/L [1].

Arsenic enters the environment from geothermal and ground waters, as a result of weathering, soil erosion, and volcanic activity. In addition, arsenic contamination has anthropogenic origins, such as the use of pesticides, mining processing, and burning of fossil fuels [1, 2, 3].

Although most of the indicated methods, provided that they are carried out under optimal conditions, allow reducing the arsenic concentration below 10 μg/L, the majority of them are rather costly, especially the membrane technologies [1, 2].

At present, a wide range of materials was tested for the purpose of removing As at low concentrations: natural ores, minerals, activated carbons (AC), ion exchange resins, agricultural and industrial waste, natural biopolymer chitosan [1, 2, 7, 8, 9, 10].
Among the materials recommended for use as adsorbents in water treatment, the following transition metal oxides were studied: Al₂O₃, TiO₂, MnO₂, and iron oxides/hydroxides [6], [11], [12], [13]]. The latter ones are of the greatest interest, since their application allows isolating powders (nanopowders) from the media to be decontaminated by magnetic separation on the condition that the oxide has magnetic properties. Of iron oxides, goethite (α-FeOOH) and hematite (α-Fe₂O₃) are non-magnetic, whereas magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and hydrated iron oxides are characterized magnetic properties [13], [14]].

The separation of iron hydroxides, which are considered as among the most effective sorbents for arsenic, requires sedimentation or filtration and is hard to perform due to their low mechanical strength [13], [15]].

The solution to this problem consists in the immobilization of iron oxides into a carbon or polymer matrix to obtain composite materials [13], [14], [15], [16], [17], [18]].

Another group of materials that are widely studied as sorbents for arsenic includes carbon materials (CM) in various forms like conventional commercial carbons or carbon nanotubes. However, activated CM, despite their high specific surface area, the presence of surface functional groups, and a well-developed porous structure, are not very suitable for removing anionic pollutants, which include arsenic compounds. At the same time, CMS comprise one of the most suitable matrices for the production of composites, even despite their high cost and the method of their production, which is not particularly environmentally friendly [19], [20]].

In recent years, numerous works were devoted to nanoscale metal (hydro)oxides, such as Fe₃O₄, hydrated iron oxide (HGO), TiO₂, MnO₂, etc., which demonstrate high sorption efficiency towards heavy metals. However, these hydroxides cannot be directly used in the flow-through systems due to high pressure in the columns caused by the ultra-fine particle sizes. These technological disadvantages can be avoided by placing the oxide on to conventional porous adsorbents, including activated carbons, cellulose granules, alginate beads, or polymer adsorbents to produce hybrid sorbents for further application [15].

Another approach to obtaining composite materials consists in the immobilization of iron oxides directly into polymer matrices. Cation-exchange and anion-exchange synthetic resins are used for immobilization [13], [15], [16], [21], [22], [23], [24], [25], [26], [27]],

Commercial arsenic sorbents were synthesized on the basis of industrial ion-exchange resins by immobilization of iron oxides in them. Among these, the ArsenX® hybrid sorbents show high efficiency in removing arsenic from model solutions [21], [23], [24].

Currently, the development of highly effective sorbents is tending to low-price sorbents based on natural biopolymers, the most preferred of which is the natural polymer chitosan (CS) [7], [10], [28], [29], [30], [31], [32], [33]].

The use of biopolymers as sorbents is determined by their unique combination of properties: non-toxicity, biodegradability, biocompatibility, bioactivity, and production from renewable sources [30], [31]].

Chitosan is a natural aminopolysaccharide synthesized by alkaline hydrolysis of chitin (a cheap natural raw material, among other sources, it is a by-product of the fishery industry). Chitosan can be considered as the most suitable material for the removal of anions (including some charged forms of arsenic), since it contains a large number of amino groups protonated in an acidic medium. This ensures the removal of anionic forms of arsenic by an ion exchange mechanism [29].

However, there are several factors that prevent the full-scale use of chitosan. The modification of CS is necessary to overcome its solubility in an acidic medium, low porosity, and residual crystallinity.

The best sorption properties are demonstrated by the materials based on modified chitosan, which include grafting functional groups or compounds of other compounds (that have a strong affinity for arsenic) incorporated into a biopolymer matrix [10].

Impregnation with metal oxides or metals was suggested to increase the sorption capacity or improve the selectivity towards arsenic [10], [30], [31], [32], [33], [34]]. A large group of modifier compounds consists of metal oxides (Al, Ti, Mn, Fe, Ce, Cu, and Mo) [5], [7], [10], [31], [34]]. Molybdenum oxide is especially remarkable of these due to the different mechanism of interaction with As as a result of the formation of an arsenomolybdate complex [6], [10].

It is necessary to single out a group of sorbents in which the biopolymer (polysaccharide) chitosan is modified with molybdenum, which has a strong affinity for both chitosan and As: this allows the use of Mo-containing chitosan as a sorbent for arsenic [6], [7], [10], [31], [35], [36]]. Mo-containing
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Table 1 - Examples of hybrid sorbents based on metal oxides

| Sorbent                                                                 | Initial concentration | Solution | Mode          | Passed volume* | Final concentration, μg/L | Reference |
|------------------------------------------------------------------------|-----------------------|----------|---------------|----------------|--------------------------|-----------|
| Polystyrene (polyHIPE) coated with iron hydroxide                       | 50-200 μg/L As(III), As(V) | deionized and tap water | dynamic      | <10            | [38]                      |
| Layers of sand coated with manganese oxide and iron oxide              | 1 mg/L As(III), As(V) | 0.01 M NaNO₃ solution | pilot unit, dynamic | <50            | [39]                      |
| Iron coated chitosan flakes, Iron doped chitosan granules              | 500 μg/L As(III), As(V) | real ground water | dynamic      | 147 b.v. As(III) 180 b.v. As(V) | <10 | [40] |
| TiO₂/montmorillonite                                                  | 120-410 μg/L          | real ground water | column       | 4300-10500 b.v. | <10 | [41] |
| FeO/activated carbon                                                  | 0.5 mg/L              | potable water | column       | 1,250 ml of solution | <10 | [42] |
| Al₂O₃/chitosan                                                        | 91 mg/L As(III), 101 mg/L As(V) | deionized water | dynamic    | 40 b.v. As(III) 120 b.v. As(V) | <10 | [43] |
| Activated carbons impregnated with iron hydroxide                     | 40-60 μg/L 70-75% As(V) 25-30% As(III) | real ground water | dynamic | 20000 b.v. | <10 | [44] |
| Activated carbon fiber impregnated with nanosized magnetite           | <1000 μg/L            | water solution | static       | m/v = 0.7 g/L  | <10 | [45] |
| Macroporous anion exchanger D-201 loaded with hydrated ferric oxide   | 1 mg/L As(V)          | solution in the presence of SO₄²⁻, Cl⁻, PO₄³⁻, SiO₂, HCO₃⁻ | dynamic | max 2000 b.v. | <10 | [15] |
| npRio gel-type strong base anion exchange resin Impregnated iron oxide | 20 μg/L               | solution in the presence of 30 μg of SiO₂ | dynamic | ~7500 b.v. 17500 b.v. | <23 | [23] |
| Strong base anion exchange resin based on styrene-divinylbenzene loaded hydrated ferric hydroxide | 600 μg/L As(V) | solution in the presence of PO₄³⁻, SiO₂ | dynamic | ~12000 b.v. | <10 | [22] |
| ArsenX²⁺                                                              | 80-100 μg/L 140-180 μg/L | 25000 b.v. 20000 b.v. | <50          | [21] |
| Natural zeolite coated with nanocomposites of Mn-Fe oxides             | 50 μg/L As(III), As(V) | potable water | pilot unit, dynamic | 10000 b.v. | <3 | [46] |
| Purolite A-500P resin filled with hydrated iron oxide                  | 100 μg/L As(III)      | solution in the presence of SO₄²⁻, Cl⁻, HCO₃⁻ | 12000 b.v. 10 | [47] |

Note: *) b.v - empty bed volumes, m/v – mass to volume ratio

chitosan resins can be synthesized in the form of magnetic sorbents [37]. Some examples of the use of hybrid sorbents for the removal of arsenic at low concentrations close to the MPC are shown in Table 1.

The objective of the present work was to study the sorption properties and stability of Mo-
containing sorbents based on both pristine carbon fiber and fiber modified with chitosan during the processes of arsenic removal from model solutions with low concentrations in bidistilled and tap water.

**Experimental part**

Carbon fiber and chitosan-carbon materials modified with molybdenum oxide were chosen as the objects of the research. To produce chitosan carbon materials, chitosan (in various forms) was deposited by different methods on the initial carbon fiber Aktilen (grade brand B) produced by St. Petersburg Research Institute Chemical Fiber “Khimvolokno”.

The chitosan-carbon material CCM(-900) was produced by depositing chitosan from a solution on a carbon fiber (CF), which was used as a working electrode, in a standard electrochemical cell, while it was polarized into the cathode region with holding at the reached potential of -900mV for a given time. The deposition potential was measured relatively to the Ag/AgCl reference electrode.

The sample of CCM(SO$_4$) was prepared by deposition of nanoscale chitosan on the surface of CF by ionotropic gelation method. To do this, the carbon fiber was pre-soaked in a chitosan solution and then the wet fiber was treated with a concentrated solution of the strong electrolyte Na$_2$SO$_4$. The fiber was washed with water to remove the excess of the electrolyte and dried in the air.

The preparation of chitosan-carbon materials is described in detail in [48].

The modification of carbon fiber and chitosan-carbon materials with molybdenum oxide was performed by adsorption of molybdenum from solutions of sodium molybdate with different concentrations at pH 3, at which the maximum sorption of molybdenum from the solution was observed. The adsorption of molybdenum was carried out under static conditions at a ratio of m : V = 1 : 1000. The concentration of molybdenum in the sorbent was determined by the difference between the initial and equilibrium concentrations from a given volume of the solution to the carbon sample.

The sorption properties of composite sorbents were studied under static conditions with a phase ratio of S : L = 1 : 1,000. The sorption kinetics was studied on the model solutions prepared with tap water by the limited volume method (0.05 mg sorbent: 50 ml solution, pH 3.0). In accordance with this method, probes were taken from the solution, the initial concentration of which is known, at certain intervals of time, in which the concentration of the element was determined during its extraction by the sorbent. Arsenic(V) sorption isotherms were obtained by the method of variable concentrations in the solutions prepared with bidistilled water from 50 to 1000 µg/L (pH 3.0) and tap water from 50 to 1500 µg/L (pH 6.4–6.5). To prepare model solutions, a standard solution of Na$_2$HAsO$_4$·7H$_2$O in 1 M HCl with 25 mg/L As was used. Standards for the determination of arsenic were prepared with tap and bidistilled water.

To study the sorption dynamics, a model solution was prepared with bidistilled water with a concentration of arsenic(V) of ~100 µg/L, pH 2.9. Arsenic breakthrough curves were taken in a polyethylene column of a diameter of 0.9 cm and a height of 5.8 cm at a solution passing rate of 1 ml/min. The volume of the loaded sorbent layer was 1 cm$^3$ with a packing density of 0.15-0.16 g/cm$^3$. The samples were analyzed for the content of As(V) as 50 ml of the solution was passed. The following sorbents were tested in the dynamic mode: initial CF–Mo, CCM(-900)–Mo, CCM(SO$_4$)–Mo.

**Results and discussion**

Despite the advantages of using chitosan as a sorbent for the removal of certain pollutants, there are a number of objective reasons that prevent its widespread use as a sorbent for the removal of arsenic, in particular. These include: 1) weak stability of chitosan at pH optimal for As extraction, 2) low sorption capacity, especially towards As(III), 3) difficulty in standardization of initial chitosans due to heterogeneity depending on the degree of deacetylation, 4) low porosity of chitosan and, accordingly, low availability of sorption sites, 5) physicochemical characteristics of granules that prevent their use in industrial units in a dynamic mode ([30], [31]).

Although chitosan can sorb arsenate ions ([29], [49], [50]), the sorption capacity towards arsenic is very low, it rarely reaches 10 mg of As (V)·g$^{-1}$, and only a few mg of As(III)·g$^{-1}$[35]. Therefore, chitosan undergoes modification by physical or chemical methods [7]. The choice of a metal modifier (specifically, a metal oxide) is determined by both the nature of the interaction of this metal directly with the matrix and its interaction with the extracted toxic agent. The immobilization of metal oxides into chitosan implies an increase in arsenic sorption capacity and the emergence of selectivity over other metals and related ions [7]. As was mentioned above, metals such as molybdenum and iron are...
effectively used to obtain sorbents due to their strong affinity for chitosan.

The removal of arsenic using granules of a chitosan sorbent containing molybdenum depends on the characteristics of the granules, as does the sorption of molybdenum by granules of the original chitosan. This is related to the fact that the sorption of molybdenum is influenced by both the degree of deacetylation and the molecular weight of chitosan. The correlation between the parameters is not direct. However, it was shown that the sorption of molybdenum depended on the degree of crystallinity of the polymer. High degree of crystallinity reduces the availability of water and metal ions to binding (reactive) amino groups [51].

On the other hand, the sorption of molybdenum is completely controlled by the pH of the solution and the concentration of molybdenum in the solution, which determine the appearance of charged poly-nuclear hydrolyzed forms of molybdenum at pH 3-3.5, which are most preferable for its sorption by chitosan [52], [53].

Thus, some part of molybdenum is well sorbed due to electrostatic interactions with polymer molecules, while the other part is in the form of clusters adjacent to the polymer structure [54].

Chitosan sorbents containing molybdenum can be prepared in various ways: 1) impregnation of chitosan granules with molybdate, 2) coagulation of CS granules in a solution of molybdate. The first process is essentially an adsorption process and is largely determined by the properties of chitosan, which cause different sorption of molybdate. The second method of production is based on ion gelation of chitosan using molybdate as gelling agent, which leads to the formation of micro and nanoparticles of chitosan [35], [36], [55]). Ionic gelation with molybdate is an analog of the processes of ionotropic gelation of chitosan in solutions of tripolyphosphate or sodium sulfate. The difference between the materials obtained in different media was confirmed by electron microscopy. The granules obtained in sodium hydroxide are characterized by large open porous structure (with a thin outer layer). When the gel is coagulated with molybdate, then treated with sodium hydroxide solutions, the structure is heterogeneous. The external layer is relatively compact (100 µm) without obvious pores, and the inner part is characterized by a small pores structure [54], [56]].

The sorbents used in the work were based on activated carbon fiber (ACF) and were obtained using these fiber modification techniques. Chitosan deposition on the fiber surface in the base form was performed by electrodeposition on the cathode from CF, that is, by gelation of chitosan with sodium hydroxide generated at the cathode at a potential of -900 mV [57]. Another sample was prepared by coagulation of chitosan with sodium sulfate in the presence of CF as a carrier [48]. The modification of the prepared samples with molybdenum was carried out by adsorption of Mo from a solution of sodium molybdate. The use of CF as a carrier creates favorable conditions for the sorption of arsenic. The deposition of CS on a highly developed CF surface contributes to the increase of the chitosan surface and, accordingly, the availability of amino groups of CS molecules [58], [59].

The features of Mo sorption by carbon fiber and chitosan-carbon materials, and the characterization of materials by atomic adsorption and electron microscopy were described in [58], [59], [60]. In order not to repeat the published data, we included only the part related to the sorption of arsenic.

The surface morphology of the initial CF and composite chitosan-carbon materials with chitosan deposited in various forms were characterized by scanning electron microscopy (Figure 1). When carbon fibers are modified with chitosan, two different films are deposited: an insoluble chitosan film in the base form under cathodic polarization and a film in the sulfate form, both of them are solid, homogeneous, completely covering the pores of the original carbon fiber.

The non-modified materials (in the absence of Mo) do not virtually sorb arsenic. On the contrary, as the test results show, the materials modified with Mo effectively decontaminate solutions from arsenic under static conditions: at initial arsenic concentrations of 50–1500 µg/L, the equilibrium concentration reaches 10 µg/L. The effectiveness of Mo-containing sorbents can be explained by the formation of an open porous structure formed in a film deposited on the carbon fiber surface, similar to the structure in chitosan gels, which were prepared by the interaction of chitosan with molybdate polyoxyanions as crosslinking agents [54], [61]].

Figure 1 - SEM image of the surface of composite sorbents based on CF modified with molybdenum: a) CF–Mo; b) CCM(900)–Mo; c) CCM(SO4)–Mo
The difference between the sorbents is displayed in the processes of arsenic(V) extraction. From the analysis of the sorption isotherms, it can be seen that in bidistilled water in the studied concentration range, the sorbents differ slightly from each other (Figure 2a). While in tap water, the best sorbent is a Mo-containing chitosan-carbon material in which the polymer is deposited on the carbon fiber surface in the sulfate form (Figure 2b).

The difference in the behavior of chitosan-carbon materials is clearly displayed in the dynamic mode of arsenic removal from aqueous solutions.

As follows from the data presented in Figure 3, the sorbents CCM(–900)–Mo and CF–Mo have approximately the same full dynamic capacity, which is achieved when passing 900-950 bed volumes of the solution.

At the same time, the total exchange capacity of sorbent CCM(SO₄)–Mo is not achieved even when passing 1800 ml (b.v.) of the solution. The numbers at the intersection of the output curves with the line of 50 μg/L correspond to the dynamic capacity before the slip. Here, at the selected sorbent loading density and a given solution passing rate, sorbents containing Mo, in which CF is coated with a chitosan film in various forms, show satisfactory characteristics: CCM(–900)–Mo retains a concentration of up to 10 μg/L when passing 300 bed volumes, and CCM(SO₄)–Mo when passing 750 bed volumes.

The isolation of arsenic is known to be based on a complexation reaction in a solution between Mo(VI) and As(V). The structure of these complexes, the so-called heteropolyanions, is very complex and depends on both the initial Mo/As ratio and the pH of a solution [6].

However, the monolybdate ion, which is located in the chitosan film in various bound forms (strongly bound and labile), can be released into the solution, leading to secondary contamination. Also, a weakly bound form of molybdate, partially released into the solution, can form complexes with arsenic, thereby reducing the efficiency of the sorption process.

The curves of Mo leaching from the sorbents in comparison with the kinetic data of arsenic extraction are shown in Figure 4.

As follows from the above data, during the sorption of arsenic, labile molybdate is washed out of the sorbent into the solution, which leads to contamination of the solution with molybdenum in concentrations significantly exceeding the MPC of molybdenum (250 μg/L). Mo leaching is not accompanied by an increase of the concentration of As in the solution, which is probably due to the bond strength of the arseno-molybdate complex with the carbon matrix. The problem of reducing the leaching of molybdate and increasing the bond strength of molybdate with the sorbent can be solved by treating the sorbent with phosphate ions before using the Mo-chitosan sorbent to prevent the leaching of mobile molybdate [6, 36, 55].
Conclusions

1. Oxides of transition polyvalent metals in an ultradispersed state in the composition of composite sorbents, being deposited on an inorganic carrier or included in a polymer matrix, can be successfully used to remove arsenic from solutions with low concentrations to a level that meets WHO standards.

2. Sorption of As(V) by Mo-containing sorbents based on carbon fiber and chitosan-modified fiber in various forms under static and dynamic conditions has been studied.

3. The determining role of the form of chitosan deposited on the surface of carbon fiber on the sorption properties of composite Mo-containing sorbents has been shown.

4. During the removal of As(V) from acidic solutions, the composite sorbents are destroyed, which is accompanied by the release of Mo into the solution to be cleaned. Therefore, the synthesized sorbents can be used in combined schemes of purification of industrial water and technological solutions.

Conflict of interests. On behalf of all the authors, the corresponding author declares that there is no conflict of interest.

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Figure 4 - Kinetics of the sorption of As(V) (a, c, e) and the kinetics of leaching of molybdenum (b, d, f) from the composite sorbents: a, b) CF–Mo; c, d) CCM(-900)–Mo; d, e) CCM(SO₄)–Mo; C/Co – the ratio of the concentration of As(V) at the time t to the initial concentration, CMo is the concentration of molybdenum at time t.

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Мышьякты кетірге арналған гибридті сорбенттер

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Гибридные сорбенты для удаления мышьяка

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АННОТАЦИЯ

В работе анализируются данные по извлечению мышьяка сорбционными методами с использованием материалов, имеющих перспективы широкомасштабного применения в водоподготовке. К ним отнесены оксиды переходных металлов в микрон- и наноразмерном состоянии, в том числе в составе композитных материалов с неорганическими матрицами, или гибридных сорбентов в составе с полимерными смолами или природными биополимерами. Приведены примеры использования композитных (гибридных) сорбентов для извлечения мышьяка из растворов с низкими концентрациями (на уровне ПДК). Цель настоящей статьи – обобщить актуальную информацию о наиболее важных особенностях Мо-содержащих хитозановых и разработанных нами хитозан-углеродных материалах для использования их в процессах удаления мышьяка на уровне низких концентраций до концентраций, удовлетворяющих требованиям ВОЗ. В работе представлены данные по сорбционным свойствам Мо-содержащих активированных углеродных волокон и хитозан-углеродных композиционных материалов по отношению к мышьяку (V) при извлечении его из дистиллированной и водопроводной воды, полученные в статических и динамических условиях. Обсуждаются причины различного поведения сорбентов в зависимости от формы осажденного на волокно биополимера и устойчивость сорбера в процессе сорбции мышьяка.

Ключевые слова: мышьяк, сорбция, композиты, гибридные сорбенты, углеродное волокно, хитозан.

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