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ADDITIONAL RESEARCH INTO ARSENIC (III) EFFECTIVE CATALYTIC OXIDATION IN AN AQUEOUS SOLUTION ON A NEW CALCIUM DOPED ACTIVE MANGANESE DIOXIDE IN A FLOW COLUMN

In many places in the world, groundwater contains arsenic compounds. To purify water containing arsenic effectively, arsenic (III) compounds must be oxidised. The subject of this study is oxidation of arsenic (III) compounds in an aqueous solution in a flow column mode.

The industrial arsenic oxidation technology involving aggressive oxidising agents such as chlorine or ozone, which is used most commonly today, has a number of serious disadvantages. The most problematic include extremely high risks for human health and the environment, the process cost and overall complexity. Catalytic oxidation of arsenic (III) compounds with atmospheric oxygen is an alternative that is free from the above disadvantages. Previously, the author studied the process of effective catalytic oxidation of arsenic (III) on the new active manganese dioxide (NADM) he had synthesised.

Later, however, it turned out that NADM has a significant drawback: during prolonged flow column stops, its catalytic activity drops sharply. This work proposes both a theoretical justification for and a solution to this problem. A new calcium-doped active manganese dioxide NADM-Ca0.5 was synthesised. It was shown that NADM-Ca0.5 demonstrates high catalytic activity towards arsenic (III). The fact that flow column long stops do not affect its catalytic activity was also experimentally confirmed. On the basis of the study results, some theoretical aspects are also discussed of the mechanism for catalytic oxidation of arsenic (III) with oxygen on active manganese dioxide in an aqueous solution.

For successful industrial implementation of the technology for catalytic oxidation of arsenic (III) compounds on NADM-Ca0.5, experimental work on pilot plants in the field is required and further laboratory research is needed in order to develop a detailed theoretical basis for the mechanism of catalytic oxidation of arsenic in aqueous solutions.

The results of this work are of interest for both industrial companies specialising in water purification from arsenic compounds, and scientists and researchers studying catalytic oxidation of arsenic (III), as well as heterogeneous catalytic oxidation with oxygen in general.

Keywords: groundwater, water purification from arsenic, arsenic (III) oxidation, arsenic (III) oxidation catalysts, arsenic sorption.

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1. Introduction

In many parts of the world, natural waters contain various arsenic compounds (III) and (V) in concentrations many times higher than the values permissible for drinking water. In some countries, such as India and Bangladesh, arsenic levels in drinking water are still far above the permissible level set by the WHO [1].

The problem of industrial water purification from arsenic (V) compounds is generally successfully resolved, for example, by conversion of these compounds into an insoluble phase using concentrated solutions of iron (III) and subsequent filtration. Since it is impossible to convert arsenic (III) compounds into an insoluble phase under industrial conditions or use ion exchange technologies,

there is a need to convert arsenic (III) compounds into arsenic (V) compounds, i. e., arsenic (III) compounds must be oxidised [2–7].

The high efficiency of catalytic oxidation of As(III) on new active manganese dioxide (NAMD) has been previously confirmed experimentally in both a limited volume and a flow column mode in the author's work [8].

During this work, however, it turned out that prolonged shutdowns of the flow column significantly reduce the catalytic activity of NAMD.

This NAMD behaviour would undoubtedly have a negative impact on the prospects for its industrial implementation.

So, it would be of great practical importance to resolve the problem of loss of catalytic activity by NAMD during possible technological flow column shutdowns.

The aim of research is to offer an explanation for the sharp decrease in the catalytic activity of NAMD during prolonged stops in flow column operation and to eliminate the catalyst shortcoming identified. To do this, the effect of a new active calcium-doped manganese dioxide (NAMD-Ca0.5) on the oxidation of arsenic (III) must be studied and its high catalytic activity towards arsenic (III) in a flow column mode experimentally confirmed. Absence of influence of prolonged stops in column operation on its catalytic activity must also be confirmed.

2. Materials and Methods

In this work, chemically pure reagents produced by Merck-Sigma-Aldrich and Fluka were used.

2.1. Oxidation of As(III) on NAMD in the presence of As(V).

900 ml of deionised water (pH=5.0) was placed in a flat-bottomed conical flask equipped with a magnetic stirrer, then 170 mg of NAMD added to the flask; after 10–15 minutes of intensive stirring at room temperature, 50 ml of an aqueous solution of Na_2HAsO_4 was added to the flask, containing 25,000 μg As(V), and, after 24 hours of intense stirring at room temperature, 50 ml of an aqueous solution of NaAsO_2 containing 16,000 μg As(III) was added; the concentrations of Mn(II), As(III) and total arsenic content, As(III)+As(V), were then measured after certain intervals.

2.2. Synthesis of NAMD-Ca0.5. In the same way as during development of the method for producing NAMD [8], the oxidation reaction of Mn(II) according to the methods of Karyakin [9] and Murray [10] was taken as the basis.

The complete method for obtaining NAMD-Ca0.5 is the author's «know-how».

2.3. Initial assessment of the catalytic activity of NAMD-Ca0.5.

950 ml of deionised water was placed in a flat-bottomed conical flask equipped with a magnetic stirrer, and 380 mg of NaHCO_3 (pH=7.6) was added. Then 100 mg of NAMD-Ca0.5 was added to the flask and, after 10–15 minutes of intense stirring at room temperature, 50 ml of an aqueous solution of NaAsO_2 containing 10,000 μg As(III) was added to the flask. After this, the concentrations of Mn(II), As(III) and total arsenic content, As(III)+As(V) were measured at certain intervals.

2.4. Study of arsenic (V) sorption on NAMD-Ca0.5.

Experiments were carried out at initial values of pH=5.0 and pH=8.0. 950 ml of deionised water (pH=5.0) was placed in a flat-bottomed conical flask equipped with a magnetic stirrer, and the pH was adjusted to 8.0 using NaHCO_3 . Then 100 mg of NAMD-Ca0.5 was added to the flask and, after 10–15 minutes of intense stirring at room temperature, 50 ml of an aqueous solution of Na_2HAsO_4 was added to the flask. The final concentration of As(V) was measured after 48 hours. The experiment was carried out twice for each value of the initial As(V) concentration.

2.5. Flow column. Washed sea sand, after thorough mixing with NAMD or NAMD-Ca0.5 in a small amount of water, was placed in a cylindrical column with a height of 8 cm and a cross-section of about 10 cm^2 .

The column was filled with deionised water, the contents allowed to settle and washed with a slow flow of water until

leaching of the working substance stopped completely (the substance washed out of the column was dried and weighed). Then, an aqueous solution of NaAsO_2 was fed from top to bottom into the column at room temperature using a peristaltic pump from a container previously prepared as follows.

A 25-litre container was filled with ordinary running tap water (pH=7.5–7.8), 33–35 mg of sodium hydrosulphite was added to it to neutralise the remaining chlorine present in the tap water, allowed to settle for several hours and, immediately before being fed into the column, 50 ml of fresh NaAsO_2 stock solution was added to it.

The concentrations of Mn(II) and As(III) at the column outlet were measured twice a day.

2.6. Determination of Mn(II), As(III) and As(V) concentration in solutions. During this work, the content of Mn(II), As(III) and As(V) in solutions was determined as follows.

All solution samples were pre-filtered through a 0.22 micrometre filter.

The Mn(II) content was determined photometrically using an analytical Mn(II) kit from Merck (vendor code 114770). The range of detectable Mn(II) concentration declared by the manufacturer is 0.01–10.0 mg/l.

Total arsenic content (As(III)+As(V)) was determined using a portable Arsenator Digital Arsenic Test Kit from Palintest.

A sample of the test solution was first passed through an ion exchanger to determine the As(III) content, with all As(V) retained on the ion exchanger, and then also examined using the Arsenator Digital Arsenic Test Kit. As(V) concentration was determined as the difference between the total arsenic (As(III)+As(V)) and As(III) concentrations. The range of detectable arsenic concentration declared by the manufacturer is 2.0–100.0 $\mu\text{g}/\text{l}$.

3. Results and Discussions

3.1. As(III) oxidation mechanism on NAMD. General considerations and an attempt at rethinking.

Previously, two experimental situations in a limited volume [8] were described, in which a very significant sorption of As(III) on NAMD was recorded: when As(III) does not undergo rapid oxidation in the case of a drop in catalytic activity or when there is a large excess of As(III) in the system, which takes some time to be completely oxidised.

On this basis, it is possible to conclude that the first stage in the catalytic oxidation of arsenic is sorption of As(III) on the surface of manganese dioxide, including both «catalytic centres» [8] and inactive sites. In this case, the predominant molecules among the sorbed particles are, due to their structure, molecules of tribasic ortho-arsenic acid $\text{As}(\text{OH})_3$, rather than monobasic meta-arsenic acid HOAsO (Fig. 1).

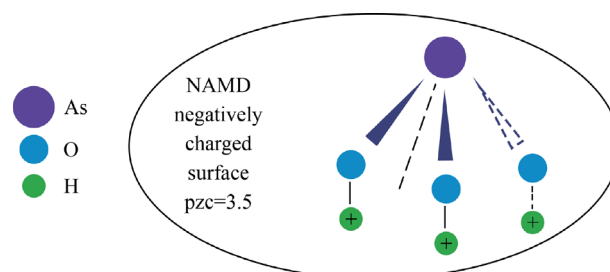


Fig. 1. Sorption of $\text{As}(\text{OH})_3$ molecules on the surface of manganese dioxide

At the second stage (Fig. 2, 3), the $\text{As}(\text{OH})_3$ molecule is oxidised at catalytic sites. In this case, inversion occurs of the resulting H_3AsO_4 molecule in a manner similar to organic $\text{S}_{\text{n}}2$ substitution reactions. Furthermore, its dissociation to the dihydroarsenate anion $(\text{HO})_2\text{AsO}_2^-$ and its repulsion from the also negatively charged surface of manganese dioxide, and finally re-emission into the solution, and at the same time the catalytic centres are released for oxidation of the next portion of $\text{As}(\text{III})$. So, the oxidation process produces mainly the dihydroarsenate anion $(\text{HO})_2\text{AsO}_2^-$, not the hydroarsenate anion HOAsO_3^{2-} .

Those H_3AsO_4 molecules that manage to be re-coordinated spatially by hydroxyl groups towards the manganese dioxide surface before dissociation occurs and the resulting anion moves away from the manganese dioxide surface are sorbed on its surface (Fig. 4, 5). Over time, the cumulative effect of this minor sorption (in [8] an estimate is given of about 1 % of the total oxidised arsenic) reduces catalytic activity, leading to a decrease in the oxidation rate – this is the third stage.

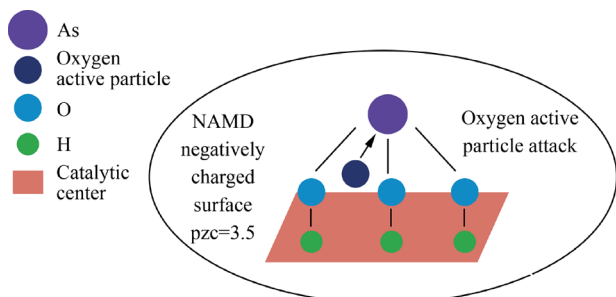


Fig. 2. Attack on the $\text{As}(\text{OH})_3$ molecule by an active oxygen particle

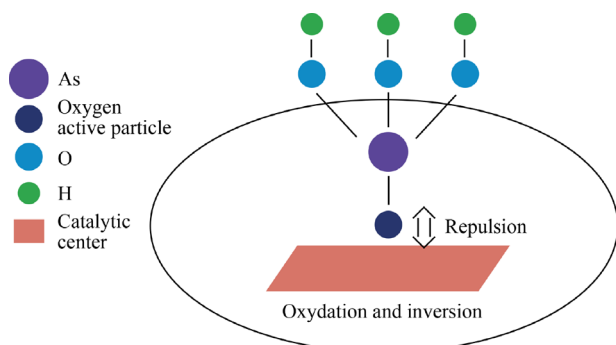


Fig. 3. Oxidation of the $\text{As}(\text{OH})_3$ molecule, its inversion and repulsion from the manganese dioxide surface

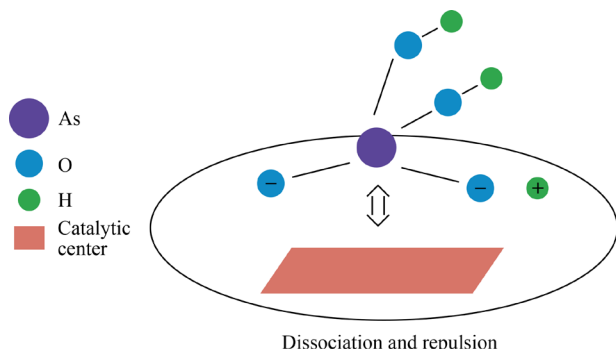


Fig. 4. Dissociation of the H_3AsO_4 molecule and its repulsion from the manganese dioxide surface

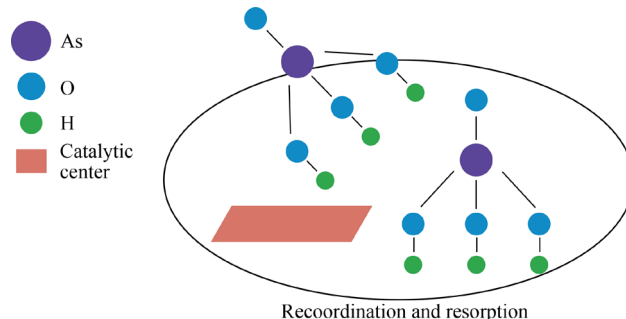


Fig. 5. Re-coordination of the H_3AsO_4 molecule spatially and its sorption on the manganese dioxide surface

At the fourth and final stage, there are two possible scenarios [8]. With an excess of $\text{As}(\text{III})$, a complete loss of catalytic activity and attenuation of catalytic oxidation occurs; the slow direct oxidation reaction becomes dominant, accompanied by an extremely slow reduction in the concentration of $\text{As}(\text{III})$ in the solution, appearance of $\text{Mn}(\text{II})$ ions in the solution, plus an extremely slow increase in their concentration. At the same time, it is possible to note once again that significant, time-stable sorption of $\text{As}(\text{III})$ is observed because manganese dioxide has lost its activity. When there is an excess of manganese dioxide, $\text{As}(\text{III})$ sorbed at the first stage is completely oxidised, then re-emitted into the solution, where the concentration of $\text{As}(\text{V})$ is fixed equal to the initial concentration of $\text{As}(\text{III})$.

At this point, however, the next question arises. How is $\text{As}(\text{III})$, which was initially sorbed on the inactive surface area of manganese dioxide, oxidised?

It is possible to believe that $\text{As}(\text{III})$ particles sorbed on inactive sites of manganese dioxide migrate chaotically over the surface and, upon reaching the «catalytic centre», are oxidised on it, unless the «catalytic centre» has not yet lost its activity.

If our assumption is correct, an interesting question appears to be what the rate-limiting factor is at various stages of $\text{As}(\text{III})$ oxidation, the decrease in catalytic activity as a result of $\text{As}(\text{V})$ sorption or the rate of migration of $\text{As}(\text{III})$ to the «catalytic centres».

More substantial arguments in favour of our assumption about migration of sorbed arsenic compounds over the surface of manganese dioxide are discussed below.

3.2. Oxidation of $\text{As}(\text{III})$ on NAMD in the presence of $\text{As}(\text{V})$. $\text{As}(\text{V})$ sorption. Table 1 and Fig. 6 data confirm the above conclusions about the four-stage mechanism of catalytic oxidation of $\text{As}(\text{III})$. So, in the first two minutes of the experiment, the concentration of $\text{As}(\text{V})$ in the solution remains constant, while that of $\text{As}(\text{III})$ drops sharply, $\text{As}(\text{III})$ was sorbed on the surface of the NAMD, but has not yet been oxidised – the first stage. After the next time interval of the experiment, 2–10 min, $\text{As}(\text{III})$ is quickly oxidised and is re-emitted into the solution in the form of $\text{As}(\text{V})$, an increase is observed in the concentration of $\text{As}(\text{V})$ but a significant part of $\text{As}(\text{III})$ remains sorbed and migrates over the surface of the catalyst. The total concentration of arsenic in the solution is still significantly lower than the initial one – stage two. Then, at 10–30 min, the «catalytic centres» begin to be blocked by $\text{As}(\text{V})$ formed during the oxidation process; the oxidation rate drops, only a small part of $\text{As}(\text{III})$ remains

sorbed, residual migration of As(III) – that is the third stage. Finally, the fourth stage, 30–180 minutes, sees slow completion of oxidation, almost complete re-emission of the formed As(V) into the solution, total concentration of arsenic in the solution becoming equal to the initial one.

When comparing the oxidation curves of As(III) on NAMD in the presence of As(V) (Fig. 6) and not in its presence [8] (Fig. 7), it is clear that the initial presence of As(V) in the system in no way affected the catalytic activity NAMD.

The As(III) oxidation curves are almost identical in both cases. Consequently, it is possible to believe that only the As(V) particles that appeared in the system as a result of As(III) oxidation and were not initially present in it are capable of sorbing on the surface of NAMD and leading to loss of its activity. This conclusion, if correct, has important practical implications.

Natural groundwater containing As(III) also always contains As(V) [2, 3, 4, 11–14]. The data obtained are indicative that the presence of As(V) should not have a negative effect on the efficiency of the catalytic oxidation of As(III) on NAMD in a flow column [8] when groundwater is purified from arsenic compounds at pilot or industrial plants.

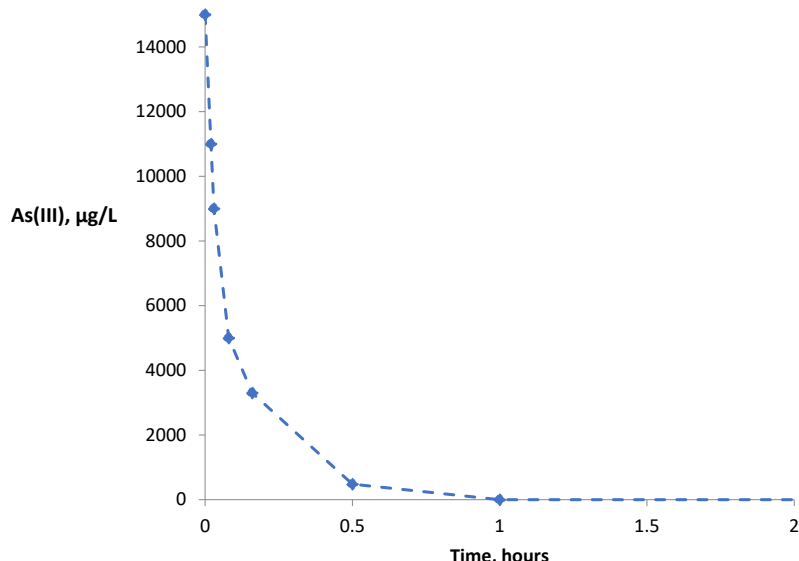


Fig. 7. Oxidation of As(III) on NAMD in a limited volume [8]

Table 1

Oxidation of As(III) on NAMD in the presence of As(V) in a limited volume

Minutes	As(III), µg/L	As(V), µg/L	As(III)+As(V), µg/L	Mn(II), µg/L
0	16000	25000	41000	0
2	10000	25000	35000	0
5	7400	28800	36200	0
10	5400	32100	37500	0
30	1600	38700	40300	0
60	400	40600	41000	0
180	0	41000	41000	0

3.3. Flow column. «Catalytic centres». Migration. Previously [8], an experimental analysis was performed of the catalytic activity of NAMD towards As(III). It was shown that, in a limited volume, loss of catalytic activity by NAMD occurs at a mass ratio of oxidised As(III) to catalyst As(III)/NAMD=0.23. While in the flow column, when it stopped, oxidation of As(III) continued with 100 % efficiency with a ratio reaching As(III)/NAMD=0.88.

The explanation proposed for this [8] was that catalytic oxidation does not occur over the entire surface of NAMD, but only at particularly active «catalytic centres». During the oxidation process, the resulting As(V) is sorbed to an extremely small extent on the NAMD surface and in a limited volume ultimately blocks these «catalytic centres», but not in the flow column mode.

It is possible to believe that sorbed As(V) particles migrate chaotically in a limited volume (Fig. 8, a, b) across the surface of the catalyst and, upon reaching the «catalytic centres», block them. The key factor ensuring the ability of As(V) particles to migrate in this way is, apparently, a chain of reversible transformations:

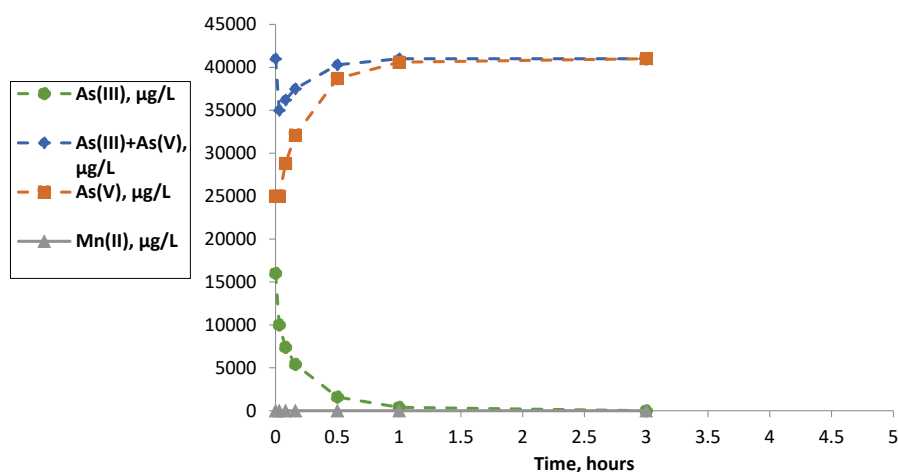


Fig. 6. Oxidation of As(III) on NAMD in the presence of As(V) in a limited volume

Transforming alternately from one equilibrium configuration to another, the As(V) particle moves along the surface like a kind of «walking tripod» (Fig. 8, a, b).

In a flow column, the directed flow of the solution prevents such migration in all directions.

As(V) particles migrate co-directionally with the flow and most «catalytic centres» remain active (Fig. 9).

The experiment carried out in this work with NAMD in a flow column confirms these conclusions.

The results of the experiment are presented in Table 2.

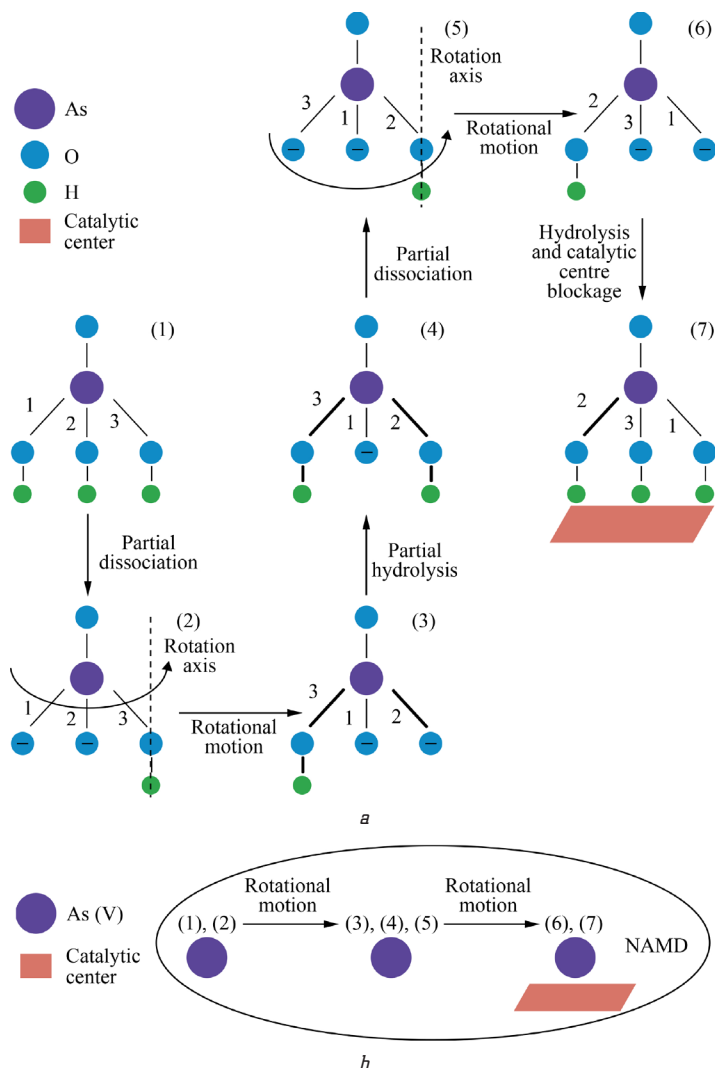


Fig. 8. Migration of the H_3AsO_4 molecule across the surface of manganese dioxide: a – step-by-step illustration; b – general scheme

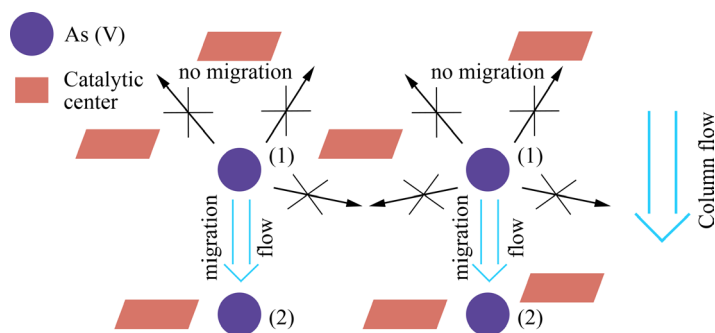


Fig. 9. Directed migration of the H_3AsO_4 molecule along the surface of manganese dioxide in a flow column

After extended operation in continuous mode, the column was washed with water until there was no $As(V)$ at all at the column outlet, and then stopped, full of water, for a long time. During the shutdown, the migration of sorbed $As(V)$ particles over the entire surface of the catalyst resumed and a significant number of «catalytic centres» were blocked by them. As a result, when the column resumed operation, a sharp drop was recorded in catalyst activity. This flow column experiment, from loading the NAMD, starting, rinsing with water, stopping, to restarting, was repeated twice more with identical results.

3.4. Flow column. NAMD-Ca0.5. Suppression of migration. A significant loss of catalytic activity by NAMD as a result of $As(V)$ migration during prolonged shutdown of the flow column would undoubtedly have a negative impact on the prospects for its industrial implementation. So, solving the problem of migration and loss of catalytic activity during possible technological flow column shutdowns would be of great practical importance. It is possible to hypothesise that the presence of a free metal cation, such as Ca^{+2} , on the surface of NAMD could limit $As(V)$ migration sharply. Such a cation would act as a kind of «trap», binding migrating $As(V)$ particles tightly (Fig. 10).

For this purpose, the author synthesised active manganese dioxide doped with calcium, with a total molar ratio of calcium and manganese of $Ca/Mn=0.42-54$ – NAMD-Ca0.5.

The results of initial assessment of the catalytic activity of NAMD-Ca0.5 in a limited volume are presented in Fig. 11, 12 and sorption curves – in Fig. 13 (during these experiments, no presence of $Mn(II)$ ions was ever detected in the solution).

Calcium doped NAMD-Ca0.5 was also tested in flow column mode with repeated long stops. The results of this experiment are provided in Table 3.

Table 2

Catalytic oxidation of arsenic (III) on NAMD in a flow column with shutdown

Duration, hours	Active work	Water wash	Interruption	Active work resumption			
	720	24	216	24	48	72	96
As(III) influent, $\mu g/l$	170	0	–	170	170	170	170
As(III) effluent, $\mu g/l$	0	0	–	30	50	60	50
Mn(II) effluent, $\mu g/l$	0	0	–	0	0	0	0

Notes: Waterpipe – pH 7.5–7.6; NAMD mass – 600 mg; Bed volume – 77 ml; Flow rate – 28.3 ml/min; EBCT – 2.72 min

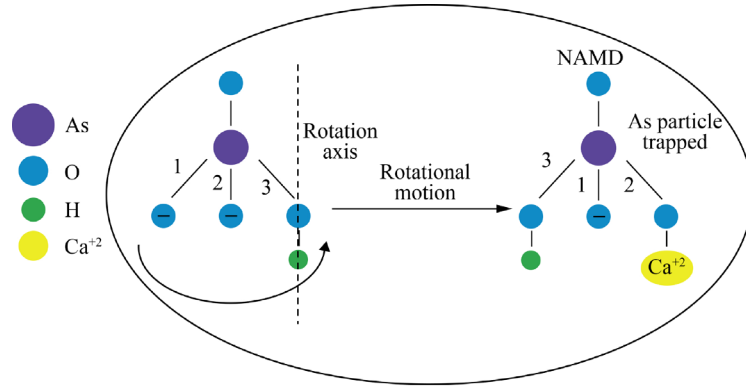


Fig. 10. Suppression of migration of H_3AsO_4 molecules over the surface of manganese dioxide by calcium ions

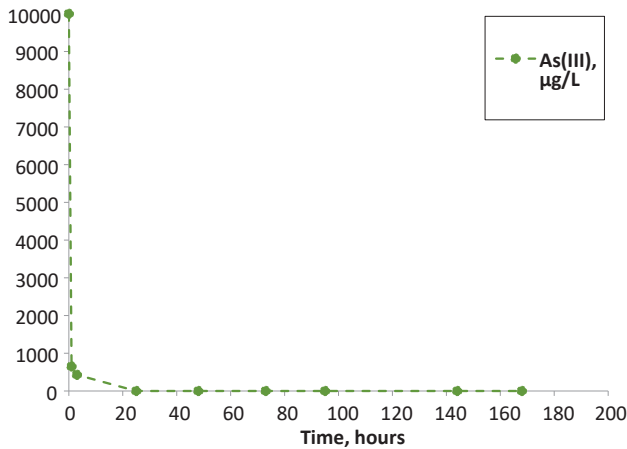


Fig. 11. Oxidation of As(III) on NAMD-Ca0.5 in a limited volume

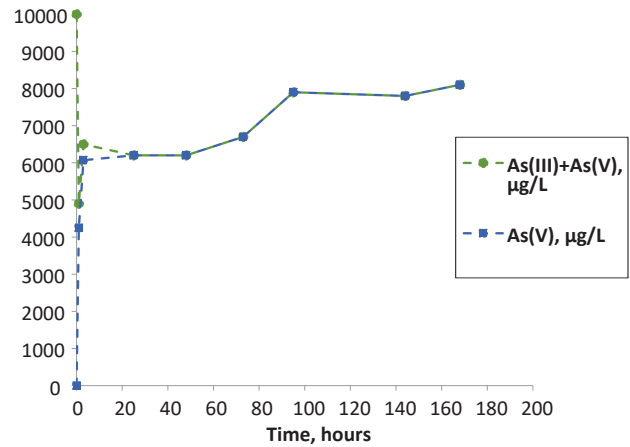


Fig. 12. Total arsenic concentration, As(III)+As(V), and As(V) concentration as a function of time during oxidation on NAMD-Ca0.5 in a limited volume

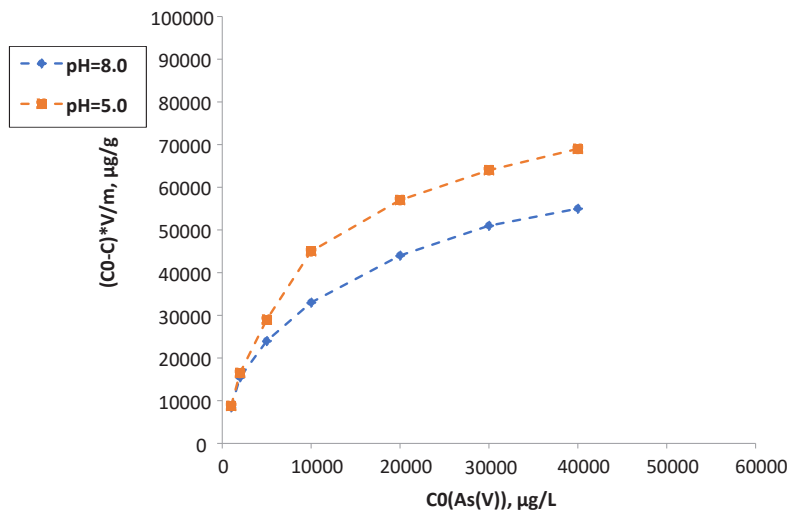


Fig. 13. NAMD-Ca0.5 sorption curves

Table 3

Catalytic oxidation of arsenic (III) on NAMD-Ca0.5 in a flow column with stops

Duration, hours	Active work	Water wash	Interrup-tion 1	Active work	Water wash	Interrup-tion 2	Active work	Water wash	Interrup-tion 3	Active work
	480	24	240	480	24	240	480	24	288	390
As(III) influent, µg/l	170	0	–	170	0	–	170	0	–	170
As(III) effluent, µg/l	0	0	–	0	0	–	0	0	–	0
Mn(II) effluent, µg/l	0	0	–	0	0	–	0	0	–	0

Notes: Waterpipe – pH 7.5–7.6; NAMD-Ca0.5 mass – 1100 mg; Bed volume – 77 ml; Flow rate – 28.3 ml/min; EBCT – 2.72 min

The experiment confirms that introduction of calcium ions into the catalyst effectively suppresses migration of As(V), as a result of which a drop in catalytic activity was never recorded during repeated long shutdowns of the column.

3.5. Discussion. *Practical significance:* successful implementation of a new calcium-doped active manganese dioxide (NAMD-Ca0.5) for catalytic oxidation of arsenic (III) compounds contained in groundwater under industrial conditions will eliminate the dangerous, labour-intensive, often ineffective stage of arsenic (III) oxidation with aggressive oxidants, such as chlorine or ozone. So, it will facilitate significantly an overall solution to the problem of industrial purification of groundwater from arsenic compounds.

Limitation of the study: additional research is needed on pilot plants in the field for NAMD-Ca0.5 to be implemented in industrial water treatment plants. This study was carried out under laboratory conditions at room temperature, and deionised water or tap water was used in the experiments. When conducting field tests, ambient and groundwater temperatures, low dissolved oxygen content and ionic composition of groundwater, organic impurities in the water, the technical parameters of industrial equipment and other features of a particular treatment plant could have a negative impact on the catalytic activity of NAMD-Ca0.5. The behaviour of NAMD-Ca0.5 in field conditions requires further study.

Prospects for further research: The present study confirmed the high oxidative potential of NAMD-Ca0.5. Along with studying the effectiveness of NAMD-Ca0.5 under field conditions, further laboratory studies seem necessary of the mechanism of catalytic oxidation of arsenic (III) on active manganese dioxides.

4. Conclusions

The resulting new active calcium-doped manganese dioxide (NAMD-Ca0.5) has high catalytic activity towards As(III) compared to analogues described in the literature. This has been confirmed experimentally, in both a limited volume and, most importantly, a flow column mode. The presence of calcium ions in the catalyst successfully suppresses migration of As(V) over the manganese dioxide surface. The resulting catalyst ensured, without any regeneration, efficient operation of a laboratory flow column at relatively high concentrations of As(III) and low contact time in the catalytic oxidation mode for a long time (about 2,000 hours) with repeated long stops in column operation.

The synthesised substance is of interest for further study of its properties and for testing as a catalyst for oxidation of As(III) compounds at pilot and industrial water treatment plants.

Conflict of interest

The author declares that he has no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

Financing

The research was performed without financial support.

Data availability

The manuscript has no associated data.

Use of artificial intelligence

The author confirms that he did not use artificial intelligence technologies when creating the current work.

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