

Abower, Denis

## Article

# Research into arsenic (III) effective catalytic oxidation in an aqueous solution on a new active manganese dioxide in a flow column

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## Kontakt/Contact

ZBW – Leibniz-Informationszentrum Wirtschaft/Leibniz Information Centre for Economics  
Düsternbrooker Weg 120  
24105 Kiel (Germany)  
E-Mail: [rights\[at\]zbw.eu](mailto:rights[at]zbw.eu)  
<https://www.zbw.eu/>

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Denis Abower

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

Groundwater in many places on Earth contains arsenic compounds. Arsenic (III) compounds must be oxidised to purify water containing arsenic effectively. The subject of this study is oxidation of arsenic (III) compounds in an aqueous solution.

Today's most common industrial arsenic oxidation method using aggressive oxidising agents such as chlorine or ozone has a number of serious disadvantages. The most problematic of these include extremely high risks to human health and the environment, the cost and overall complexity of the process. Catalytic oxidation of arsenic (III) compounds using atmospheric oxygen is an alternative free from the above disadvantages, yet, to date, no information about effective catalysts for this process has been presented in the literature.

The arsenic (III) catalytic oxidation process is studied in an aqueous solution on a new active manganese dioxide (NAMD) synthesised by the author. A comparative experimental analysis is performed with other known modifications of manganese dioxide. It is shown that the new active manganese dioxide (NAMD) has high catalytic activity towards arsenic (III), this being confirmed experimentally in both a limited volume and a flow column mode. Some theoretical aspects of the mechanism for catalytic oxidation of arsenic (III) with oxygen on active manganese dioxide in an aqueous solution are also discussed on the basis of the research results.

Experimental work is required at pilot plants in the field for successful industrial implementation of the technology for catalytic oxidation of arsenic (III) compounds on NAMD. Further laboratory research is necessary for developing a detailed theoretical basis for catalytic oxidation of arsenic in aqueous solutions.

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

**Keywords:** groundwater, removal of arsenic from water, arsenic (III) oxidation, arsenic (III) oxidation catalysts, arsenic sorption, manganese dioxide.

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## 1. Introduction

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

The problem of industrial removal of arsenic (V) compounds from water is generally successfully resolved by, for example, converting these compounds into an insoluble phase using concentrated solutions of iron (III), followed by filtration. Since arsenic (III) compounds cannot be converted into an insoluble phase under industrial conditions or ion exchange technologies used, arsenic (III) compounds

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

Arsenic (III) compounds are oxidised at industrial treatment plants most often with the help of oxidising agents that are extremely dangerous to human health and the environment, such as chlorine, sodium hypochlorite or ozone. This process is expensive, produces harmful by-products and is not always effective; arsenic (III) is often not completely oxidised, making re-oxidation necessary. In an aqueous solution, arsenic (III) compounds are oxidised by atmospheric oxygen but this process is too slow to be implemented under industrial conditions and, as far as we know, no effective catalysts have yet been proposed for this process [8–16].

So production and study of new, inexpensive, easy-to-use substances with high catalytic activity, ensuring

highly efficient catalytic oxidation of arsenic (III) compounds in an aqueous solution with atmospheric oxygen under industrial conditions, are of significant practical and scientific interest.

*The aim of the research* is to investigate the effect of new active manganese dioxide (NAMD) on oxidation of arsenic (III) and confirm experimentally its high catalytic activity towards arsenic (III) in a limited volume and a flow column mode.

## 2. Materials and Methods

Chemically pure reagents produced by Merck-Sigma-Aldrich and Fluka were used in this research.

### 2.1. Synthesis of various manganese dioxide modifications.

About two hundred different modifications of manganese dioxide were synthesised in developing the NAMD production method. The basis was provided by the oxidation reaction of Mn(II) according to the Karyakin [17] and Murray [18] methods. The synthesis was carried out in both neutral and alkaline environments in the range of  $\text{OH}^-/\text{Mn}^{2+}$  molar ratios from 0 to 45. KOH, NaOH, LiOH and CsOH were used as bases, and  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$  and NaClO were used as oxidising agents.

The complete method for obtaining NAMD is the author's «know-how». The Karjakin and Murray methods themselves were also reproduced exactly, the only difference being that the Murray substance was dried at 60 °C for 24 hours.

**2.2. Oxidation of As(III) in a limited volume. Primary assessment of the activity of the dioxides obtained.** Primary assessment of the activity of the substances obtained with respect to As(III) was carried out as follows: 950 ml of deionised water (pH=5.0) was poured into a flat-bottomed conical flask equipped with a magnetic stirrer, then 170 mg of manganese dioxide was added to the flask and, after 10–15 minutes of intense stirring at room temperature, 50 ml of an aqueous solution of  $\text{NaAsO}_2$  containing 15,000 µg of 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 specific time intervals.

### 2.3. Study of arsenic (V) sorption on manganese dioxides.

The experiments were carried out at initial values of pH=5.0, 8.0, 11.0. 950 ml of deionised water (pH=5.0) was poured into a flat-bottomed conical flask equipped with a magnetic stirrer, then 100 mg of the test manganese dioxide was added to the flask, the pH was adjusted to the desired values and, after 10–15 minutes of intense stirring at room temperature, 50 ml of an aqueous solution of  $\text{Na}_2\text{HAsO}_4$  was added to the flask. After 48 hours, the final concentration of As(V) was measured. The experiment was carried out twice for each value of the initial As(V) concentration.

**2.4. Flow column.** Washed sea sand was placed in an 8-cm high cylindrical column with a cross-sectional area of about 10 square centimetres after being thoroughly mixed with 700 mg of NAMD in a small amount of water.

The column was filled with deionised water, allowed to settle and washed with a slow flow of water until the leaching of the working substance stopped completely (the

substance washed out of the column was dried and weighed). Then, an aqueous solution of  $\text{NaAsO}_2$  was fed into the column from top to bottom, at room temperature, using a peristaltic pump, from a container previously prepared as follows.

A 25 l container was filled with ordinary running tap water (pH=7.5–7.8), 33–35 mg of sodium hydrosulphite was added to neutralise the remaining chlorine present in the tap water, allowed to settle for several hours and 50 ml of fresh  $\text{NaAsO}_2$  stock solution was added just before feeding to the column.

The column operated in continuous mode for about 2,000 hours. The concentrations of Mn(II), As(III) and As(V) at the column outlet were measured twice a day.

**2.5. Study of arsenic (V) sorption on sea sand.** 950 ml of tap water was poured into a flat-bottomed conical flask equipped with a magnetic stirrer; 50 ml of thoroughly washed sea sand from the same batch used to fill the flow column was added to the flask; 50 ml of a  $\text{Na}_2\text{HAsO}_4$  solution containing 5 mg of arsenic was then added and left for a day with gentle stirring.

The sand was then washed repeatedly with deionised water until the solution contained no arsenic and placed in a litre of solution containing 1 g of sodium hydroxide and stirred vigorously. An hour later, the arsenic concentration was measured twice: no presence of arsenic was detected in the solution.

**2.6. Oxidation of As(III) in an alkaline medium.** 950 ml of deionised water (pH=5.0) was poured into a flat-bottomed conical flask equipped with a magnetic stirrer, 0.7 g of NaOH was added, bringing the pH to 12.0, then 170 mg of manganese dioxide was added to the flask and, after 10–15 minutes of intense stirring at room temperature, 50 ml of an aqueous solution of  $\text{NaAsO}_2$  containing 100,000 µg of As(III) was added to the flask. The pH, Mn(II) concentration, As(III) concentration and total arsenic content, As(III)+As(V), were measured after 24 and 36 hours. This completed the first cycle of the experiment. A total of four cycles were performed. 0.7 g of NaOH was added to the flask before each cycle, bringing the pH to 12.0.

**2.7. Determination of the concentration of Mn(II), As(III) and As(V) in solutions.** The content of Mn(II), As(III) and As(V) in solutions during this work 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 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 µg/l.

### 3. Results and Discussions

**3.1. As(III) oxidation in a limited volume.** The results of the initial activity assessment of the most active substance we obtained (NAMD) are shown in Fig. 1, 2.

A similar experiment carried out with NAMD at higher pH values showed that increasing the pH has a slight effect on the As(III) oxidation rate, Fig. 3.

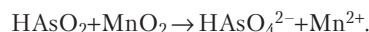
The methods described most frequently in the literature [8–16] for obtaining active manganese dioxide in the context of As(III) oxidation are variations of the Karyakin [17], Murray [18] and McKenzie [19] methods.

Two series of experiments were carried out to compare the activity of NAMD and manganese dioxides obtained using these methods: with the initial mass ratio of  $\text{MnO}_2/\text{As(III)}$  chosen by us, i. e., 170 mg/15 mg, and with the ratio found most often in the literature [16, 20], 100 mg/7.5 mg.

The results of these comparative studies (Fig. 4–6) show (for the McKenzie substance data from the work by Manning [16] are presented) that the substances according to the Karyakin and Murray methods are inferior to NAMD in activity and this according to the McKenzie method is significantly inferior.

The described experiments with NAMD never detected any Mn(II) ions in the solution. For the Karyakin and Murray substances, emission of Mn(II) ions into the solution was recorded only in the case of an initial ratio

$\text{MnO}_2/\text{As(III)} = 170 \text{ mg}/15 \text{ mg}$  and amounted to 0.32 mg and 0.64 mg, respectively, which is negligible compared to the reaction stoichiometry:



The absence of manganese (II) ions in the solution can be explained either by sorption on manganese dioxide [20] or by catalytic oxidation of arsenic, as a result of which no Mn(II) ions are formed. *This issue is discussed in more detail in subsection 3.4 below.*

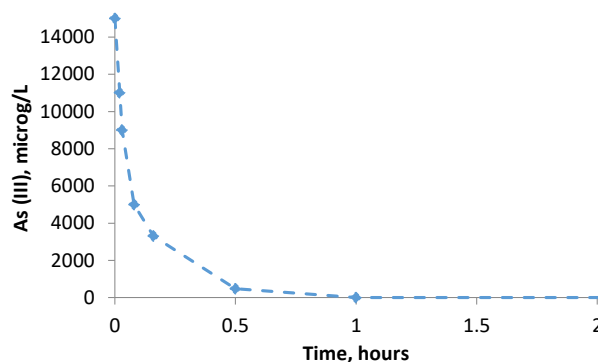


Fig. 1. Arsenic (III) concentration as a function of time during oxidation on NAMD in a limited volume

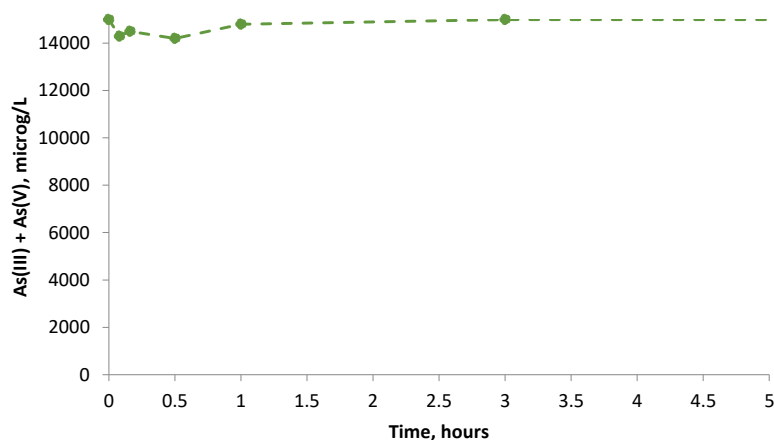


Fig. 2. Total arsenic concentration as a function of time during oxidation on NAMD in a limited volume

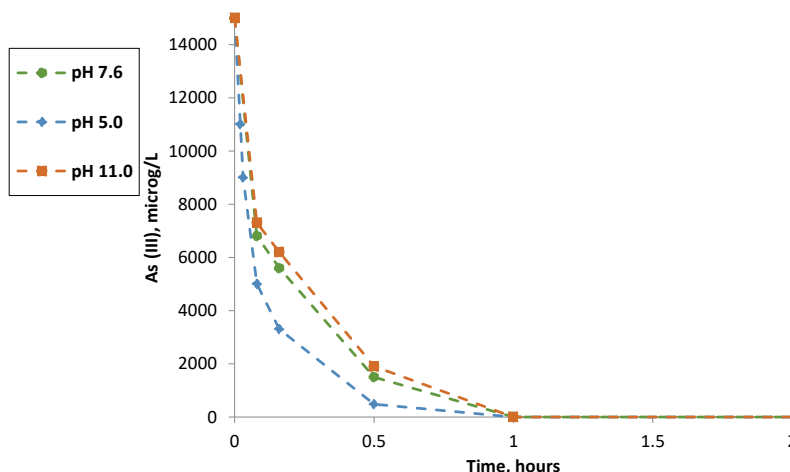


Fig. 3. Arsenic (III) concentration as a function of time during oxidation on NAMD in a limited volume at different pH

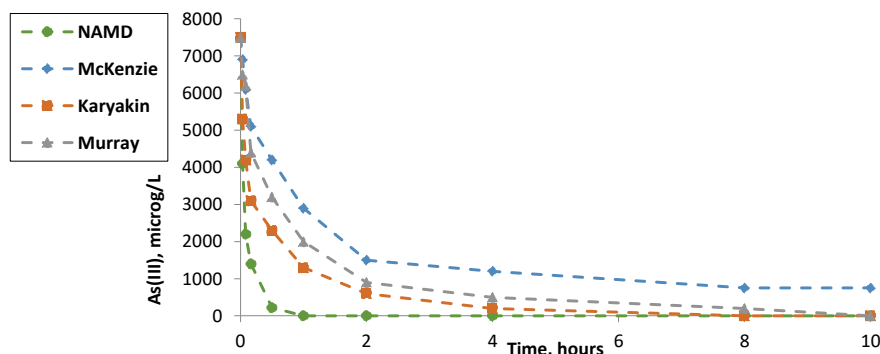


Fig. 4. Arsenic (III) concentration as a function of time during oxidation on various modifications of manganese dioxide in a limited volume,  $c_0\text{As(III)}=7.5$  mg/L

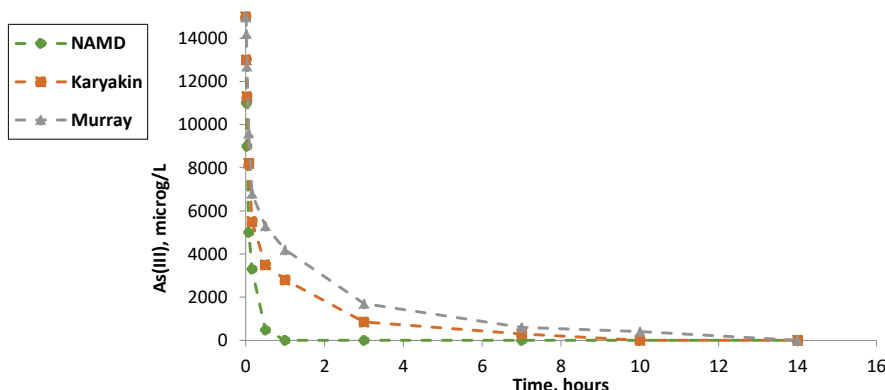


Fig. 5. Arsenic (III) concentration as a function of time during oxidation on various modifications of manganese dioxide in a limited volume,  $c_0\text{As(III)}=15$  mg/L

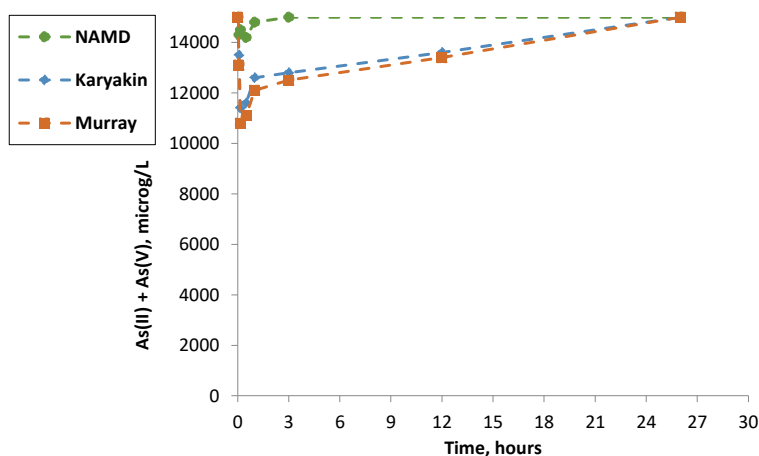


Fig. 6. Total arsenic concentration as a function of time during oxidation on various modifications of manganese dioxide in a limited volume

### 3.2. Sorption properties of active manganese dioxides in relation to arsenic (V) compounds.

The study also covered the sorption activity of NAMD, Karjakin and Murray substances in relation to As(V). No difference between the initial and final concentrations of As(V) outside measurement error was recorded at all experimental pH values for the three substances under study (Fig. 7).

So the three test substances in the indicated pH range have no significant ability to sorb As(V), and the drop in the total arsenic concentration over a certain period of time in Fig. 2, 6 can be explained by the As(III) sorption, which, having oxidised to As(V), is re-emitted into the solution.

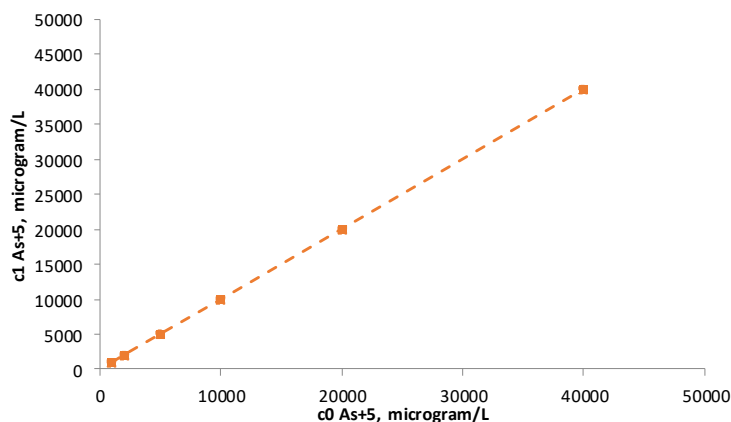


Fig. 7. Arsenic (V) concentration as a function of the initial arsenic (V) concentration on various modifications of manganese dioxide in a limited volume

The almost complete inability of these manganese dioxides to sorb As(V) is perhaps a key factor ensuring their high activity towards As(III).

*These issues are also discussed in more detail in subsection 3.4.*

### 3.3. Catalytic oxidation of arsenic (III) in a flow column.

The catalytic activity of NAMD was tested in a laboratory flow column (Fig. 8). The column operated in continuous mode for about 2,000 hours. The concentrations of Mn(II), As(III) and As(V) at the column outlet were measured twice a day. No Mn(II) or As(III) was detected in the solution at the outlet of the column from the time the column was started until it was stopped. The As(V) concentration at the outlet throughout the column operation corresponded to the input As(III) concentration to within a few per cent.

Table 1 shows the column's main parameters and the results obtained.

The absence of Mn(II) ions in the solution at the column outlet, as well as the molar ratio of NAMD to oxidised As(III) following from the data in Table 1 being less than 1, indicates unambiguously the catalytic mechanism of As(III) oxidation.

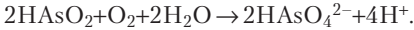
Afterwards, the column was washed with water at the same flow rate for 12 hours and then with a sodium hydroxide solution (2 g NaOH per 25 l of water) for five days. At the same time, about 5 mg of As(V) was washed out of the column, this constituting about 1 % of the total arsenic passed through the column during its operation.

The entire flow column experiment, from NAMD loading, start and up to washing with an alkaline solution, lasting 1,500–2,000 hours, was repeated another twice with identical results.

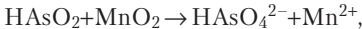
The Murray and Karyakin substances were also tested three times under identical flow column conditions. Each time, the Murray substance lost all activity after three days, the Karyakin substance – after a week.

**3.4. Mechanism.** The above experimental data, as well as those given below, prompted us to draw the following conclusions regarding the mechanism of As(III) oxidation in the presence of active manganese dioxide.

*As(III) is oxidised by oxygen catalytically, i.e., manganese dioxide is not consumed during the oxidation process:*



This is confirmed by the experimental data obtained using the column. Specifically, oxidation of 529 mg of As(III) according to the oxidation reaction:



would require 614 mg of absolutely dry manganese dioxide, while the column held 600 mg of a substance containing residual moisture. In addition, in the case of non-catalytic oxidation, by the time a third of the manganese dioxide had reacted, Mn(II) ions would have been detected in the solution at the column outlet, since the maximum molar ratio of manganese dioxide to the Mn(II) sorbed by it described in the literature is 2:1 [15, 18, 20]. In our case, from the time the column was started until it was stopped, no Mn(II) was detected in the solution at the column outlet.

*The resulting hydroarsenate anion is sorbed to an extremely small extent on the surface of manganese dioxide during oxidation. This, however, leads to the catalytic activity of manganese dioxide in a limited volume decreasing and ultimately disappearing as the reaction progresses. The transformation of the arsenate anion into a completely deprotonated state ensures arbitrarily long catalysis.*

Indeed, the results discussed above (Fig. 7) indicate that NAMD and the Karyakin and Murray substances have no significant ability to sorb As(V), at least outside the measurement error of the technique used. This is also evidenced by the data shown in Fig. 6: with complete oxidation of As(III), in all cases an equal to initial concentration of arsenic was recorded in the solution.

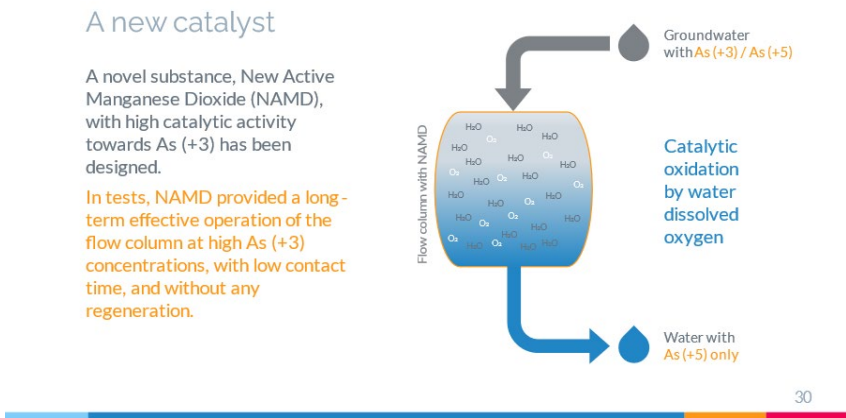


Fig. 8. Catalytic oxidation of arsenic (III) in a flow column

Main parameters of a flow column with NAMD and the results of catalytic oxidation of arsenic (III)

Table 1

Water, pH	NAMD mass, mg	Bed volume, ml	Flow rate, ml/min	EBCT, min
Waterpipe, 7.5–7.6	600	77	28.3	2.72
As(III) influent, mg/L	As(III) effluent, mg/L	Bed volumes passed	Breakthrough, L	Total As(III) oxidised, mg
0.17	0	40403	3111	529



In addition, we carried out a series of experiments for NAMD in a limited volume with higher initial concentrations of As(III) – Table 2. The presented data again show that the total concentration of arsenic in the solution in each case of complete oxidation of As(III) corresponds to the initial one, this indicating that NAMD has no significant ability to sorb As(V).

**Table 2**

Oxidation of arsenic (III) on NAMD in a limited volume  
at high initial concentrations

NAMD, 170 mg, V=1 l, pH=5.5				
c <sub>0</sub> (As+3)=15 mg/l	24 h	48 h	72 h	96 h
c <sub>1</sub> (As+3), mg/l	0	0	0	0
c <sub>1</sub> (As total), mg/l	15.0	15.0	15.0	15.0
c <sub>1</sub> (Mn+2), mg/l	0	0	0	0
c <sub>0</sub> (As+3)=23 mg/l	–	–	–	–
c <sub>1</sub> (As+3), mg/l	0	0	0	0
c <sub>1</sub> (As total), mg/l	23.0	23.0	23.0	23.0
c <sub>1</sub> (Mn+2), mg/l	0	0	0	0
c <sub>0</sub> (As+3)=30 mg/l	–	–	–	–
c <sub>1</sub> (As+3), mg/l	0	0	0	0
c <sub>1</sub> (As total), mg/l	30.0	30.0	30.0	30.0
c <sub>1</sub> (Mn+2), mg/l	0.7	0.65	0.65	0.65
c <sub>0</sub> (As+3)=40 mg/l	–	–	–	–
c <sub>1</sub> (As+3), mg/l	3.7	2.4	1.6	0
c <sub>1</sub> (As total), mg/l	35.5	37.5	38.5	40.0
c <sub>1</sub> (Mn+2), mg/l	1.9	2.3	2.6	3.8
c <sub>0</sub> (As+3)=50 mg/l	–	–	–	–
c <sub>1</sub> (As+3), mg/l	14.2	4.4	3.6	3.0
c <sub>1</sub> (As total), mg/l	45.0	46.0	47.0	48.0
c <sub>1</sub> (Mn+2), mg/l	2.0	2.9	3.6	3.8
c <sub>0</sub> (As+3)=100 mg/l	–	–	–	–
c <sub>1</sub> (As+3), mg/l	49.0	48.0	47.3	46.8
c <sub>1</sub> (As total), mg/l	92.0	93.0	93.0	93.6
c <sub>1</sub> (Mn+2), mg/l	3.2	4.0	4.4	4.8

On the other hand, when a column through which a solution with a total arsenic content of 530 mg had previously been passed is washed with an alkaline solution,

leaching of about 5 mg of As(V) sorbed in the column is recorded, which is less than 1 % of the amount of arsenic passed through the column.

A separate experiment with sea sand column filler showed that As(V) is not sorbed at all on sea sand.

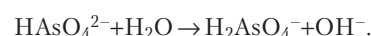
So, the hydroarsenate anion is sorbed to a negligible extent on the surface of active manganese dioxide, though we believe that this poisons the catalyst and leads to loss of catalytic activity. The Table 2 data show that, at high initial concentrations of As(III) starting from 40 mg/l or more, at a certain stage of the reaction, oxidation virtually stops and, subsequently, even over a long period of time, an extremely slow decrease is observed in the As(III) concentration in the solution.

We explain the difference in activity between different manganese dioxides (Fig. 4, 5) precisely by this factor. The less a substance sorbs the hydroarsenate anion, the more active it is.

Why is the negatively charged hydroarsenate anion still sorbed, though to a negligible degree, on the also negatively charged surface of manganese dioxide ( $PZC=3.5$ )?

We see it this way.

The hydroarsenate anion formed during As(III) oxidation is largely hydrolysed:



So, when 0.13 mmol of Na<sub>2</sub>HAsO<sub>4</sub> is dissolved in a litre of deionised water, the pH value rises from 5.0 to 7.0. So, a minimally charged anion (HO)<sub>2</sub>AsO<sub>2</sub><sup>–</sup> possessing two hydroxyl groups with positively charged hydrogen atoms at the ends appears in the system. We believe that, owing to these hydroxyl groups, minimal sorption of hydro- and, to a greater extent, dihydroarsenate anions occurs, despite the electrostatic effect of repulsion from the negatively charged manganese dioxide surface.

If this is indeed the case, then transfer of the arsenate anion to the completely deprotonated state AsO<sub>4</sub><sup>3–</sup> would provide for zero sorption, manganese dioxide would cease losing activity, and the As(III) catalytic oxidation process would continue indefinitely, as was confirmed by experiment on As(III) oxidation in an alkaline medium carried out with NAMD and Murray substance.

Table 3 shows the experimental results.

**Table 3**

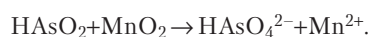
Catalytic oxidation of arsenic (III) on NAMD and on Murray manganese dioxide in a limited volume in an alkaline medium

Results for NAMD/Murray are shown in each cell						
Initial loading for both substances 170 mg, V=1 l						
Time, hours	First circle			Second circle		
	0	24	36	36	60	75
pH	11.9/11.9	11.3/11.0	10.8/10.5	12/12.1	11.3/11.4	10.4/10.4
c As(III), mg/l	100/100	13.5/0	0/0	100/100	22/0	0/0
c As(III)+As(V), mg/l	100/100	93/98	100/100	200/200	188/190	199/199
c Mn+2 mg/l	0/0	0/0	0/0	0/0	0/0	0/0
Time, hours	Third circle			Fourth circle		
	75	99	119	119	143	167
pH	12/11.9	11.5/11.35	10.6/10.5	12/12	11.3/11.4	10.4/10.3
c As(III), mg/l	100/100	28/12	0/0	100/100	35/23	0/0
c As(III)+As(V), mg/l	300/300	281/285	295/296	400/400	375/380	394/395
c Mn+2 mg/l	0/0	0/0	0/0	0/0	0/0	0/0

400 mg of As(III) were oxidised in the presence of 170 mg of NAMD or Murray substance. It is worth noting that, under these conditions, the Murray substance produces an oxidation rate slightly superior to that of NAMD (Fig. 4, 5, Table 3). The results prove:

- a) catalytic mechanism of As(III) oxidation with oxygen in the presence of active manganese dioxides;
- b) the loss of catalytic activity of manganese dioxides during As(III) oxidation in a limited volume is explained by sorption of hydrogen-containing arsenate anions;
- c) the catalytic activity of various manganese dioxides towards As(III) depends on their ability to sorb hydrogen-containing arsenate anions: the lower this ability, the higher the catalytic activity;
- d) transfer of hydrogen-containing arsenate anions to the deprotonated state  $\text{AsO}_4^{3-}$ , with the reaction carried out at pH=12, reduces sorption to zero, thereby ensuring arbitrarily long catalysis.

*During the oxidation process, when the catalytic activity decreases, the direct reaction begins of As(III) oxidation with manganese dioxide, competing with the catalytic oxidation and extremely slowly in comparison, accompanied by Mn(II) emission into the solution:*



The data in Table 2 show that, for high (more than 40 mg/l) initial concentrations of As(III), after a sharp drop recorded in the As(III) concentration in the first 24 hours of the experiment, which we attribute to the stage of rapid catalytic oxidation, the next few days see an extremely slow decrease in As(III) concentration, accompanied by appearance of Mn(II) ions in the solution and an extremely slow increase in their concentration. Our explanation for this is that the slow direct oxidation reaction becomes dominant with the loss of catalytic activity and the decay of catalytic oxidation. We also attribute the above-mentioned appearance of Mn(II) ions in low concentrations in experiments with Karyakin and Murray substances to a sharp decrease in the catalytic activity of the substance and the onset of a direct oxidation reaction.

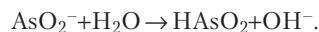
*The decrease in catalytic activity is accompanied by significant sorption of As(III). We also explain the drop in the total concentration of arsenic over a certain period of time during the initial oxidation stage by the As(III) sorption, which, having oxidised to As(V), is re-emitted into the solution.*

The data in Table 2 show that, for high initial concentrations of As(III), in each case of incomplete oxidation of As(III) a significantly lower value of the total arsenic concentration was recorded compared to the initial value. Yet it was shown above that the active manganese dioxides studied in this work lack any significant ability to sorb As(V). Consequently, the observed drop in the total arsenic concentration in cases of incomplete oxidation of As(III) is explained by As(III) sorption.

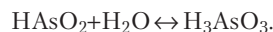
This agrees well with the structure of arsenite particles participating in the discussed oxidation process as a reducing agent and with the above considerations about the key role played by the presence or absence of hydroxyl groups in the sorbed particle.

Arsenous acid  $\text{HAsO}_2$  has an extremely low dissociation constant  $K=6 \cdot 10^{-10}$ , so all arsenite anions  $\text{AsO}_2^-$  formed in

the solution as a result of the dissociation of the reducing agent  $\text{NaAsO}_2$  are completely hydrolysed:

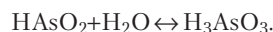


In addition, the reversible hydration of the resulting arsenous acid should be taken into account:



Although this equilibrium is strongly shifted to the left under normal conditions, the tribasic form of arsenous acid  $\text{As}(\text{OH})_3$  appears in the system. This pyramidal molecule «equipped» with three hydroxyl groups is not subject to the effect of repulsion from the negatively charged surface of manganese dioxide owing to the absence of a negative charge.

It is these structural features of the hydrated form of arsenous acid that determine the high sorption of As(III), which, in turn, entails a shift of the equilibrium to the right in the reversible reaction discussed just above:



So, in a situation where As(III) does not undergo rapid oxidation, as in the case of a drop in catalytic activity or when there is a large excess of As(III) in the system requiring a long time to oxidise completely, significant sorption of As(III) is detected on manganese dioxide.

On this basis, we explain the drop in the total arsenic concentration during a certain initial period of time in Fig. 2, 6 by As(III) sorption, which, having oxidised to As(V), is re-emitted into the solution.

*It remains unclear why, in the flow column mode, there is no drop in catalytic activity, just as happens in a limited volume (Table 2). It is possible to assume that catalytic oxidation of As(III) does not occur over the entire surface of the manganese dioxide but only at some specific points or regions.*

For convenience, we will call these special areas «catalytic centres». As discussed above, we believe that the decrease in catalytic activity in a limited volume is primarily due to sorption of the dihydroarsenate anion  $\text{H}_2\text{AsO}_4^-$ . The resulting hydroarsenate anion  $\text{HAsO}_4^-$  is located near the catalytic centre at the time of oxidation. Since the resulting anion is a tetrahedron with an arsenic atom in the centre and four oxygen atoms with a negative effective charge at the vertices, only one of which is part of the hydroxyl group, it is logical to assume that this anion is repelled from the negatively charged surface of manganese dioxide and moves away from the catalytic centre when formed. Some time is required for hydrolysis into the dihydroarsenate anion and spatial re-coordination by hydroxyl groups towards the catalytic centre. This does happen in a limited volume at a certain point and dihydroarsenate anions are sorbed on the catalytic centres of manganese dioxide, leading to a loss of catalytic activity.

In a flow column, the re-coordinating dihydroarsenate anion is carried away from the catalytic centre by the solution flow and is sorbed on another, inactive area of the manganese dioxide surface. If catalytic oxidation were to occur over the entire surface of the catalyst, not only at the catalytic centres, then the insignificant sorption of As(V), that takes place in both a limited volume and

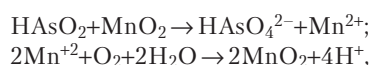


the column, would lead to a loss of catalytic activity not only in a limited volume but and in the column, too.

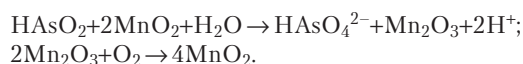
*It also remains unclear whether oxygen is the direct oxidiser of As(III) during catalytic oxidation, in which case this is a one-stage process:*



*or Mn(IV) in the composition of manganese dioxide, producing a two-stage process:*



or



As far as we know, this still remains an open question.

**3.5. Discussion.** *Practical significance:* successful introduction of a new active manganese dioxide (NAMD) for catalytic oxidation of arsenic (III) compounds contained in groundwater under industrial conditions will eliminate the dangerous, labour-intensive stage of arsenic (III) oxidation using harsh oxidants, such as chlorine or ozone, thus significantly facilitating an overall solution to the problem of industrial removal of arsenic compounds from water.

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

*Prospects for further research:* this study confirms the high oxidative potential of NAMD. In addition to studying the NAMD effectiveness in the field, further laboratory study appears necessary of the mechanism for catalytic oxidation of arsenic (III) on active manganese dioxides.

Studies of the oxidation of other difficult-to-oxidise substances using NAMD as a catalyst, in both the liquid and gas phases, also seem very appropriate.

## 4. Conclusions

The resulting new active manganese dioxide (NAMD) 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, flow column mode. This substance ensures, without any regeneration and for a protracted period (more than 2,000 hours compared to 150 hours or less for analogues under the same conditions), effective operation of a laboratory flow column at relatively high concentrations of As(III) with a low contact time in the catalytic oxidation mode.

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

This substance can also be the starting point for creating a series of effective catalysts for various oxidative processes, in both solutions and the gas phase.

## Conflict of interest

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

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## Data availability

The manuscript has no associated data.

## Use of artificial intelligence

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

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**Denis Abower**, Independent Researcher, Jerusalem, Israel, e-mail: [denis.abower@gmail.com](mailto:denis.abower@gmail.com), ORCID: <https://orcid.org/0009-0002-4546-0572>