Nanostructured Adsorbents for Arsenic Compounds' Removal

Marta Litynska, Tetiana Dontsova, Grigorii Krymets, and Anna Gusak

Abstract The paper analyzed the usage and efficiency of different types (zero-valent iron, oxides, hydroxides, oxyhydroxides, composites, etc.) of nanostructured adsorbents for arsenic compounds' removal. Increasing of arsenic content in natural waters due to changes of groundwater level and mining activities is the significant problem of drinking water treatment. Arsenic is one of the most dangerous elements in world. According to European Commission, the maximum allowable level of arsenic in drinking water is 10 μg/l. High arsenic concentration in natural water is typical for India, China, Bangladesh, Taiwan, Vietnam, Hungary, the USA, Mexico, Chile, Argentina, Ghana, Iran, etc. Chronic arsenic exposure provokes a lot of different health problems, including cancer of skin and internal organs, endocrine disorders, hyperkeratosis, melanosis, etc. It was noted that inorganic sorption materials, especially iron-based adsorbents, are effective in removal arsenic compounds from polluted water and in immobilization from contaminated soils and sediments. In the paper, various compositions and applications of nanostructured adsorbents are observed.

M. Litynska (✉) · T. Dontsova · G. Krymets · A. Gusak
Igor Sikorsky Kyiv Polytechnic Institute, Kyiv, Ukraine
e-mail: m.litynska-2017@kpi.ua

T. Dontsova
e-mail: dontsova@ua.fm

G. Krymets
e-mail: krimets@xtf.kpi.ua

A. Gusak
e-mail: maril91@ukr.net

1 General

1.1 Introduction

Arsenic compounds are often considered pollutants in environmental science due to significant toxicity and inability for natural degradation [1]. There are a lot of contamination sources and pathways, including such natural and anthropogenic processes as leaching from arsenic minerals, volcanic activity, mining, coal burning, infiltration from industrial wastes, etc. [2–4]. Mining activity and sedimentary formations are two of the main arsenic sources in Europe, Asia, the USA, and Africa (Fig. 1).

Arsenic compounds pollute air, soils, and water and eventually cause significant environmental problems and health risks. Arsenic pollution of soils often leads to obtaining of contaminated food products, including rice and other agricultural crops. Arsenic concentrations in rice grain are very significant in a lot of cases: 0.4 mg/kg in Kazakhstan, 0.53 mg/kg in Bolivia, 0.58 mg/kg in Bangladesh, and 0.87 mg/kg in Iran [5].
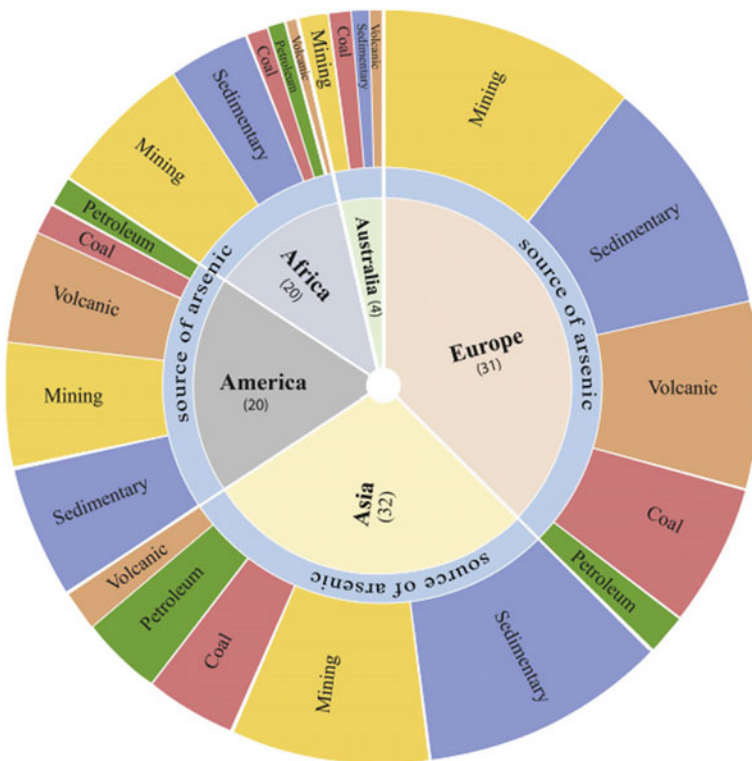

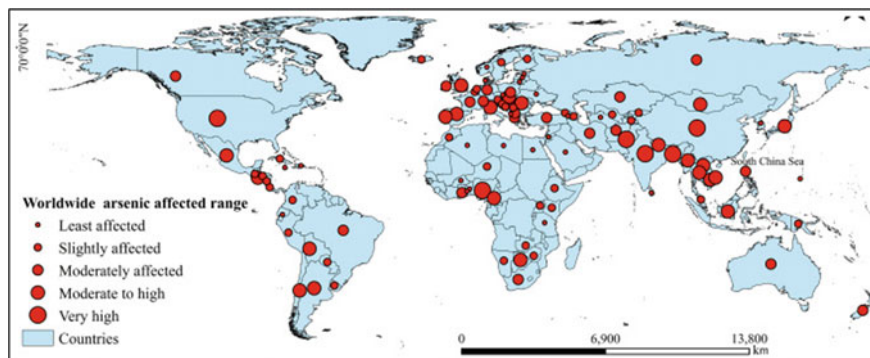**Fig. 1** Characterization of main arsenic sources [2]

Fig. 2 Arsenic affected countries [2]

Leaching from minerals and infiltration from industrial wastes, especially after mining, are among the main ways of natural water pollution and aquatic organism's contamination. Seafood often contains significant arsenic (about 10–100 mg/kg dry weight) [6]. Such processes as changes of groundwater level and acidic rains intensify arsenic leaching. Increasing of arsenic content in natural waters due to these processes is the significant problem of drinking water treatment. Arsenic is one of the most dangerous elements in world. According to European Commission and recommendations of World Health Organization, the maximum allowable level of arsenic in drinking water is 10 μg/l. High arsenic concentration in natural water is typical for India, China, Bangladesh, Taiwan, Vietnam, Hungary, the USA, Mexico, Chile, Argentina, France, Portugal, Ghana, Iran, etc. [3, 7]. Millions people are affected by arsenic exposure: 2.4 millions in Cambodia (1610 μg As/l), 13 millions in Pakistan (2620 μg As/l), 19.6 millions in China (2000 μg As/l), 50 millions in India (3880 μg As/l), 85 millions in Bangladesh (4730 μg As/l) etc. (Fig. 2).

Chronic arsenic exposure provokes a lot of different health problems, including cancer of skin and internal organs, endocrine disorders, hyperkeratosis, melanosis, genotoxic and cytotoxic effects, etc. [8–10]. Oral arsenic exposure is significantly dangerous than dermal and causes more negative health effects [11]. In addition to the path of entry, people age is also very important. In consonance with work [11], in Jinghui irrigation district (China), where the main source of arsenic is industrial wastewater, the carcinogenic risk for adults is higher than for children, but the non-carcinogenic risk for children is higher. Thereby, prevention of oral arsenic exposure is very necessary. That is why it is very important to treat polluted water and remediate soils.

Nowadays, there are a lot of treatment methods, especially dosing of different chemicals, creation of biological systems, etc., but usage of sorption materials, especially nanostructured, is one of the most popular approaches both in water treatment and soil remediation due to small particle size, high surface area, and significant adsorption efficiency [1, 12, 13].

Fig. 3 Types of adsorbents
for arsenic removal
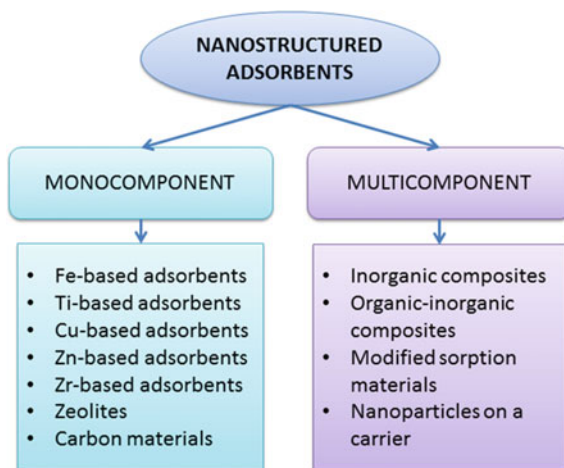
1.2   Types of Adsorbents for Arsenic Removal

Presently nanosized structures have a significant impact on technological advancements in different fields, especially environmental applications [14]. There are a lot of diverse types of nanostructured adsorbents for arsenic removal, including various oxides, hydroxides, composites, and nanoparticles on a carrier (Fig. 3).

Nanostructured adsorbents often are one-component: iron oxides, iron hydroxides, iron oxyhydroxides, zero-valent iron, titanium oxides, calcium titanate, copper oxides, zinc oxides, zirconium oxides, aluminum oxides, carbon nanotubes, zeolites, etc. [15–21]. But multicomponent adsorbents often are more effective than one-component due to combining benefits of different materials. There are a lot of both environmental and economic effective adsorbents for arsenic removal, but main part of them contains iron or its compounds due to low-cost and significant efficiency in arsenic immobilization [12, 19].

2   Usage and Perspectives of Nanostructured Adsorbents for Arsenic Compounds' Removal

2.1   Application and Perspectives of Iron-Based Nanostructured Adsorbents for Arsenic Compounds' Removal

Iron-based adsorbents can be one-component and multicomponent, which contain metal nanoparticles, oxides, oxyhydroxides, ferrites, etc.
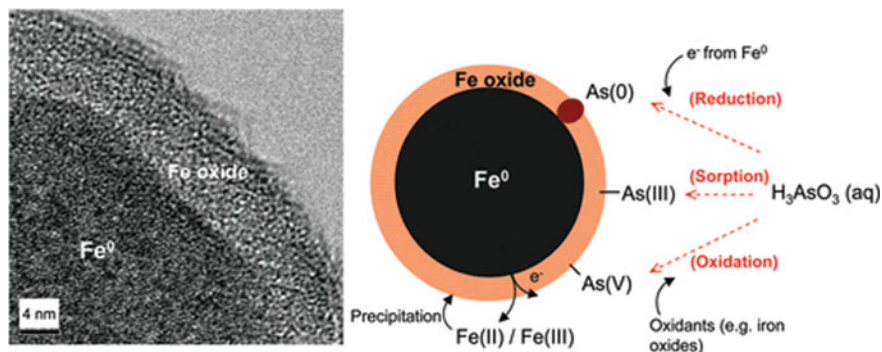
Fig. 4 Structure of ZVI nanoparticles and mechanisms of arsenic pollutants removal [23]

Zero-valent iron nanoparticles (nZVIs) and their composites have extremely wide usage for ecological purposes, including removal from water organic and inorganic arsenic compounds, soil and sediments remediation and treatment of arsenic-contaminated water in wells [17]. There are two methods to obtain treated water from polluted wells: the first one is an injection of nZVIs to form a reactive barrier, the second one is an injection of mobile nZVIs to form an nZVI plume [17].

These nanoparticles have typical core–shell structure formed in an aqueous medium due to interactions with water and dissolved oxygen [18, 22]. Zero-valent iron is the core and reducing agent in redox reactions with arsenic compounds. Iron oxides/hydroxides are the main components of shell [22]. Figure 4 demonstrates shell–core structure of nanoparticle and mechanisms of arsenic compounds' immobilization.

According to review data which are represented in [18], sizes of nZVIs increase from 5 to 10.7 nm due to corrosion processes, what is more the thickness of the oxide/oxyhydroxide layer is about 3.6 nm. Thus, nZVIs can effective immobilize both As(III) and As(V) compounds due to its specific core–shell structure [18]. For example, nZVIs can remove 102 mg As(III)/g or 118 mg As(V)/g [17].

But multicomponent sorption materials based on nZVIs often are more effective, than single nZVIs. It can be modifications, including sulfide-modified nZVIs or different combinations with other oxides, zeolites, grapheme, etc. [24–29]. Sepiolite-supported nanoscale zero-valent iron can remove 165.86 mg As(III)/g from water solution [27]. According to the work [28], adsorption capacity of zeolite-supported sulfide nanoscale zero-valent iron is 204.36 mg As(V)/g. Cu^0 nano-shell-decorated nZVIs are significantly more effective than conventional nZVIs, and its adsorption capacity is 453 mg As(III)/g [29].

Magnetite nanoparticles also are effective in arsenic compounds' immobilization, but their adsorption properties are lower than nZVIs and effective pH range is smaller [30].

Nanostructured iron oxyhydroxide is other effective adsorbent for arsenic compounds' removal. It demonstrates adsorption capacity of As(III) and As(V) about

70 mg/g [3, 19]. But iron oxyhydroxide does not have magnetic properties which makes the separation of nanoparticles more difficult than in case nZVIs or magnetite.

Manganese ferrite nanoparticles are significantly less effective in arsenic compounds' removal than nZVIs, iron oxides or oxyhydroxides. Its adsorption capacity of As(III) and As(V) is about 35 mg/g at pH 8 [31]. This is too small to compete with other iron-based sorption materials.

2.2 Usage and Perspectives of Titanium-Based Nanostructured Adsorbents for Arsenic Compounds' Removal

Titanium (IV) oxide is the most popular titanium-based nanostructured adsorbent. This material is both effective in removal of inorganic and organic arsenic compounds due to its adsorption and photocatalytic properties. According to review data which are represented in [32], hydrous TiO_2 with particle size 3–8 nm has surface area of 312 m^2/g and adsorption capacity of 83–96 mg As(III)/g; titania nanotubes with same surface area can adsorb 60 mg As(III)/g or 208 mg As(V)/g.

Iron (III) titanium (IV) mixed binary oxide has similar efficiency as hydrous TiO_2 (85 mg As(III)/g) [32]. This material is cheaper than pure titanium (IV) oxide, but less efficient in photocatalytic treatment. Well-dispersed TiO_2 nanoparticles anchored on Fe_3O_4 magnetic nanosheets have significantly smaller adsorption capacity (about 31 mg As(III)/g and 36 mg As(V)/g) although both components may be involved in photocatalytic reactions [33].

Calcium titanate nanoparticles prepared by the sol–gel method are even less efficient adsorbent. It demonstrates maximum adsorption capacity of As(III) about 11 mg/g [20].

Thereby, titanium (IV) oxide nanoparticles are not suitable for use to remove inorganic arsenic compounds from polluted water or to remediate contaminated soils and sediments due to high cost of these adsorbents, which becomes impossible to reuse after such processes.

2.3 Usage and Perspectives of Copper-Based Nanostructured Adsorbents for Arsenic Compounds' Removal

Copper oxide nanoparticles can remove arsenic under a wide range of water content without adjusting the pH and removal such competing anions as phosphate or silicate [34]. But copper nanoparticles and copper oxide nanoparticles do not use as one-component adsorbent for water treatment due to their irreversible aggregation property and a toxicity of copper compounds.

But these nanoparticles can be used in multicomponent sorption materials to improve arsenic removal properties. For example, rice-husk biochar-stabilized iron and copper oxide nanoparticles has maximum capacity of 20.32 mg As/g, but it is significantly higher than biochar without additives (about 1 mg As/g) [35].

Copper-based nanostructured adsorbents are completely unusable for remediation of arsenic-contaminated soils and sediments due to a toxicity of copper compounds, which can pollute ecosystems in this case.

2.4 Applications and Perspectives of Other Different Nanostructured Adsorbents for Arsenic Compounds' Removal

There are a lot of other adsorbents for arsenic compounds' removal, including different oxides, zeolites, carbon materials, etc., but they are less usable than iron-based.

According to work [21], γ-aluminum oxide nanoparticles are completely ineffective in arsenic removal (about 0.8 mg As(III)/g and 1.0 mg As(V)/g). Magnesium oxide nanoparticles have high arsenate adsorption capacity (98 mg/g) but do not participate in redox reactions, which improve As(III) removal [36].

Nanoscale hierarchically porous zeolitic imidazolate framework-8 produced in situ on ZnO nanoparticles is twice as effective in As(III) removal as the sample without imidazolate [37]. This material has an adsorption capacity of 104.9 mg/g, but is significantly more expensive than iron-based adsorbents and is unsuitable for remediation of arsenic-contaminated soils and sediments due to zinc pollution of ecosystems.

3 Conclusion

Therefore, there are extremely many various adsorbents for arsenic compounds' immobilization and removal, but some of these adsorbents are very expensive (titanium-based), several materials are ineffective (γ-aluminium oxide and non-modified biochars), and some adsorbents are unsuitable for wide environmental application (copper-based and zinc-based).

Iron-based sorption materials are low-cost, high-effective in arsenic compounds' immobilization or removal and environmental friendly. Also, zero-valent iron nanoparticles, magnetite, and multicomponent adsorbents based on them can be easy separated from water due to magnetic properties.

Consequently, iron-based multicomponent adsorbents are interesting for many researchers, who are working to improve arsenic compounds' immobilization and removal.

References

1. X. Wan, M. Lei, T. Chen, Review on remediation technologies for arsenic-contaminated soil. Front. Environ. Sci. Eng. **14**(2), 1–14 (2020)
2. E. Shaji, M. Santosh, K. Sarath et al., Arsenic contamination of groundwater: a global synopsis with focus on the Indian Peninsula. Geosci. Front. **12**(3), 101079 (2021)
3. M. Litynska, T. Dontsova, O. Yanushevska et al., Development of iron-containing sorption materials for water treatment from arsenic compounds. East.-Eur. J. Enterp. Technol. **10**(110), 35–42 (2021)
4. S. Koley, Future perspectives and mitigation strategies towards groundwater arsenic contamination in West Bengal, India. Environ. Qual. Manage. **4**(31), 75–97 (2021)
5. D. Moulick, S. Samanta, S. Sarkar et al., Arsenic contamination, impact and mitigation strategies in rice agro-environment: an inclusive insight. Sci. Total Environ. **800**, 149477 (2021)
6. G. Genchi, G. Lauria, A. Catalano et al., Arsenic: a review on a great health issue worldwide. Appl. Sci. **12**(12), 6184 (2022)
7. V.S.T. Ciminelli, D.C. Antônio, C.L. Caldeira et al., Low arsenic bioaccessibility by fixation in nanostructured iron (Hydr)oxides: quantitative identification of As-bearing phases. J. Hazard. Mater. **353**, 261–270 (2018)
8. A. Abejón, A. Garea, A. Irabien, Arsenic removal from drinking water by reverse osmosis: minimization of costs and energy consumption. Sep. Purif. Technol. **144**, 46–53 (2015)
9. M. Litynska, N. Tolstopalova, I. Astrelin et al., Influence of foreign ions on the adsorption of arsenate on iron(III) oxides and hydroxides. Voprosy Khimii i Khimicheskoi Tekhnologii **3**, 22–29 (2019)
10. E.A. Hull, M. Barajas, K.A. Burkart et al., Human health risk from consumption of aquatic species in arsenic-contaminated shallow urban lakes. Sci. Total Environ. **770**, 145318 (2021)
11. Y. Zhang, B. Xu, Z. Guo et al., Human health risk assessment of groundwater arsenic contamination in Jinghui irrigation district, China. J. Environ. Manage. **237**, 163–169 (2019)
12. J. Fan, X. Chen, Z. Xu et al., One-pot synthesis of nZVI-embedded biochar for remediation of two mining arsenic-contaminated soils: arsenic immobilization associated with iron transformation. J. Hazard. Mater. **398**, 122901 (2020)
13. J. Nikić, A. Tubić, M. Watson et al., Arsenic removal from water by green synthesized magnetic nanoparticles. Water **11**(12), 2520 (2019)
14. I. Bonadies, (2019) Nanoscale materials in water purification, in *Nanoscale Materials in Water Purification,* pp. 231–246
15. R. Soni, A.K. Pal, P. Tripathi et al., An overview of nanoscale materials on the removal of wastewater contaminants. Appl Water Sci **10**(8), 189 (2020)
16. T.A. Dontsova, S.V. Nahirniak, I.M. Astrelin, Metaloxide nanomaterials and nanocomposites of ecological purpose. J. Nanomater. **2019**, 5942194 (2019)
17. T. Pasinszki, M. Krebsz, Synthesis and application of zero-valent iron nanoparticles in water treatment, environmental remediation, catalysis, and their biological effects. Nanomaterials **10**(5), 917 (2020)
18. U.S. Rashid, B. Saini-Eidukat, A.N. Bezbaruah, Modeling arsenic removal by nanoscale zero-valent iron. Environ. Monit. Assess. **192**(2), 110 (2020)
19. M. Litynska, T. Dontsova, Suspension sorbents for removal of arsenic compounds and humates from water. Water Water Purif. Technol. Scien. Tech. News **3**(28), 14–25 (2020)

20. R. Tamayo, R. Espinoza-González, F. Gracia et al., As(III) removal from aqueous solution by calcium titanate nanoparticles prepared by the sol gel method. Nanomaterials **9**(5), 733 (2019)
21. S. Ghosh, R. Prabhakar, S.R. Samadder, Performance of γ-aluminium oxide nanoparticles for arsenic removal from groundwater. Clean Technol. Environ. Policy **21**(1), 121–138 (2018)
22. G. Sappa, M. Barbieri, P. Viotti et al., Assessment of zerovalent iron nanoparticle (nZVI) efficiency for remediation of arsenic-contaminated groundwater: two laboratory experiments. Water **14**(20), 3261 (2022)
23. M.A.V. Ramos, W. Yan, X.Q. Li et al., Simultaneous oxidation and reduction of arsenic by zero-valent iron nanoparticles: understanding the significance of the core−shell structure. J. Phys. Chem. C **113**(33), 14591–14594 (2009)
24. P. Singh, P. Pal, P. Mondal et al., Kinetics and mechanism of arsenic removal using sulfide-modified nanoscale zerovalent iron. Chem. Eng. J. **412**, 128667 (2021)
25. J. Raez, A. Arencibia, Y. Segura et al., Combination of immobilized TiO_2 and zero valent iron for efficient arsenic removal in aqueous solutions. Sep. Purif. Technol. **258**, 118016 (2021)
26. J. Suazo-Hernández, P. Sepúlveda, K. Manquián-Cerda et al., Synthesis and characterization of zeolite-based composites functionalized with nanoscale zero-valent iron for removing arsenic in the presence of selenium from water. J. Hazard. Mater. **373**, 810–819 (2019)
27. M. Ainiwaer, X. Zeng, X. Yin et al., Thermodynamics, kinetics, and mechanisms of the co-removal of arsenate and arsenite by sepiolite-supported nanoscale zero-valent iron in aqueous solution. Int. J. Environ. Res. Public Health **19**(18), 11401 (2022)
28. C. Zhou, C. Han, X. Min, T. Yang, Enhancing arsenic removal from acidic wastewater using zeolite-supported sulfide nanoscale zero-valent iron: the role of sulfur and copper. J. Chem. Technol. Biotechnol. **96**(7), 2042–2052 (2021)
29. L. Xu, K. Yan, Y. Mao et al., Enhancing the dioxygen activation for arsenic removal by Cu_0 nano-shell-decorated nZVI: synergistic effects and mechanisms. Chem. Eng. J. **384**, 123295 (2020)
30. T.K. Das, A.N. Bezbaruah, Comparative study of arsenic removal by iron-based nanomaterials: potential candidates for field applications. Sci. Total Environ. **764**, 142914 (2021)
31. J. López-Luna, L.E. Ramírez-Montes, S. Martinez-Vargas et al., Linear and nonlinear kinetic and isotherm adsorption models for arsenic removal by manganese ferrite nanoparticles. SN Appl. Sci. **1**(8), 950 (2019)
32. S. Ashraf, A. Siddiqa, S. Shahida et al., Titanium-based nanocomposite materials for arsenic removal from water: a review. Heliyon **5**(5), e01577 (2019)
33. M. Deng, X. Wu, A. Zhu et al., Well-dispersed TiO_2 nanoparticles anchored on Fe_3O_4 magnetic nanosheets for efficient arsenic removal. J. Environ. Manage. **237**, 63–74 (2019)
34. K. Reddy, K. McDonald, H. King, A novel arsenic removal process for water using cupric oxide nanoparticles. J. Colloid Interface Sci. **397**, 96–102 (2013)
35. N. Priyadarshni, P. Nath, N. Chanda, Sustainable removal of arsenate, arsenite and bacterial contamination from water using biochar stabilized iron and copper oxide nanoparticles and associated mechanism of the remediation process. J. Water Process Eng. **37**, 101495 (2020)
36. L. Guo, R. Lei, T.C. Zhang et al., Insight into the role and mechanism of polysaccharide in polymorphous magnesium oxide nanoparticle synthesis for arsenate removal. Chemosphere **296**, 133878 (2022)
37. L. Shi, Z. Shu, K. Wang, et al., Nanoporous zeolitic imidazolate framework-8 nanoparticles for arsenic removal. ACS Appl. Nano Mater. (2023)