




# Water Pollutants Removal by Coated Quartz Sand †

Vesna S. Cvetković \* , Nataša M. Petrović  and Jovan N. Jovičević 

Department of Electrochemistry, Institute of Chemistry, Technology and Metallurgy, National Institute, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia; vukicevic@ihtm.bg.ac.rs (N.M.P.); jovicevic@ihtm.bg.ac.rs (J.N.J.)

\* Correspondence: v.cvetkovic@ihtm.bg.ac.rs

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**Abstract:** Presence of major environmental pollutants in water can cause a variety of harmful effects on living organisms in ecosystems. Very often, apart from the ubiquitous arsenic (As), organic compounds, iron, manganese, hydrogen sulfide, ammonia, and similar pollutants may reach dramatically high levels in originally unpolluted waters due to various anthropogenic activities. These elevated levels have major negative effects on the environment and require action. The aim of this research was to propose a new approach to the development and production of cost-effective water pollutant removal media based on natural minerals. The synthesis process is based on chemical and subsequent thermal treatment of quartz sand with a magnesium carbonate water solution. The MgO-coated sand in a 5 min. interaction in column operation with 250 mL of synthetic water with  $200 \mu\text{gL}^{-1}$  of As(V),  $0.51 \text{ mgL}^{-1}$  of Fe(III), and  $1.41 \text{ mgL}^{-1}$  of Mn(II) removed more than 90% of the As(V). The final concentrations of arsenic, iron, and manganese in treated waters were very close to zero after 10 min of contact with active materials. The removal process is based on redox and sorption processes on the surface and inside the pores of the active material.

**Keywords:** arsenic; manganese; iron; removal; MgO-coated quartz sand



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## 1. Introduction

Since water contamination caused by organic and inorganic pollutants has become a serious worldwide environmental issue, in 2015, the United Nations announced a new Agenda with 17 Sustainable Development Goals (SDG). SDG sixth call should ensure clean and accessible water for present and future generations. Arsenic (As), a toxic metalloid whose reservoir pool is in the earth's crust, is one of the contaminants that have originally occurred in low quantities in unpolluted surface water, but may reach dramatically increased levels due to anthropogenic activities [1]. Very often, apart from ubiquitous As, organic compounds, iron, manganese, hydrogen sulfide, ammonia, and similar pollutants may reach much higher concentrations than permissible levels, which causes water quality deterioration. Ravenscroft et al. announced that around 140 million people in 50 countries have already been drinking waters containing arsenic at levels above the World Health Organization provisional guideline value of  $10 \mu\text{g/L}$  [2,3]. Despite the strong global advocacy of prevention and control of high water contaminant exposure, especially exposure to arsenic, this is still a large-scale problem that is recognized as a major public health concern. It is crucial to develop viable and economical technologies for waste water treatments in order to overcome the harmful impact of contaminated waters for human and animal consumption. In the meantime, techniques based on adsorption processes have attracted considerable attention in the attempts to remove pollutants from various aqueous systems [1,4,5]. A number of adsorbents, including activated alumina, coated sand, kaolinite-bentonite ceramics, zerovalent iron, metal oxides, and among them, highly porous  $\text{Mg}(\text{OH})_2/\text{MgO}$ , etc., have been used to remove targeted pollutants [1,4,6–8]. It has

been shown that a well-designed and carefully operated sand filter can be very effective in removing pollutants and especially arsenic from water [7]. In most cases, the efficiency of adsorbent materials in the removal of pollutants from waters relies on the recyclability of materials and reduction of waste volume by using solid adsorbents [1]. In this study, a new approach to the development and production of water pollutant removal media was adopted. As a result, an inexpensive and effective sorbent based on natural minerals, such as quartz sand, has been synthesized for the treatment of contaminated waters. Moreover, the fabricated active material exhibits a high sorption capacity towards, not only arsenic, but also manganese and iron species' removal from treated waters.

## 2. Materials and Methods

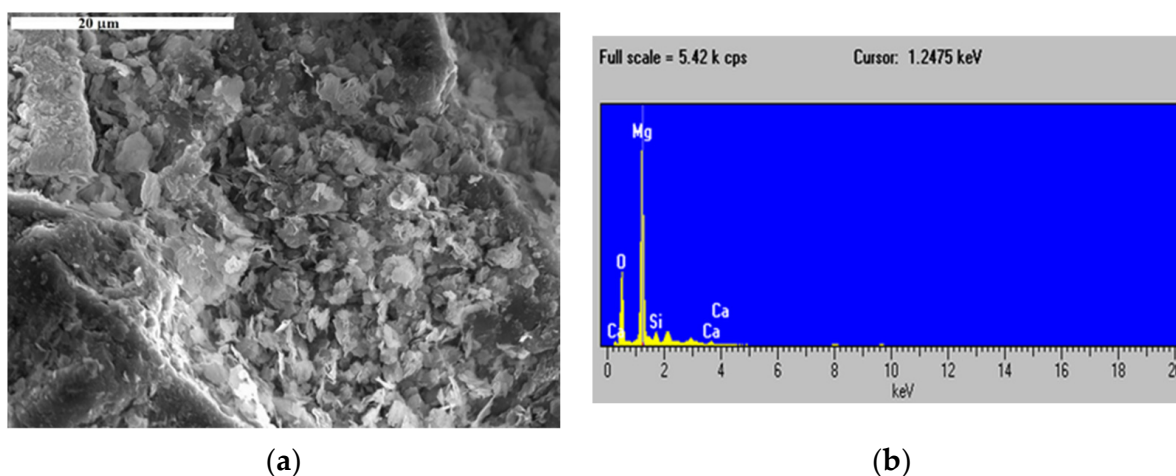
The mineral chosen in this work was a low cost and naturally abundant quartz sand (98.50 wt.% of SiO<sub>2</sub>, grain average size 0.278 mm), with the assumption that there would be no requirement for additional regeneration after polluted water treatment. In order to remove impurities, the quartz sand was washed with deionized water and dried at 105 °C. A freshly prepared concentrated solution of Mg(CO<sub>3</sub>)<sub>4</sub> Mg(OH)<sub>2</sub> × 5H<sub>2</sub>O was then added to the sand in the amount that ensures that Mg in the synthesized material represents the desired mass percentage, for example, 2 wt.% of magnesium. Suspension was then vigorously stirred until it was well homogenized and was dried in an oven at 170 °C for 30 min. After drying, the material was heated at 800 °C for one hour, left to cool down to room temperature, and was powdered in a mortar. In this study, the experiments were performed at room temperature, by bringing into contact 5 g of composite active material with 250 mL of a model water solution. For that purpose, the model water solution was made as follows: appropriate amount of arsenic standard solution (H<sub>3</sub>AsO<sub>4</sub> in HNO<sub>3</sub> 0.5 mol/L 1000 mg/L As Certipur<sup>®</sup>, Sigma Aldrich, St. Louis, MO, USA), MnCl<sub>2</sub> × 4H<sub>2</sub>O, and FeCl<sub>3</sub> × 6H<sub>2</sub>O (Merck, p.a, Darmstadt, Germany) were dissolved in deionized water in the following concentrations: 200 µg As(V) L<sup>-1</sup>, 1.41 mg Mn(II) L<sup>-1</sup>, and 0.51 mg of Fe(III) L<sup>-1</sup>. The model water solution (250 mL) was placed in a glass column and 5 g of composite materials was added. The contact time of the solid and liquid phases were predetermined for each experiment and separation was conducted by filtration. Concentrations of arsenic, manganese, iron, and other pollutant cations were determined by Atomic Absorption Spectrometer (AAS, Varian spectra A-20, Palo Alto, CA, USA). Scanning electron microscopy (SEM-JEOL JSM-5300, Tokyo, Japan), in conjunction with Energy dispersive spectroscopy (EDS) capabilities (LINK QX-2000 Oxford Instruments-XR400, Abingdon, UK), was used to assess the resulting appearance and perform compositional and semi-quantitative chemical analysis of the active material in the composite before and after contact with model water solutions.

## 3. Results and Discussion

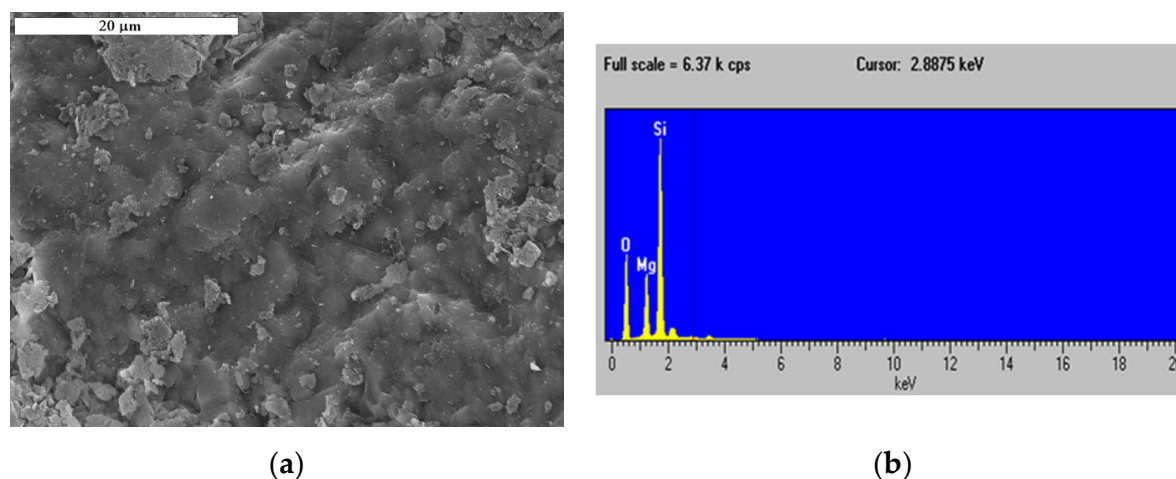
Figure 1 shows the image of the modified quartz sand surface and corresponding EDS analysis. As observed, the quartz sand grains are completely covered with microcrystalline and amorphous stoichiometric and non-stoichiometric oxides with an excess of magnesium in our case. The grains are randomly grouped into more or less separate agglomerates, which are manifested by a highly developed surface area. According to EDS analysis, Figure 1b) apart from magnesium (42.67 at.%) and oxygen (55.96 at.%), a small quantity of Ca (0.21 at.%) and almost no detectible Si were found at the surface of the composite. After contact with the model water solution, the structure and the surface appearance of the MgO-coated quartz sand changed greatly, as shown in Figure 2. It is evident from SEM results Figure 2a) that the unique porous microstructure of the coated quartz sand disappeared, while a more uniform and flatter surface was created. This indicated that, when placed in contact with the model water solution, MgO from the composite dissolved.

This was confirmed by EDS and AAS analyses of the quartz sand and model water solutions, respectively, taken after active contact. EDS analysis of the newly formed surface

revealed the presence of Si in a substantial quantity, 23.41 at.%, suggesting that that amount of active material (mainly MgO) on the surface of the coated sand was reduced.



**Figure 1.** (a) SEM image (magnification 2.500×); (b) EDS analysis of the modified quartz sand before treatment with the model water solution.



**Figure 2.** (a) SEM image (magnification 2.500×); (b) EDS analysis of the modified quartz sand after contact with the model water solution.

Removal of As(V), Fe(III), and Mn(II) by MgO-coated quartz sand as a function of contact time is shown in Table 1. During contact, magnesium oxides from the surface of the active material are dissolved in model water solutions, providing the electrons in the solution that can participate in a number of reduction processes. The electrochemical reduction processes of As(V), Mn(II), and Fe(III)/Fe(II) are driven by the difference in the electrochemical potential of Mg atoms and pollutants whose standard reduction potentials in this solution are more positive than the standard potential of Mg. Such reduced species are most likely adsorbed/deposited on the surface of the composite material. The reduction process takes place until  $\text{Mg}^{2+}$  ions continue to solvate themselves in the model water solution. Most likely, part of  $\text{Mg}^{2+}$  ions react with  $\text{OH}^-$  ions to form  $\text{Mg}(\text{OH})_2$ , resulting in a rapidly increased pH value, immediately above 10 at the beginning of the process, as seen in Table 1. On the other hand, it can be presumed that the total pH value of the model water solution after treatment is a result of the manganese and iron hydroxide being formed, also with hydroxyl ions present.

According to Wu et al., removal of As(V) could be the result of the As(V) reaction with  $\text{Mg}(\text{OH})_2$  and other magnesium arsenate formations [9]. This was also revealed in our

study when the modified quartz sand after treatment with model water solution containing a very high As(V) concentration (200 mg/L As(V)) was subjected to XRD analysis. Apart from Mg(OH)<sub>2</sub> and SiO<sub>2</sub>, the analysis showed the presence of Mg<sub>3</sub>As<sub>2</sub>. It is interesting to note that the As(V) removal efficiency did not decrease with an increase in pH values, as shown in Table 1, which is contrary to the observations made by others [10]. This may be attributed to the precipitation of magnesium, manganese, and even Fe hydroxide on the surface of the solid material, leading to a more effective process [7,11]. In addition, the presence of sludge at the bottom of the column after a prolonged contact time of more than 30 min was observed. Finally, used composite material (coated quartz sand) does not have to be recycled. Instead, it can be used as a component of the materials for road building or similar construction applications, where the adsorbed contaminants can remain captured.

**Table 1.** Change of As(V), Fe(III), and Mn(II) concentration in model water solution after treatment with MgO-coated quartz sand.

Species and Concentration	Model Water Solution	Contact Time (min)					
		5	10	15	20	25	30
Na (mg/L)	0.025	6.02	3.6	5.12	4.58	4.6	4.52
K (mg/L)	<0.02	0.83	0.86	0.75	0.78	0.69	0.71
Ca (mg/L)	<0.062	9.45	10.45	9.3	9.95	9.9	9.85
Fe (mg/L)	0.51	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Mn (mg/L)	1.41	<0.018	<0.018	<0.018	<0.018	<0.018	<0.018
Mg (mg/L)	0.027	9.9	8.1	9.2	8.7	12.75	12.35
As (µg/L)	200	9	7.7	2.6	1.75	1.35	<0.5
pH	4.27	10.49	10.60	10.55	10.59	10.61	10.64

#### 4. Conclusions

Removal of contaminants As(V), Fe(III), and Mn(II) from water by MgO-coated quartz sand was investigated. When placed in contact with model water solutions, MgO from the composite material dissolves, providing electrons for the reduction of present pollutant species. After 5 min of interaction of the MgO-coated quartz sand with 250 mL of model water solution with 200 µg/L of As(V), 0.51 mg/L of Fe(III), and 1.41 mg/L of Mn(II), nearly 95% of the As(V) was removed. Final concentrations of arsenic, iron, and manganese in treated waters after 10 min of contact with active materials were very close to zero. The MgO-coated sand exhibited a strong ability to remove both ionic and colloidal forms of pollutants from treated waters. The removal process is based on redox and sorption processes on the surface and inside the pores of the active composite material.

**Author Contributions:** Conceptualization and methodology, V.S.C.; investigation, V.S.C. and N.M.P.; data curation, V.S.C. and N.M.P.; writing—original draft preparation, V.S.C.; review and editing, V.S.C. and J.N.J.; All authors have read and agreed to the published version of the manuscript.

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