

Zero-Valent Iron Used for Radioactive Waste Water Treatment

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Abstract: The paper presents the researches on the synthesis, characterization and decontamination capacities tests of the nanostructured zero-valent iron, which can be used for the radioactive contaminated water treatment from the uranium ore processing plant. There were synthesized two types of nanostructured iron namely: nanostructured zero-valent iron obtained by the boron hydride reducing method and nanostructured iron laid-down on the solid support - activated carbon Purolite resin type AG 20G and Purolite resin type C 160. The research for testing the decontamination capacity of the synthesized materials, which were added commercial resin Purolite ARSEN-Xnp impregnated with iron nanoparticles, have led to a decontamination capacity varied directly as the amount of nanostructured iron from the reactive material. Distribution coefficient values (for uranium) obtained after experiments are related both to the content of nano-iron material reagent and their adsorption properties. Utilization of these types of materials leads to a process with a decontamination efficiency of over 99.99% according to the environmental quality standards in the field of water policy.

Keywords: nano-particles, water decontamination, zero-valent iron, uranium

1. Introduction

In early 1990 the research about reductive capabilities of metal substances, such as zero-valent iron, were directed towards the depollution of waste water [1-8]. It proved to be particularly suitable for the decontamination of halogenated organic compounds, but subsequent studies have confirmed the possibility of using zero-valent iron for the reduction of nitrate, bromated, chlorate, nitro aromatics compounds, brominated pesticides. Zero-valent iron proved to be effective in removing arsenic, lead, uranium and hexavalent chromium.

Studies have demonstrated that the efficient removal of contaminants depends essentially on the iron particles size because the reactions arise from the iron particle surface [9].

The most reactive iron nanoparticles, are obtained by reduction of borohydride of iron salts in aqueous solution [11] and on solid support, in our case activated carbon Purolite type AG 20G and Purolite type C 160. Presented paper research offers information regarding the synthesis, characterization and testing the decontamination capacity of nanostructured zero-valent iron (in discontinuous regime), which can be used for the radioactive contaminated water treatment from the uranium ore processing plant [12]. The researches were performed for the commercial resin Purolite ARSEN-X^{np} impregnated with iron nanoparticles, too.

2. Experimental

Synthesis of iron nanoparticles by reducing iron sulphate (II) in aqueous medium - the method consists in reducing ions Fe (II) to zero-valent iron using borohydride according to reaction 1:

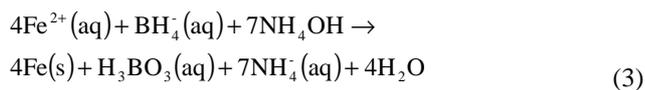


Some of zero-valent iron formed is consumed according to reaction 2:



It is therefore necessary excess of borohydride ion for direct the reactions in a zero-valent iron formation. The yield of precipitation of iron using this method was 74.5%. Iron content determined by volumetric method obtained in dry compound was 52.34%.

Synthesis of iron nanoparticles by reducing iron (II) sulphate in aqueous medium with hydroxide addition - since the yield obtained by the method above, was quite low it is tried to neutralize the hydrogen ions responsible for zero-valent iron resolubilization. The method consists in the reduction of iron (II) ions with borohydride in the presence of ammonium hydroxide according to reaction 3:



The precipitation yield of iron using this method was 94.5 %. Iron content determined by volumetric method was 61.45 %. For the characterization of nanoparticles obtained in both situations, was used Zetasizer Nano-ZS ZEN 3600.

Synthesis and characterization of nanostructured iron laid-down on solid support - method used was the reduction of iron (III) ions by sodium borohydride in the presence of sodium hydroxide, in contact with the solid support. As solid supports were chosen activated carbon Purolite type AG 20G and a polymer resin type Purolite C 160. Products characterization was made using electron microprobe analyzer by comparing the initial samples impregnated with iron.

Tests in the discontinuous behaviour - The discontinuous tests were used to determine the distribution coefficient, K_d , for different types of reactive material and to determine the speed of contaminants removal. The distribution coefficient is defined as the ratio between the amount of contaminant adsorbed on the solid and the amount of contaminant left in solution at equilibrium. Distribution coefficient was calculated as follows:

$$K_d = \frac{c_i - c_f}{m} \cdot \frac{V}{c_f} \quad (4)$$

Where: c_i = initial concentration of contaminants in solution; c_f = concentration of contaminants in the final solution; m = mass of solid reagent material; V = solution volume (density of waste water can be considered 1g/cm^3). Contaminants concentration associated with the solid phase is made by the difference between the initial and final concentration. The main advantage of the method is that it allows fast determination of reactive capacity to retain contaminants. The method is used only for selecting the most suitable reactive materials, not for extrapolation of data in continuous behaviour that because through a water column the water speed is different. Therefore K_d values can be much higher in discontinuous behaviour than those obtained in continuous behaviour. Were tested the following reactive materials: synthesized nanostructured iron; nanostructured iron on activated carbon type Purolite AC 20G; nanostructured iron on macroporous resin type Purolite C 160; Purolite resin ARSEN X^{np}. For the experimental tests was used a standard solution with similar concentration as contaminated water. The chemical composition of standard solution is: U: 1.16 mg/L, Mo: 1.61 mg/L, NaCl: 1.52 g/L, Na₂CO₃: 1.48 g/L, NaHCO₃: 2.77 g/L, NO₃⁻: 0.13 g/L, Na₂SO₄: 1.46 g/L.

3. Result and Discussions

For the synthesis of iron nanoparticles by reducing iron (II) sulphate in aqueous medium, particle size distribution depending on the intensity and volume,

indicates that the average of the obtained particle size is 211.5 nm. For the synthesis of iron nanoparticles by reducing iron (II) sulphate in aqueous medium with the addition of hydroxide, particle size distribution as a function of volume and intensity indicates that the average particle size is obtained by the 211.5 nm. The two synthesis methods used, lead to obtain the particles with the same size, but with different precipitation yield. Comparing the image enlarged by 50,000 times of initial activated carbon (untreated with iron) were the incidence of individual particles less than 1 micron is rare, and the iron content is 0.39% (Figure 1), with iron nanoparticles deposited on activated carbon support type Purolite AC20G, enlarged images of 2000, 10,000 and 50,000 times clearly indicate that the deposition of iron particles occurred and the incidence of particles below 1 micron is high. Fe content is 5.99% and confirms the submission of iron particles on the activated carbon (Figure 2).

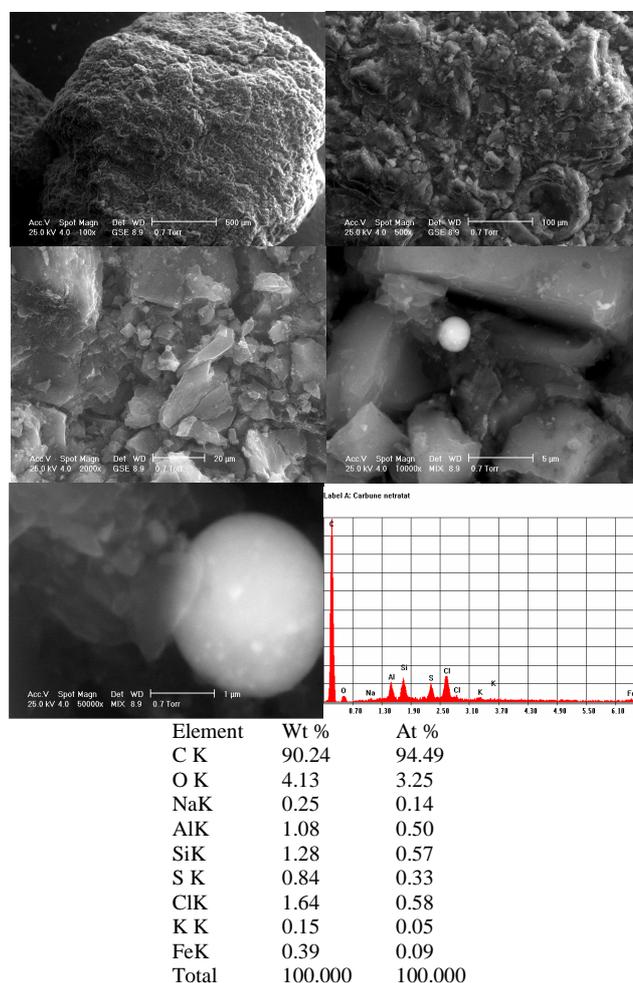
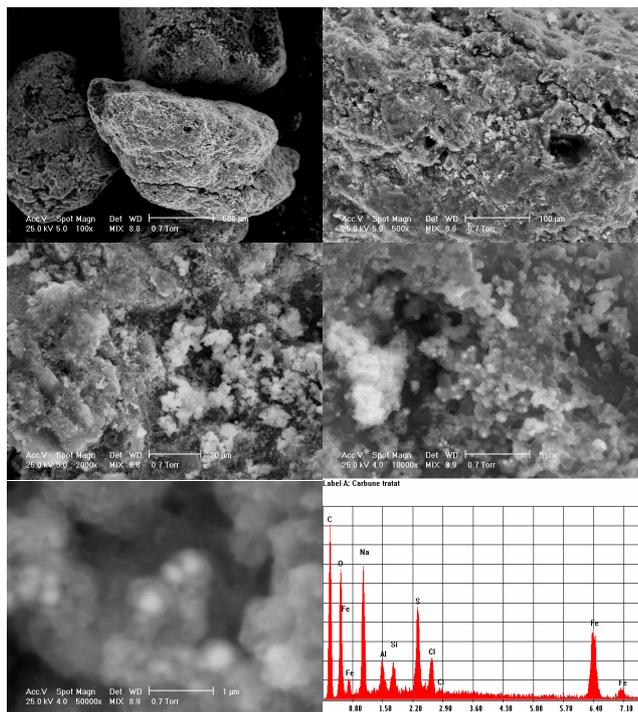


Figure 1. Activated carbon – initial structure

For the iron nanoparticles deposited on support of macroporous polymeric resin, in the image enlarged by 10,000 and 50,000 times is observed that in the Purolite C 160 pores were deposited iron particles with dimensions less than 1 micron. Iron content in treated resin is 21.64%

while untreated resin does not contain iron (Figure 3 and Figure 4).

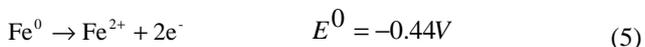


Element	Wt %	At %
C K	56.34	68.49
O K	24.85	22.68
NaK	7.35	4.67
AlK	1.10	0.59
SiK	0.90	0.47
S K	2.38	1.08
ClK	1.10	0.45
FeK	5.99	1.57
Total	100.000	100.000

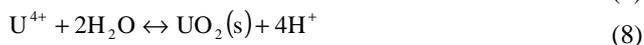
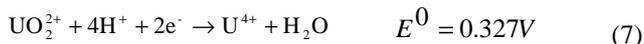
Figure 2. Nano-iron on activated carbon

To compare the iron nanoparticle treated Purolite C 160 resin with the commercial resin Purolite ARSEN X^{np} (with iron nanoparticles) was analyzed using electronic device. Purolite ARSEN X^{np} resin is a macroporus polystyrene resin impregnated with iron nanoparticles having particle size ranging from 0.300-1.200 mm, at pH 4.5 - 8.5. In Figure 5 is observed a similitude to those of impregnated resin Purolite C 160, iron content was approximately of 20.1%.

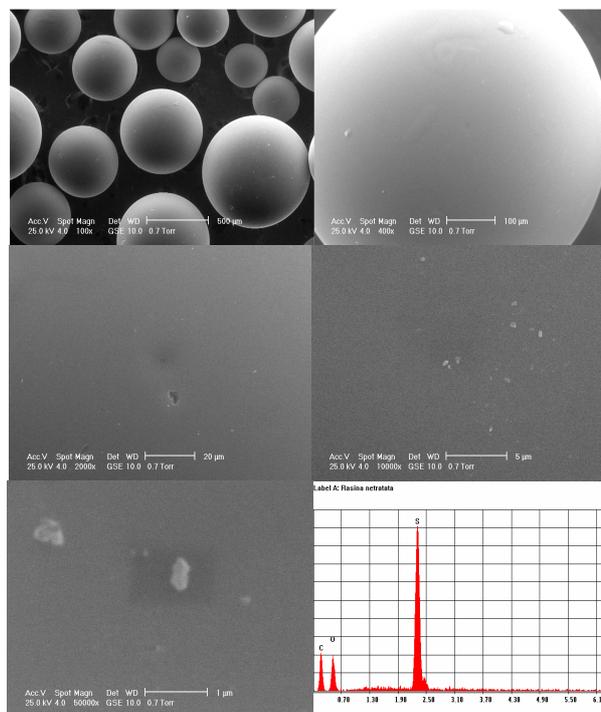
The uranium distribution coefficient depends both to the content of nano-iron reactive material and to the adsorptive properties of the reactive material. There are a lot of studies [6] on the uranium (VI) immobilization on the surface of zero-valent iron. In the first stage Fe⁰ reacted as a reducing agent, facilitating removal of uranium by precipitation under reductive reactions 5 and 6:



Zero-valent iron dissolution forms the necessary electrons for uranium precipitation:



While as zero-valent iron is attacked, the formation of oxidation products of Fe (II) and Fe (III) leading to the formation of adsorption centres. Reducing U (VI) to U (IV) may take place in solution near interface Fe⁰-solution, as soon as electrons are released by corrosion, followed by reduced solid precipitation on iron surface. Alternatively, the adsorption of complexes U (VI) may be followed by their reduction to a mixture solid U (VI) / U (IV) or a solid phase U (IV). Currently is accepted that uranium immobilization by zero-valent iron can take place by tetravalent uranium precipitated reduction and by adsorption of uranium (VI) complexes on the corrosion products of zero-valent iron.



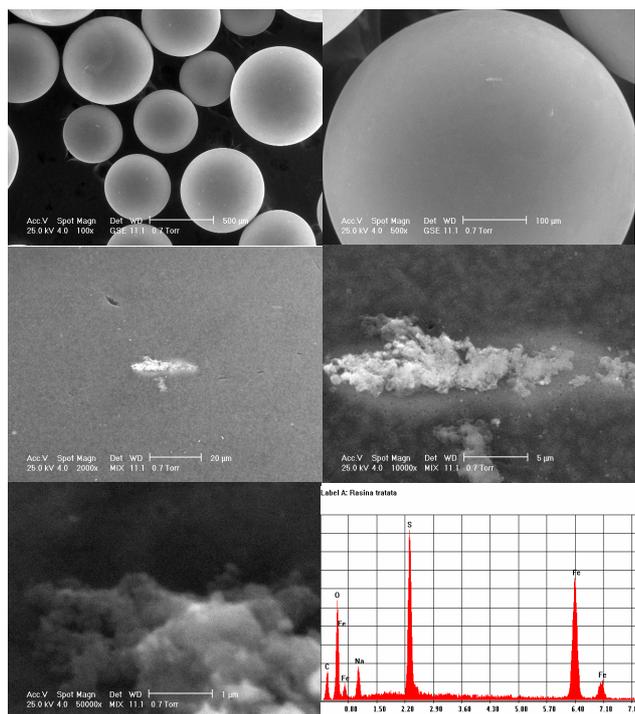
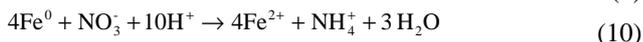
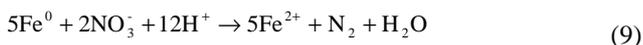
Element	Wt %	At %
C K	59.19	70.20
O K	26.16	23.29
S K	14.65	6.51
Total	100.000	100.000

Figure 3. Untreated resin

For the experiments performed with zero-valent nano-iron and with nano-iron deposited on solid support (activated carbon and cationic resin Purolite C160) distribution coefficient is proportional to the amount of iron. For the resin ARSEN X^{np} the distribution coefficient indicates an accumulation of nano-iron deposited on the

resin with the adsorption properties for uranium of the macroporous resin used.

For molybdenum removal, which is found in solution like sodium molybdate, from the reactive material (containing nano-iron) tested, are appropriate only material based on activated carbon. In fact, molybdate is adsorbed from solution and immobilised by activated carbon. Experiments regarding nitrates ions from contaminated water experiences showed that zero-valent iron can reduce the content of NO₃⁻ ions. The two possible reactions are:

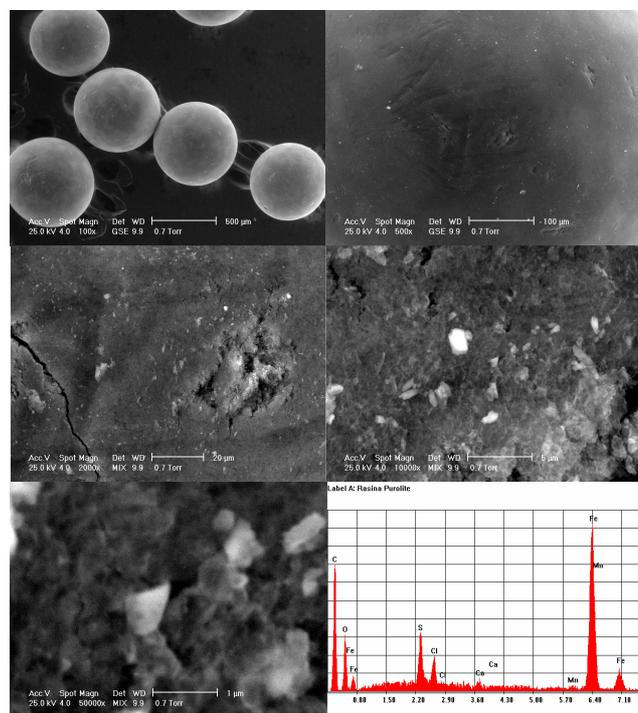


Element	Wt %	At %
C K	30.47	46.19
O K	32.27	36.73
NaK	5.14	4.07
S K	10.48	5.95
FeK	21.64	7.06
Total	100.000	100.000

Figure 4. Resin treated with nano-iron

Most probable reaction is reaction 10 with the formation of ammonium as the final product. Reaction is fast even at a relatively high pH (8-10), while this pH is an inhibitor of different iron oxidation reaction. It is assumed that in alkaline medium, oxo-iron anionic species (Fe(OH)_y^{2-y}, Fe(OH)_x^{3-x}) are dissolved and precipitate containing iron is magnetite (Fe₃O₄). Transformation phase may expose a fresh surface of the zero-valent to nitrate, which leads to a reaction speed relatively stable. The experiments showed that the nitrate ion degradation is in

direct ratio to the amount of nano-iron from reactive material. Experimental data showed that for uranium and nitrate the maximum distribution coefficients are obtained for ARSEN-X^{DP} and for molybdenum activated carbon Purolite AC 20 G



Element	Wt %	At %
C K	59.34	76.48
O K	16.77	16.23
S K	2.18	1.05
ClK	1.19	0.52
CaK	0.30	0.12
MnK	0.11	0.03
FeK	20.10	5.57
Total	100.000	100.000

Figure 5. Purolite resin type ARSEN X^{DP}

4. Conclusions

Soluble uranium, present in waste water for uranium ore processing may be removed by two processes: adsorption on different types of materials and reductive precipitation. Depending on the type of used reactive material the two mechanisms can be individual or combined. For decontamination by reductive precipitation studies have focused on the use of zero-valent iron nano-compounds. Testing depollution capacity on the synthesized materials has led to the following conclusions:

1) depollution capacity of materials based on nanostructured iron is directly proportional to the amount of nanostructured iron from reactive material and to the adsorptive capacity of the support;

2) the uranium distribution coefficient values are related both to the content of nano-iron from reactive material and to the adsorption properties of the reactive material. The most effective proved to be resin ARSEN X^{np}. Distribution coefficient indicates an accumulation of nano-iron amount deposited on the used resin with uranium adsorption properties;

3) in case of molybdenum, which is found in solution in the form of sodium molybdate, only material containing reactive nano-iron from those tested, which can remove molybdenum is the compound containing activated carbon; this compound adsorb molybdate from solution by immobilising;

4) nitrate ion degradation is directly proportional to the amount of nano-iron from reactive material;

5) tests concerning the speed of uranium removal using nano-iron from waste water indicate that the best kinetics is obtained for ARSEN X^{np} and after only 24 hours the uranium content decreases to 0.096 mgU/L (Figure 6).

Using this type of microporous materials, the efficiency of depollution process is 99.99%, which remove the risks of radioactive cations remains in waters.

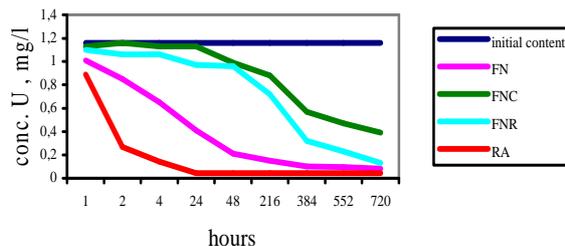


Figure 6. Uranium residual content against contact time

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