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SYNTHESIS AND CHARACTERIZATION OF ZEROVALENT IRON INTENDED TO BE USED FOR DECONTAMINATION OF RADIOACTIVE WATER

Răzvan-Ioan PANȚURU[1], Gheorghița JINESCU[2], Eugenia PANȚURU[3], Antoaneta Filcenco-Olteanu[4], Rozalia RĂDULESCU[5]

În lucrarea de față sunt prezentate cercetările întreprinse privitor la sinteza şi caracterizarea fierului zerovalent nanostructurat, care poate fi utilizat în tratarea apelor contaminate radioactiv provenite de la uzina de prelucrare alcalină a minereurilor uranifere. Au fost sintetizate două tipuri de fier nanostructurat şi anume fierul zerovalent nanostructurat prin metoda reducerii cu borohidrură şi fier nanostructurat depus pe suport solid - cărbune activ Purolite tip AG 20 G şi răşina Purolite C 160. Cercetările întreprinse pentru testarea capacității de depoluare a materialelor sintetizate, la care s-a adăugat şi răşina comercială Purolite ARSEN-X np, impregnată cu nanoparticule de fier, au condus la o capacitate de depoluare, direct proportională cu cantitatea de fier nanostructurat prezent în materialul reactiv.

The paper presents the researches on the synthesis and characterization of the nanostructured zero-valent iron, which can be used for the radioactive contaminated water treatment from the uranium ore processing plant. synthesize Two types of nanostructured iron hase been synthetized 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 increasing directly to the amount of nanostructured iron from the reactive material.

Keywords: uranium, environmental impact, zero-valent iron, decontamination

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-

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[1] Phd student, Chemical Engineering Dept., University POLITEHNICA of Bucharest, Romania, e-mail: ioanpanturu@yahoo.com

[2] Prof., Chemical Engineering Dept., University POLITEHNICA of Bucharest, Romania

[3] PhD eng., R&D National Institute for Metals and Radioactive Resources-Bucharest, Romania

[4] PhD student, R&D National Institute for Metals and Radioactive Resources-Bucharest, Romania

[5] Chem., R&D National Institute for Metals and Radioactive Resources-Bucharest, Romania

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, brominates 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].Generally, several methods are used to obtain iron nano-particles, namely [10]: reduction of dissolved iron in solution using a reducer to transform the dissolved metal into the zero-valent iron nano-particles,(the particles are amorphous or polycrystalline or composed of a layer of magnetic core around the Fe^0); grinding of metallic iron particles of micron size to nanometre dimensions;reduction of iron oxides with hydrogen at high temperature;iron pentacarbonyl decomposition ($Fe\ (CO)_5$) in organic solvent or argon;electrodepositing of Fe (II) salts; spraying in vacuum.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. The researches in this paper offers information regarding the synthesis and characterization of nanostructured zero-valent , 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

2.1. 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:

$$4Fe^{2+}(aq) + BH_4^-(aq) + 3H_2O \rightarrow 4Fe(s) + H_3BO_3(aq) + 7H^+(aq) \qquad (1)$$

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

$$Fe(s) + 2H^+ \rightarrow Fe^{2+} + H_2 \uparrow \qquad (2)$$

It is therefore necessary an excess of borohydride ion for directing the reactions towards the zero-valent iron formation.The method consists in solubilization of 15g $FeSO_4 \cdot 7\ H_2O$ in 200 ml water cooled at 2-3^0C for 30 min. in a Erlenmeyer glass (750 ml). In another glass was prepared the reducing solution consisting of 4 g $NaBH_4$ dissolved in 200 ml cooled water. Reducing solution was added slowly under stirring to the solution containing iron (II) ions. The black precipitate is obtained which quickly settles down. The precipitate is immediately filtered through a Gooch crucible no. 5, washed with water and then with ethanol. The sample is preserved in 10^{-4} M HCl solution to avoid oxidation. To obtain the powder of iron nanoparticles, the precipitate washed with alcohol was dried in a dessicator connected to vacuum, for 24 hours. 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%.

2.2. Synthesis of iron nanoparticles by reducing iron (II) sulphate in aqueous medium with hydroxide addition

Since the yield obtained by the method above mentioned, was quite low it was 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:

$$4Fe^{2+}(aq) + BH_4^-(aq) + 7NH_4OH \rightarrow 4Fe(s) + H_3BO_3(aq) + 7NH_4^-(aq) + 4H_2O \quad (3)$$

The method consists in solubilization of 15g $FeSO_4 \cdot 7\,H_2O$ in 200 ml cooled water to 2-3^{O}C for 30 min. (for decreasing the content of dissolved O_2, which is consuming the reducing agent) in an Erlenmeyer glass (750 ml). Into another glass was prepared the reducing solution consisting of 4 g $NaBH_4$ dissolved in 200 ml water 10 ml and cooled NH_4OH (25%). Reducing solution was added slowly under stirring to the solution containing iron (II) ions, and then it was shaken for further 20 min. A black precipitate it was obtained which quickly settles down. The precipitate is immediately filtered through a Gooch crucible no.5 (1-2 micron pore size), washed with water and then with alcohol. The sample is preserved in 10^{-4} M HCl solution to avoid oxidation. To obtain the powder of iron nanoparticles, the precipitate washed with alcohol was dried in a dessicator connected to vacuum, for 24 hours. 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, a Zetasizer Nano-ZS ZEN 3600 was used.

2.3. Synthesis and characterization of nanostructured iron laid-down on solid support

The method used for synthesis 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 carried out using electron microprobe analizer by comparing the initial samples impregnated with iron. To achieve deposition of iron nanoparticles on the activated carbon supportet is necessary first to prepare the support. Activated carbon type Purolite AC20G is washed with 4M HCl for 30 min., then washed with water to remove acid in excess and dried at 80^0C for 4 hours. 11 g FeCl3 x 6H2O are dissolved in 140 ml distilled water and cooled to 2-3^oC, then is added 60 ml ethyl alcohol. Activated carbon is added (4 g), pH is adjusted to 7 (with NaOH 3N). Gradually is added 2 g sodium borohydride powder and agitation continued for 20 min. Activated carbon is separated by decantation and finally washed with alcohol. To prevent iron oxidation the support is stored in tightly closed containers.For iron nanoparticles laid-down on the macroporous resin (type Purolite C 160) the following method was used: 11 g $FeCl_3$ x $6H_2O$ are dissolved in 200 ml distilled water and cooled to 2-3^oC. The pH is adjusted to 2 with NaOH 3N. It is added 4 g of resin Purolite 160 by agitation for 20 min., the pH is adjusted to 6.8 and gradually added 2 g sodium borohidrura powder. The agitation continues for 20 min. The resin is separated by decantation and then it washed with water and finally filtered through a sieve with appropriate mesh size. To prevent iron oxidation the support is stored in tightly closed containers. Agitation was carried out in all cases using a magnetic stirrer.

3. Results and Discussion

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 (Fig. 1 and Fig. 2).

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 was 211.5 nm(Fig. 3 and Fig. 4).

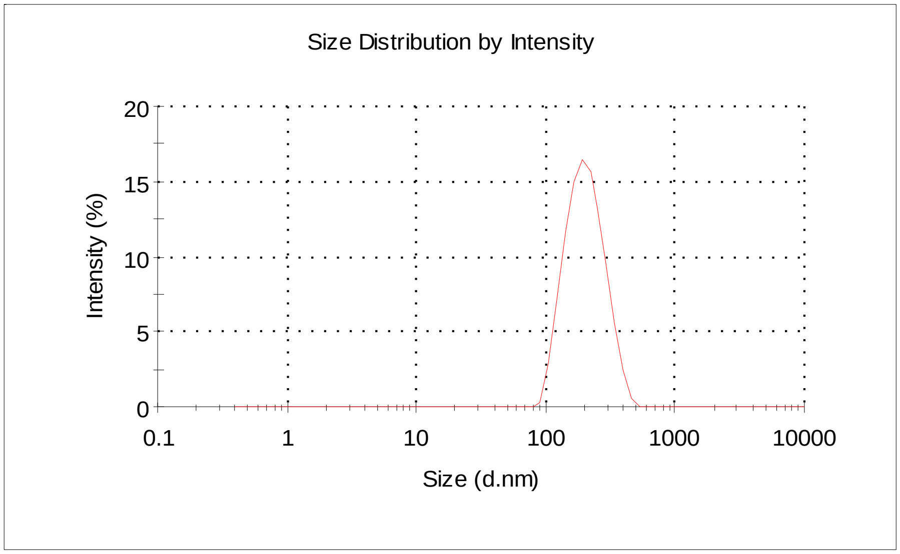


Fig. 1 - Particle size distribution depending on intensity in aqueous medium

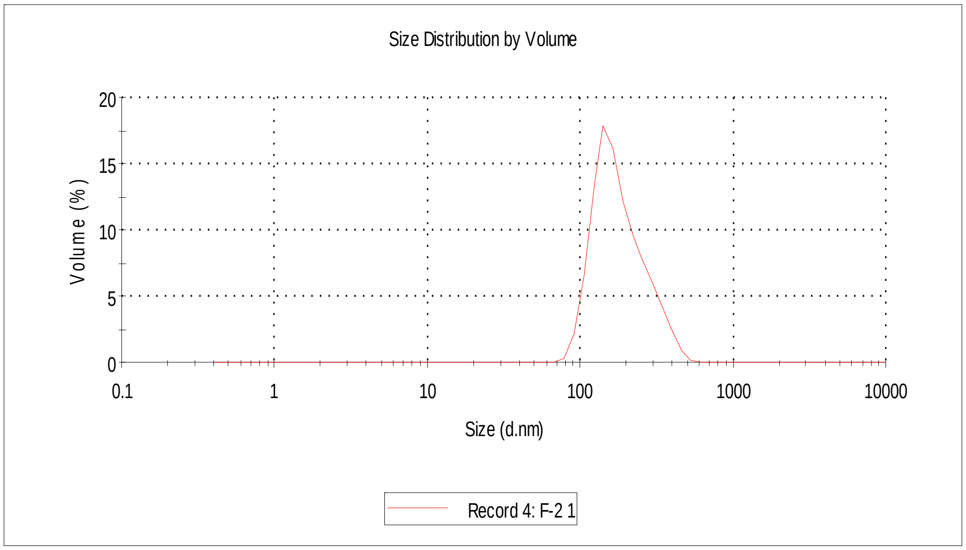


Fig. 2 - Particle size distribution depending on volume in aqueous medium

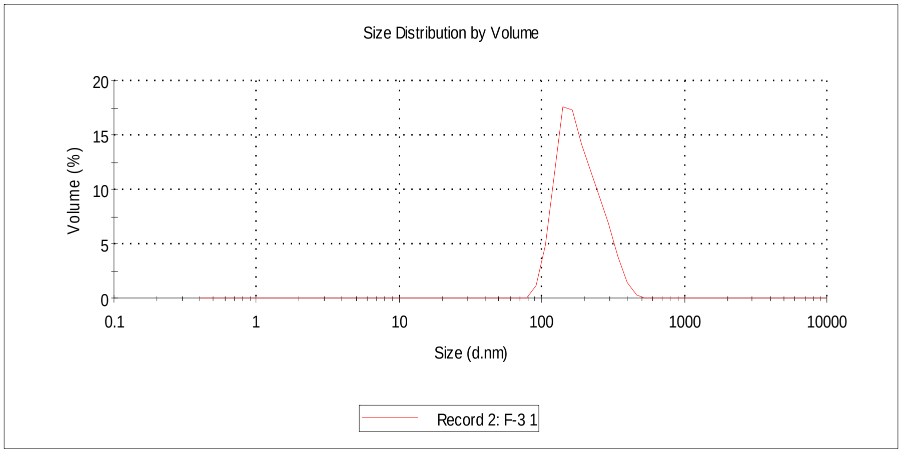


Fig. 3 - Particle size distribution depending on intensity in aqueous medium with hydroxide addition

The two synthesis methods used, lead to obtain the particles with the same size, but with different precipitation yield. Comparing the S.E.M (Scanning Electron Microscopy) image enlarged by 50,000 times of initial activated carbon (untreated with iron, were the incidence of individual particles is less than 1 micron is rare, and the iron content is 0.39%, Fig. 5) with iron nanoparticles deposited on activated carbon support, type Purolite AC 20 G (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.

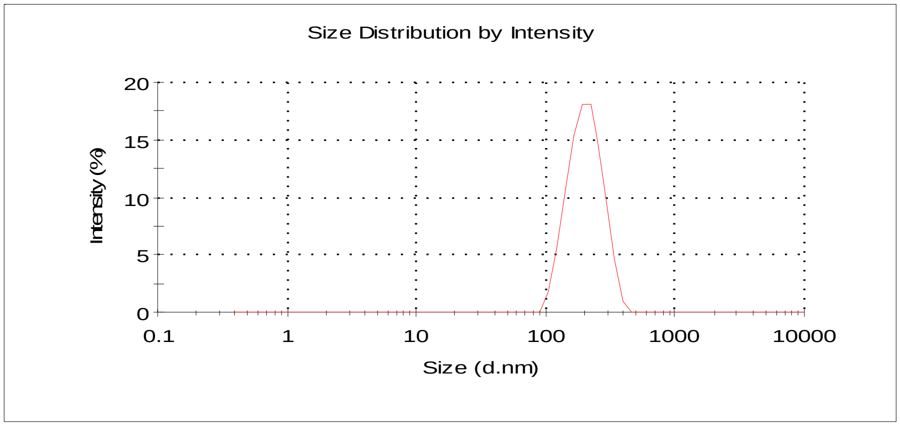
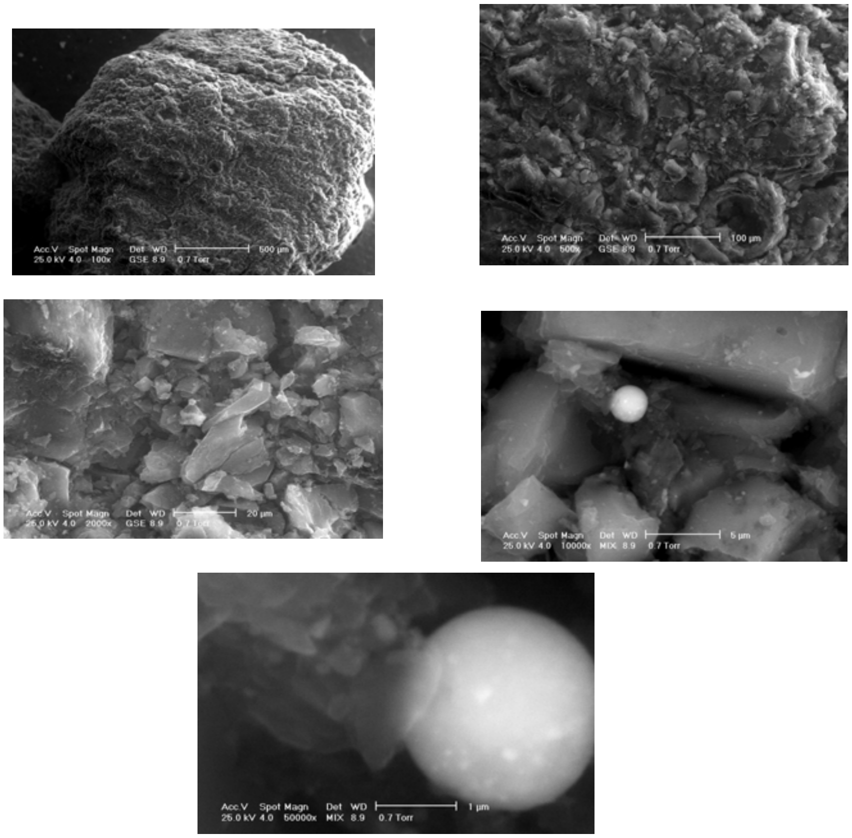
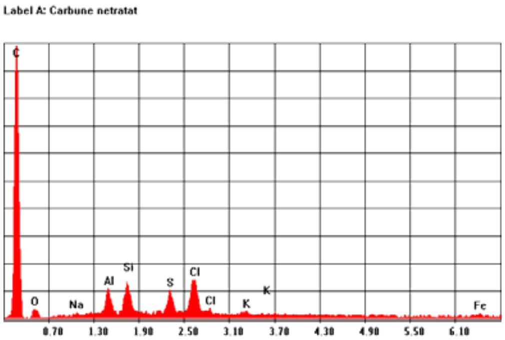


Fig. 4 - Particle size distribution depending on volume in aqueous medium with hydroxide addition

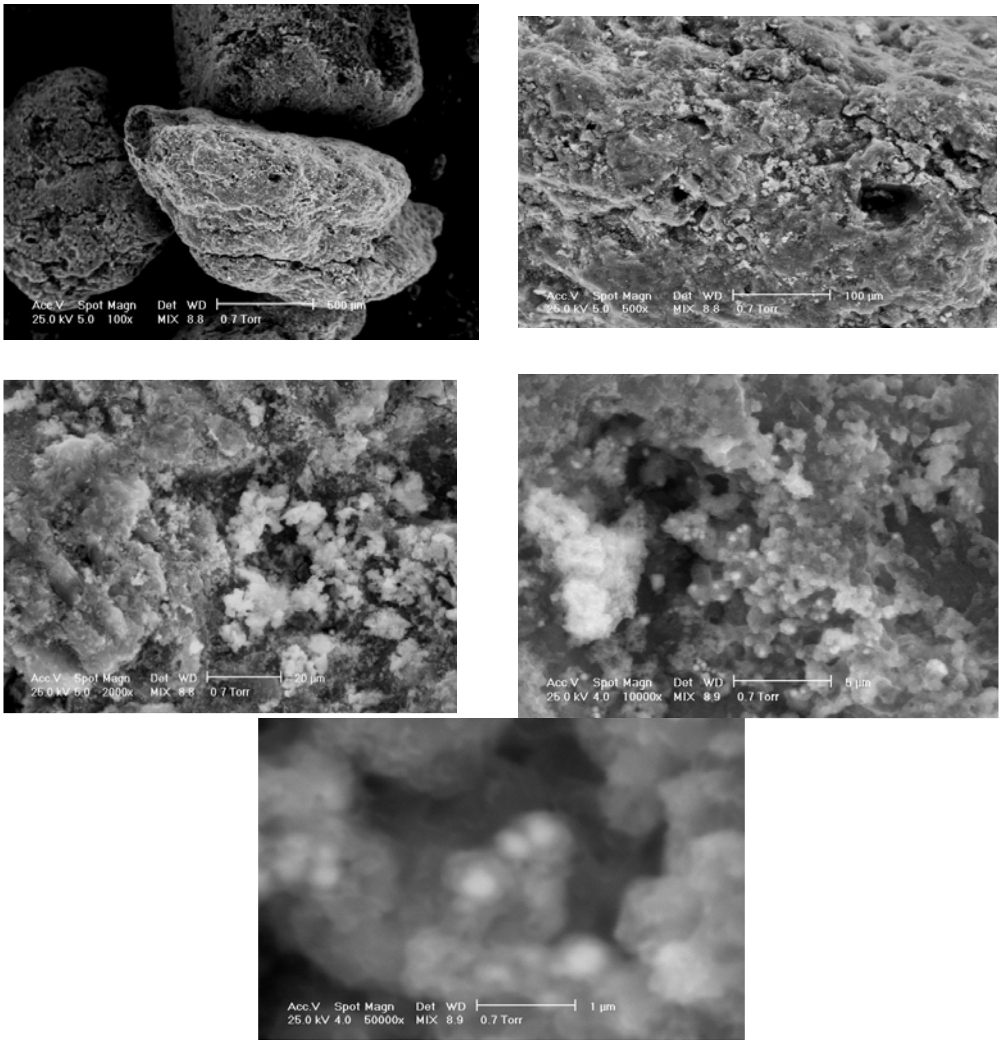
Fe content is 5.99% and confirms the submission of iron particles on the activated carbon (Fig. 6).

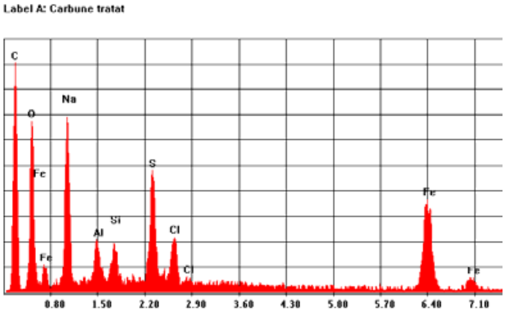




Element	Wt %	At %
C K	90.24	94.49
O K	4.13	3.25
NaK	0.25	0.14
AlK	1.08	0.50
SiK	1.28	0.57
S K	0.84	0.33
ClK	1.64	0.58
K K	0.15	0.05
FeK	0.39	0.09
Total	100.000	100.000

Fig. 5 - Activated carbon – initial structure and composition

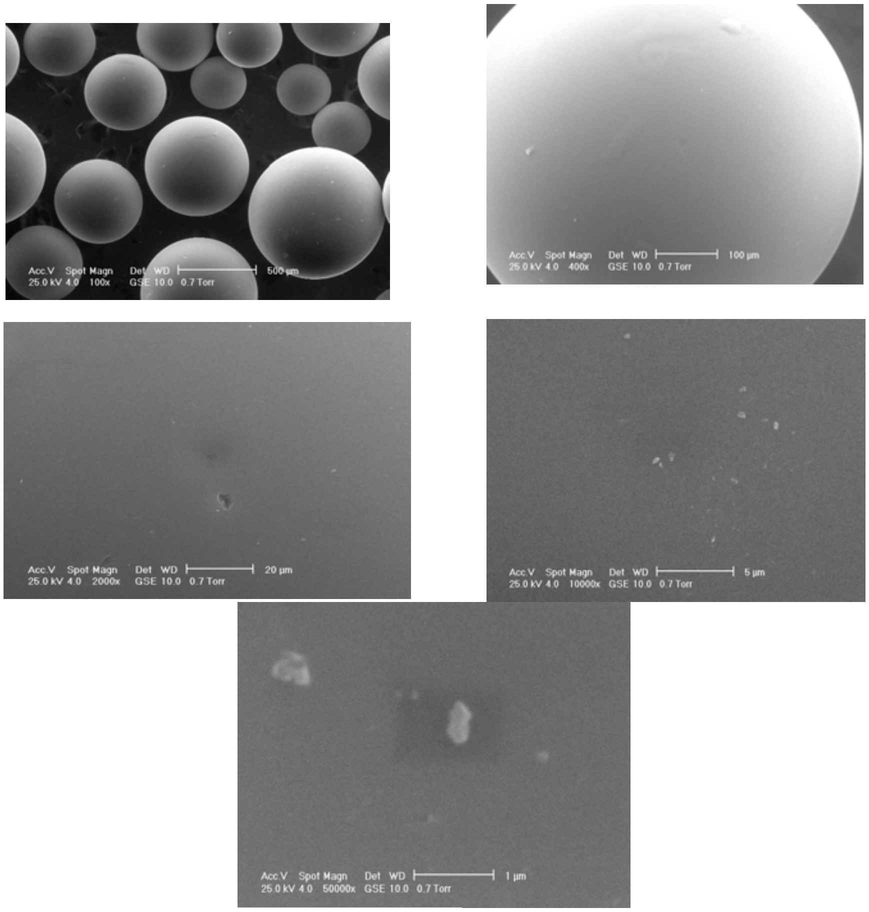


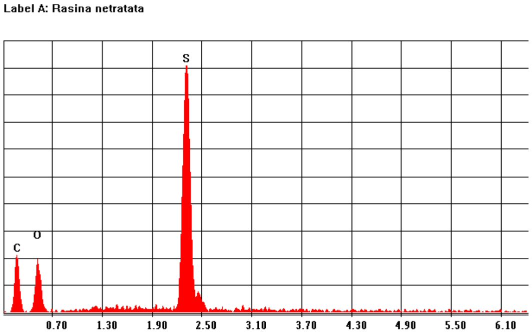


Element	Wt %	At %
C K	56.34	68.49
O K	24.85	22.68
NaK	7.35	4.67
AlK	1.10	0.59
SiK	0.90	0.47
S K	2.38	1.08
ClK	1.10	0.45
FeK	5.99	1.57
Total	100.000	100.000

Fig. 6 - Nano-iron on activated carbon , structure and composition

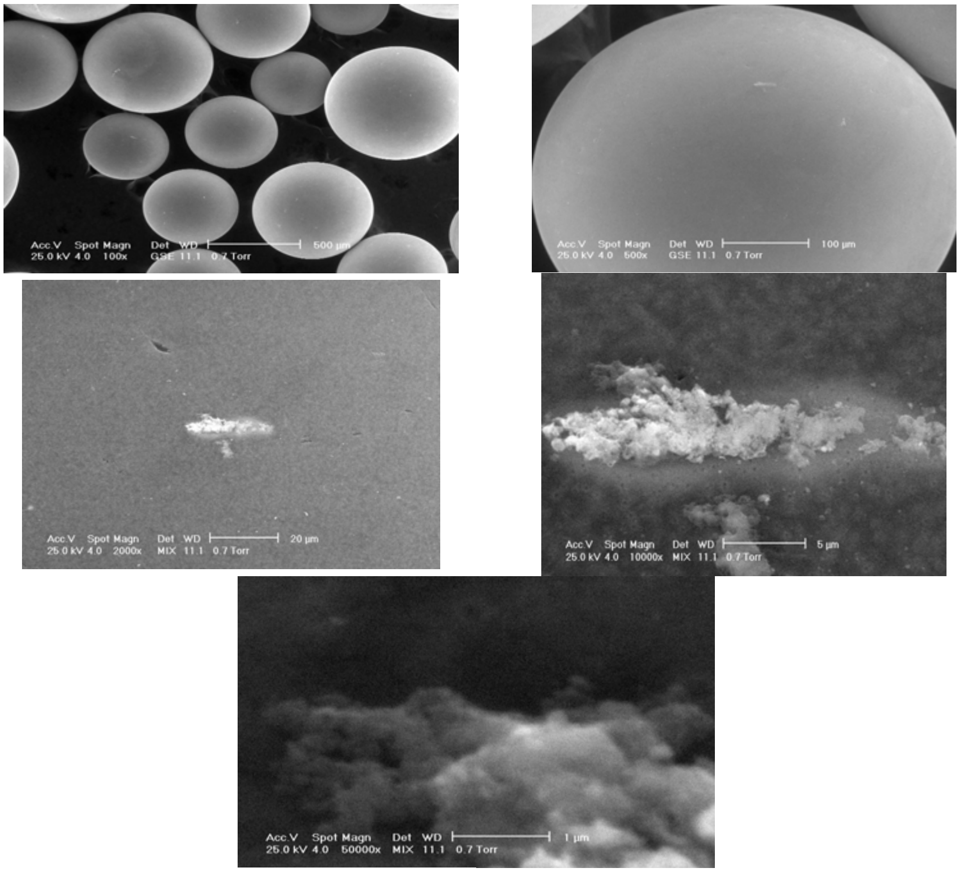
Iron content in treated resin is 21.64% while untreated resin does not contain iron (Fig. 7 and Fig. 8).

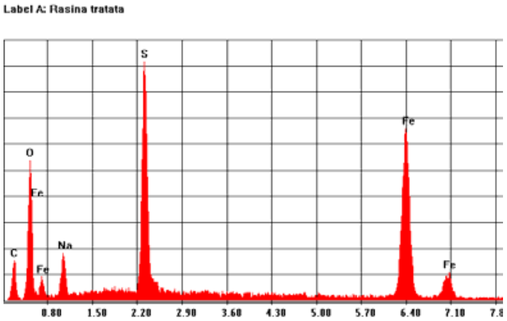




Element	Wt %	At %
C K	59.19	70.20
O K	26.16	23.29
S K	14.65	6.51
Total	100.000	100.000

Fig. 7- Untreated resin, structure and composition



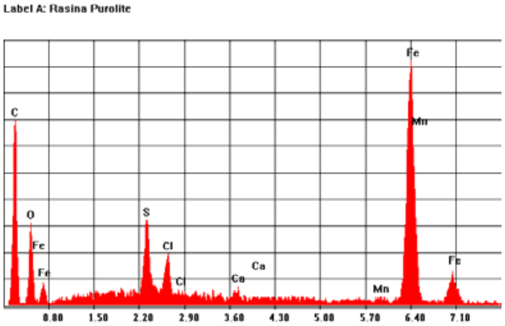


Element	Wt %	At %
C K	30.47	46.19
O K	32.27	36.73
NaK	5.14	4.07
S K	10.48	5.95
FeK	21.64	7.06
Total	100.000	100.000

Fig. 8 - Resin treated with nano-iron

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 then 1 micron.(Fig. 7, Fig. 8)

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 Fig. 9 is observed a similitude to those of impregnated resin Purolite C 160, iron content was approximately of 20.1%.



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

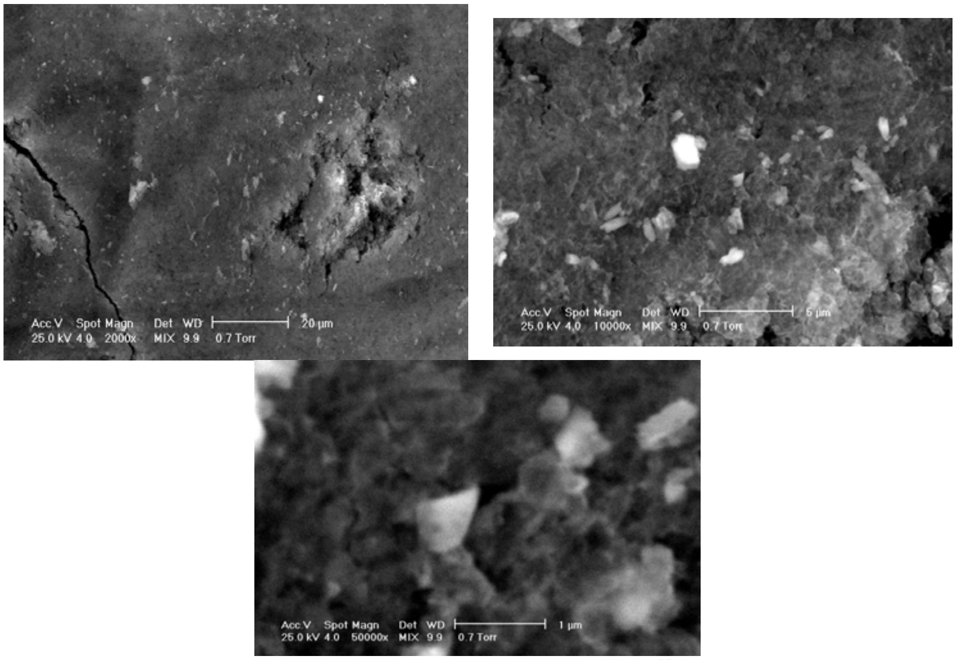


Fig. 9 - Purolite resin type ARSEN X^{np}

4. Conclusions

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. Soluble uranium, present in waste water resulting from 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. From materials group based on nanostructured iron were synthesized:

- zerovalent iron nanostructured by reducing borohydride method of iron soluble salts using two synthesis methods, which both lead to particle size of 211 nm according characterization performed with Zetasizer Nano-ZS ZEN 3600;
- nanostructured iron deposited on solid support, namely: activated carbon Purolite AG 20G type, Purolite C 160 resin against commercial Purolite ARSEN X^{np}; the characterization by scanning electron microscopy method, indicate the deposition of nanostructured iron on the two types of solid support.

In an article future will be presented results of tests on the ability of depollution capacity of the materials synthesised.

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