

# Ultrasound-assisted synthesis of nanosized zero-valent iron for metal cations extraction and wastewater treatment applications

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**Abstract.** Nanosized zero-valent iron has shown good results in wastewater treatment and activation of physicochemical processes. Its applications in modern industry are complicated by high production costs of nanomaterials produced via existing synthesis routes. Therefore there is a need of cheap and high-productive methods of nanosized zero-valent iron with advanced functional properties. Improvement of oxidative conditions with additions may find its place in extraction of rare-earth metals, where high cost of nanomaterials could be viable. In this paper we studied an effect of ultrasonic irradiation on specific surface area and particle size of nanosized zero-valent iron synthesized by methods of chemical precipitation with high-temperature reduction in hydrogen flow and sodium borohydride reduction. Obtained results showed significant decrease of particle size and differences in particles morphology depending on presence of ultrasonication during synthesis and on chosen method. For ultrasonic-assisted synthesis with 100 % amplitude, particle size calculated from specific surface area was 70 nm for sample synthesized by chemical precipitation with high-temperature reduction and 35 nm for borohydride reduction method compared to 63 nm for reference sample without ultrasonication.

## 1. Introduction

Rare-earth metals have critical role in production of almost all electronic devices, magnets, batteries etc. On the other hand, raw sources of rare-earth metals are geographically dispersed and concentrated irregularly depending on countries. Recycling of waste electrical and electronic equipment (WEEE), fluorescent lamp waste, industrial wastes, municipal solid waste (MSW) and other rare-earth containing wastes became one of the most important issues in modern industry [1-4]. According various researchers, recovery of rare-earth methods is often performed by acid leaching and takes a few hours. Thus there is a need for activation of leaching kinetics and thereof improvement in performance and yield capacity of existing methods.

On the other hand Fenton-like processes and nanosized zero-valent iron (nZVI) as Fenton-like catalyst have presented promising potential for applications requiring strong oxidative conditions. Formation of extremely reactive hydroxyl radical ( $\text{OH}^*$ ) and high reactivity of nZVI during Fenton-like reactions established nZVI applications as rapidly growing [5-10].

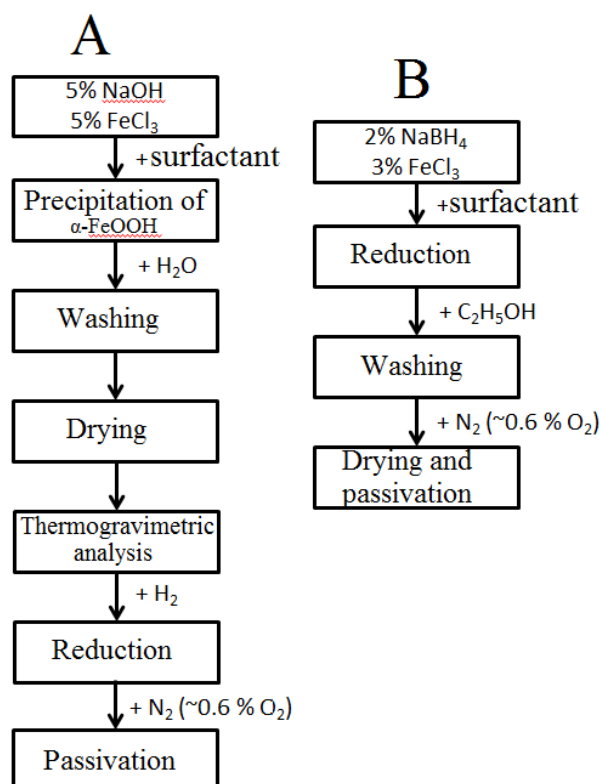


For wastewater treatment, at the moment there is a common route of treatment consisting of four main steps: pretreatment, primary treatment, secondary treatment and fining. Most of existing technologies require construction of wastewater treatment purification plants as well as Great scientific interest for research in this area is represented by recovery agents and Fenton catalysts, such as nanoparticles based on iron, which has high values of reactive surface area. First of all, formation of hydroxyl radicals allows oxidizing of organic pollutants. On the other hand, strong sorption and reducing properties allows sequestration of cations from the solution. Unlike conventional methods, nZVI treatment allows to treat water and soil in situ via direct injection into the hot spots of the pollution [6]. At the same time, rapidly developing technologies based on nZVI usually associated with the expansion of persistent organic pollutants (POPs) in the presence of iron cations (Fenton-like processes) [11]. However, possible applications of nZVI are not limited to wastewater treatment. There could also be included: ultrasonic disinfection of groundwater («sono-Fenton process»), treatment of leachates from municipal landfills, pharmaceutical wastewater treatment and others. Therefore, recent advances and trends in the development of water treatment technologies allow us to conclude that nZVI has undoubted relevance in today's industry.

In this study we investigated the effect of ultrasonic cavitation during synthesis via chemical precipitation with high-temperature reduction and sodium borohydride reduction methods on specific surface area, particle size and morphology of formed nZVI.

## 2. Materials and methods

In present research we focused on synthesis of nZVI by two different methods: chemical precipitation with high-temperature reduction in continuous hydrogen flow and subsequent passivation in technical grade nitrogen and sodium borohydride reduction. Comparison of experimental procedures for each of investigated methods is presented in figure 1.



**Figure 1.** Experimental procedures:  
A: Chemical precipitation with high-temperature reduction; B: sodium borohydride reduction

As it could be seen from experimental procedures (figure 1), method of chemical precipitation with high-temperature reduction (figure 1A) includes 7 main steps. The first one is chemical precipitation ( $\alpha$ -FeOOH is preferable due to higher values of dispersity compared to other iron hydroxide phases). Next step is washing with bi-distilled water from ions of  $\text{Na}^+$  and  $\text{Cl}^-$  (from 5 to 10 times, controlled by pH value). After that washed precipitate should be dried at temperature of 60 °C for 10-12 h. In order to determine an optimal reduction temperature, dried powder is analyzed by thermogravimetric analysis (TA Instruments, USA, model SDT Q600, heating rate 10-15°C/min, in  $\text{Ar}+\text{H}_2$  flow). Reduction is made in tube furnace made by Carbolite, UK (model HZS 12/900 with quartz reactor, linear heating and holding at reduction temperature, continuous  $\text{H}_2$  flow with rate approximately 80  $\text{dm}^3/\text{h}$ ) with subsequent passivation in technical grade  $\text{N}_2$  (room temperature, approximately 0.6 % of  $\text{O}_2$ ). Such a long procedure allows us to produce air-stable nZVI with different particle size (from 20 to 100 nm, depending on pH, surfactant additions, reduction temperature) and morphology (i.e., chain or dumbbell shaped structure, depending on reduction temperature) with high reproducibility.

Compared to chemical precipitation with high-temperature reduction, sodium borohydride reduction (figure 1B) is rather unsophisticated. It includes only direct reduction of metallic iron from the solution, washing with 98 % ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ , from 3 to 5 times), drying and passivation in technical grade  $\text{N}_2$  (2-3 h at 40-60 °C and 10-12 h at room temperature, approximately 0.6 % of  $\text{O}_2$ ). Besides of apparatus and procedure simplicity, sodium borohydride reduction allows us to control the particle size (from 3-5 to 100 nm, depending on feed rates, concentrations of reactants and surfactant additions) and morphology (depends on external pressure, feed rates and concentrations of reactants). Main disadvantage of sodium borohydride reduction method is low yield of nZVI production.

All chemicals used in the experiments were purchased from local supplier (Labteh, Moscow, Russia), were analytical grade and used without any purification.

Experimental parameters used during synthesis of nZVI samples are shown in table 1. During synthesis as surfactant 0.1 % additions of sodium dodecylsulfate (SDS) was used.

**Table 1.** Experimental parameters

Parameter	Method	
	Chemical precipitation with high-temperature reduction	Sodium borohydride reduction
$\text{FeCl}_3$ , %	5.0	3.0
$\text{NaOH}$ , %	5.0	-
$\text{NaBH}_4$ , %	-	2.0
SDS, %	0; 0.1	0; 0.1
Precipitation temperature, °C	25	-
Reduction temperature, °C	405	25
Drying temperature, °C	60	60
Passivation temperature, °C	25	25
Amplitude of ultrasonic vibrations, %	0; 50; 100	50; 100

A sample party of nZVI was prepared following the experimental procedures and parameters presented earlier (figure 1 and table 1 respectively). First 3 samples were obtained by chemical precipitation with high-temperature reduction (without surfactant and 50 % amplitude, with 0.1 % of surfactant and 50 % or 100 % amplitude) and other 3 samples were obtained by sodium borohydride reduction with same parameters. Besides that, 1 reference sample of nZVI was synthesized by chemical precipitation with high-temperature reduction with same experimental

parameters (figure 1B, table 1) without ultrasonication (500 RPM, mechanical stirrer made by Heidolph, Germany, model RZR-1).

All synthesis experiments were performed using an ultrasonic unit consisting of ultrasonic generator, piezoceramic transducer and titanium sonotrode (industrial grade ultrasonic device made by Hielscher, Germany, model UIP2000hdV); flow cell with a working volume of 150 ml with a cooling jacket; peristaltic pump (made by Heidolph, Germany, model PD 5201), worm pump, thermostat (made by Lauda, Germany, model RS232 Eco Silver), sliding stand, hoses, fittings and other peripherals. The experimental set-up is shown in figure 2.



**Figure 2.** Ultrasonic unit with Hielscher UIP2000hdV

After synthesis, all nZVI samples were characterized by low-temperature adsorption of nitrogen according to the Brunauer-Emmett-Teller theory of multimolecular adsorption (BET, device made by Quantachrome Instruments, USA, model Nova 1200e), X-ray diffraction analysis (XRD, powder diffraction with Bragg-Brentano geometry, device made by Scientific Instruments, Russia, model Diffrei 401), scanning electron microscopy (SEM, with device made by JEOL, Japan, model JSM-6700F, 15 kV of accelerating voltage) for samples synthesized under ultrasonic irradiation and transmission electron microscopy (TEM) for reference sample (JEOL, Japan, model JEM-2000 EX, 100 kV of accelerating voltage).

Particle size was calculated (assuming that all particles have spherical morphology) as follows:

$$d_{SSA} = \frac{\rho}{6 \cdot S} \quad (1)$$

where  $\rho$  – density, kg/m<sup>3</sup> and  $S$  – specific surface area, m<sup>2</sup>/kg.

SEM and TEM images are presented in figure 1.

Mean crystalline size of nZVI was calculated from XRD data using well-known Scherrer equation as follows:

$$d_{\text{Sher}} = \frac{K_{hkl} \cdot \lambda}{\beta \cdot \cos \theta} \quad (2)$$

where  $d_{\text{Sher}}$  – mean size of the crystalline domains, nm;  $K_{hkl}$  – dimensionless shape factor;  $\lambda$  – X-ray wavelength,  $10^{-10}\text{m}$ ;  $\beta$  – line broadening at half the maximum intensity, radians;  $\theta$  – Bragg's angle.

### 3. Results and discussions

Results for specific surface area measurement of nZVI samples are shown in table 2. XRD patterns for obtained samples are not presented due to irrelevance.

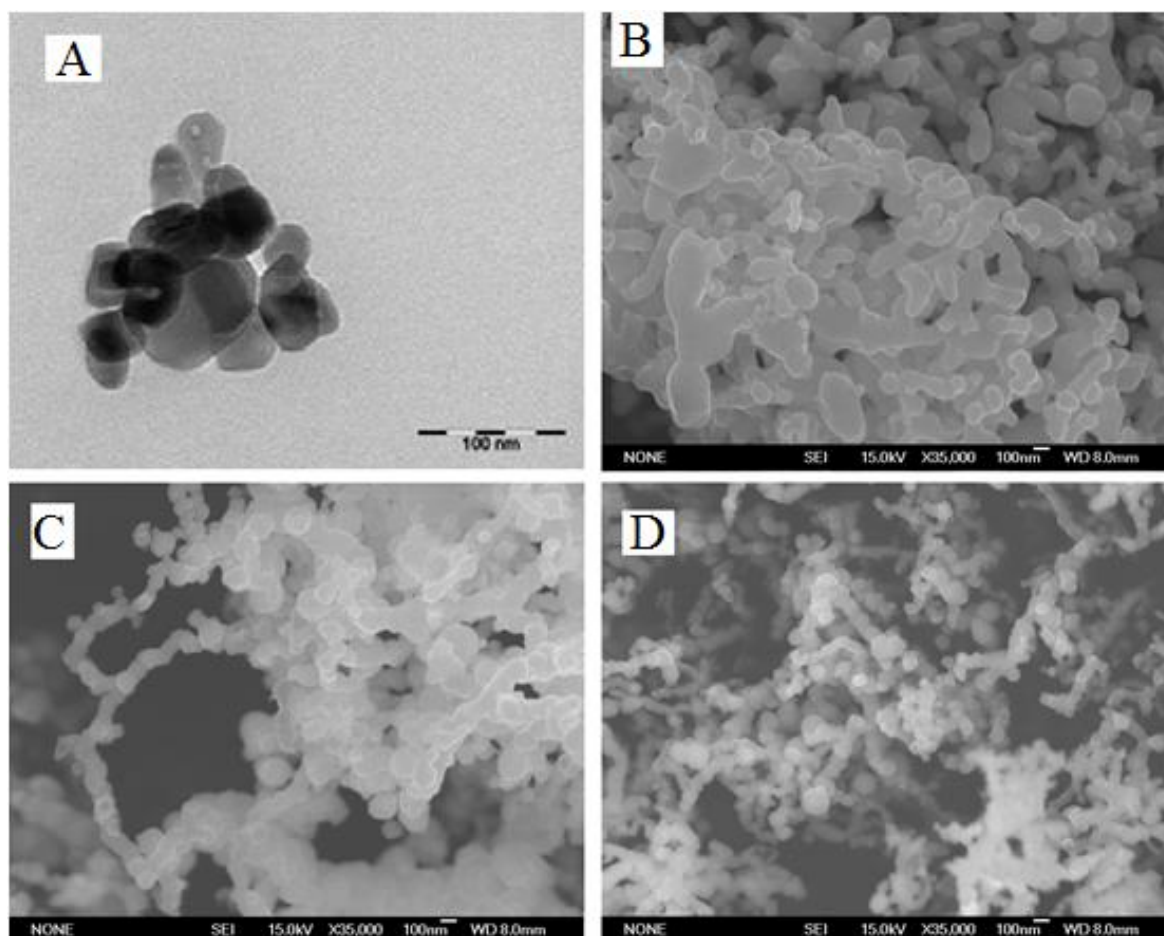
It should be noted that results of calculations from specific surface area and XRD data using (1) and (2) have good correlation for almost all samples, which corresponds that iron nanoparticles have monocrystalline or close to monocrystalline structure. That also means that most of presented agglomerates should be formed from separate nanoparticles.

**Table 2.** Specific surface area, calculated particle and crystalline sizes of synthesized nZVI samples

Method	SDS, %	Amplitude of ultrasonic vibrations, %	$S_p$ , $\text{m}^2/\text{g}$	$d_{\text{SSA}}$ , nm	$d_{\text{sher}}$ , nm
Chemical precipitation with high-temperature reduction (reference)	0.1	0 %	12.0	63	59
	0	50 %	8.6	90	72
Chemical precipitation with high-temperature reduction	0.1	50 %	12.2	75	69
	0.1	100 %	12.9	70	64
Sodium borohydride reduction	0	50 %	11.3	67	59
	0.1	50 %	18.2	42	34
	0.1	100 %	21.6	35	23
	0.1	100 %	21.6	35	23

SEM images of the obtained nZVI samples are shown in figures 3 and 4. As it could be seen, size of iron nanoparticles sufficiently correlates with calculated values from specific surface area measurement and XRD structure analysis.

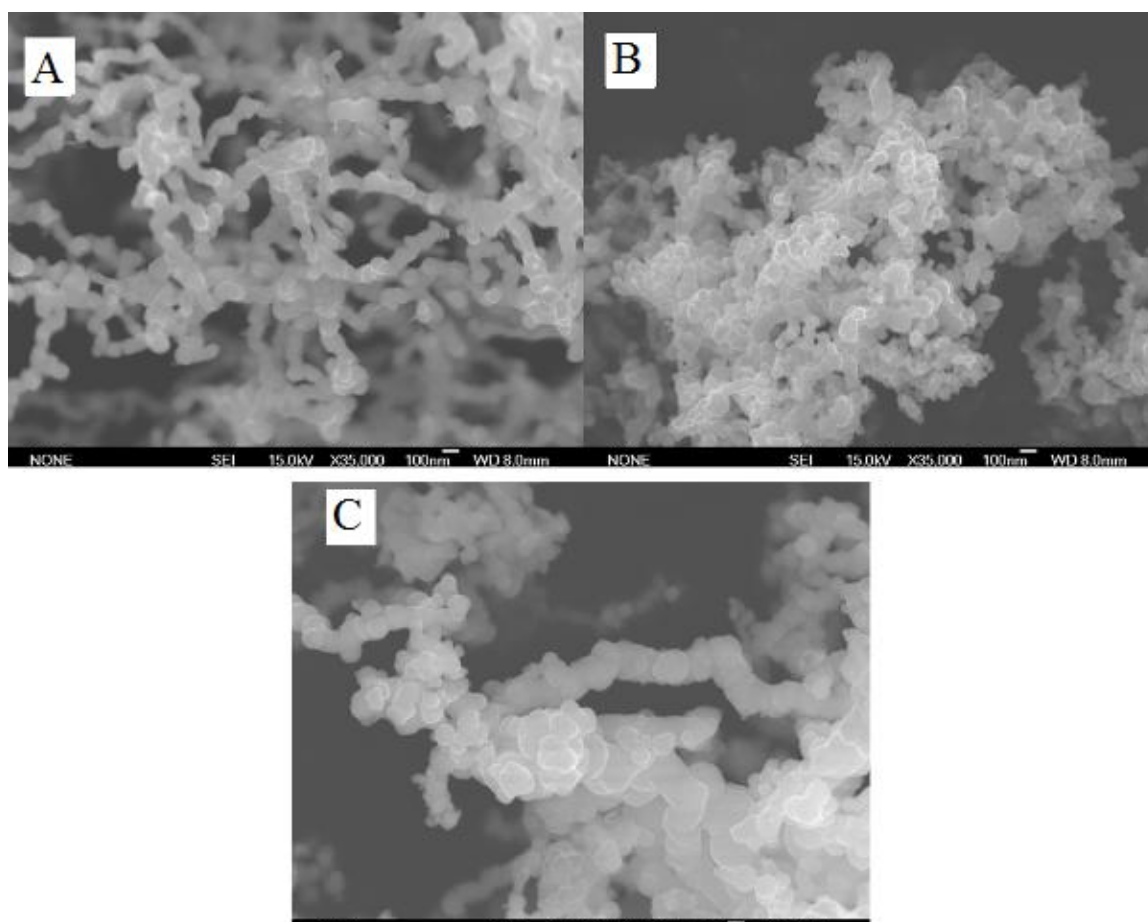
Morphology of nZVI samples, obtained by chemical precipitation with high-temperature reduction, varies from quazi-regular shape for the reference sample (figure 3A) to dumbbell shape for 50 % amplitude without surfactant and finally to chain (figure 3C) and agglomerated (figure 3D). It is clear that presence of ultrasonic irradiation, as well as SDS additions, led to more dispersed structure of nZVI and therefore to higher values of specific surface area and dispersity.



**Figure 3.** Microphotographs of the samples: A: TEM image of nZVI sample (reference, no US), B: SEM image of nZVI (0% SDS, 50 % amplitude), C: SEM image of nZVI (0.1% SDS, 50 % amplitude), D: SEM image of nZVI (0.1% SDS, 100 % amplitude)

Morphology of samples obtained by sodium borohydride reduction is mostly chain-shaped (figures 4A and 4B), but for 100% amplitude of ultrasonic irradiation morphology changes to agglomerated. It is curious, that in spite of quite coarse size of agglomerates (approximately), measures values of specific surface area and crystalline size are best of all experiments. This could be explained by taking into account the assumption, that all of the particles have relatively small size (20-30 nm), but as in order to compensate the excess surface energy they formed an agglomerated structure.





**Figure 4.** A: SEM image of nZVI (0% SDS, 50 % amplitude), B: SEM image of nZVI (0.1% SDS, 50 % amplitude), C: SEM image of nZVI (0.1% SDS, 100 % amplitude)

#### 4. Conclusions

Sample party of nZVI with different particle size and morphology have been prepared under ultrasonic cavitation via chemical precipitation with high-temperature reduction and sodium borohydride reduction methods.

During the study an impact of ultrasonic irradiation on specific surface area, particle size and morphology of nZVI has been observed. Results showed that compared to the sample obtained via synthesis without ultrasonic irradiation, presence of ultrasonic cavitation provides decreasing in particle size without significant changes in morphology.

Achieved values of nZVI particle size make it appropriate for use in environmental applications (wastewater treatment) as well as in development of novel processes for rare-earth metals extraction, requiring higher values of oxidation-reduction potential or efficient separation via sorption on the nanoparticles surface.

#### Acknowledgements

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#### References

- [1] Binnemans K, Jones P T, Blanpain B, Van Gerven T and Pontikes Y 2015 *J. Clean. Prod.* **99** 17
- [2] Funari V, Braga R, Bokhari S N H, Dinelli E and Meisel T 2015 *Waste Manag.* **45** 201

- [3] Tunsu C, Ekberg C and Retegan T 2014 *Hydrometallurgy* **144** 91
- [4] Binnemans K, Jones P T, Blanpain B, Van Gerven T, Yang Y, Walton A and Buchert M 2013 *J. Clean. Prod.* **51** 1
- [5] Su C, Pulsa R W and Krug T A 2012 *Water Res.* **46** 5071
- [6] Taha M R and Ibrahim A H 2014 *J. Env. Chem. Eng.* **2** 1
- [7] Yan W, Herzing A A, Kiely C J and Zhang W X 2010 *Journal Contam. Hydrol.* **118** 96
- [8] Crane R and Scott T B 2012 *J. Hazard. Mater.* **211-212** 112
- [9] Li X and Zhang W 2012 *J. Phys. Chem. C* **111** 6939
- [10] Yang G C C and Chang Y-I 2011 *Sep. Purif. Technol.* **79** 278
- [11] Gan S and Ng H K 2012 *Chem. Eng. J.* **213** 295