Synthesis and Application of Zeolite and Glass Fiber Supported Zero Valent Iron Nanoparticles as Membrane Component for Removal Nitrate and Cr (+6) Ions

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In the present paper the synthesis and characterization of zeolite and glass fiber supported zero valent iron nanoparticles (Ze-ZVI, GF-ZVI NPs) are reported.ZVI, Ze-ZVI and GF-ZVI NPs size, composition and morphology were characterized by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Energy Dispersive Spectroscopy (EDS). Synthesized nanostructures were tested as reducing agents of nitrate and hexavalent Chromium. Batch experiments were carried for revealing of efficacy of prepared nanomaterials (ZE-ZVI NPs and GF-ZVI NPs). Nitrate removal efficiency (at initial concentration 50 mg/mL) was rapidly increased from 26% to 76% for GF-ZVI NPs at 60-240 min time interval for and from 34% to 90% for ZE-ZVI NPs at the same time interval.Also was studied the efficacy of prepared nanostructures ZE-ZVI and ZE-ZVI NPs as membrane component with 5% of ZVI NPS weight contentfor the removal of nitrate from water solution that made 85% for ZE-ZVI NPs and 76% for GF-ZVI NPs, respectively. The results of this study indicate that the application of GF-ZVI and ZE-ZVI NPs as membrane component is advantageous because it allows to prevent the additional pollution of treated solution caused by unreacted ZVI NPs.

1. Introduction

The interest to nano scale particles applicable for the solving of environmental problems grow day by day. The different routes of synthesis of nanostructures have been developed and they reveal the high application potential in various fields. Particularly in the recent years zero valent iron nanoparticles ZVI NPs attract the significant interest as a soft reducing agent, and due to its biocompatibility it can be used in green environmental technologies. There are different synthetic procedures are developed for obtaining ZVI NPs(Di Palma et al., 2015; Karlsson A et al.,2005; Glavee GN et al.,1995). Among them the practical importance have the methods of engineering of nanopartciles surface in order to avoid their oxidation, agglomerationand as consequence the increase the efficiency in situ reactions (Khalil H, et al., 2004; Xu J, Dozier A et al.,2005; Schrick B et al., 2002).Many field tests have demonstrated the promising results for in situ remediation (Elliott D and Zhang, 2001; Quinn J, Geiger C et al.,2005).

The excess amount of nitrate has become a serious problem affecting waterquality. Nitrates are potential harmful contaminants towards living organisms, and due to high solubility, theycan easily contaminatesoil and groundwater. Nitrates can be introduced into environment mainly as a result of excessive use of fertilizers and through industrial wastes. It has been found that nitrate in living organisms is enzymatically reduced to nitrite, thus causing cancer (J.H. Barrett et al., 1998). The maximum allowed level of nitrate in drinking water in accordance to the World Health Organization should not exceed 10 mg/L^{-1} NO_3-N. There are some studies reporting of successful application of ZVI NPs for removal of nitrates from the ground and water (Hwang Y.H et al., 2011). But at the same time the authors underlined the drawbacks of use of ZVI NPs, that is they can also act, in turn, as contaminant of the environment. In order to apply ZVI NPs as reducer for the purification of soil and water, the development of new nano formulation containing ZVI NPs is a matter of practical interest.

Recently, the use of some supportive materials has been suggested in order to prevent their agglomeration and their release into the environment.

Another most common environmental contaminants is hexavalent chromium, Cr(VI). While trivalent chromium, Cr(III), naturally occurs in soil and it is comparatively friendly towards environment, Cr(VI) has severe toxicity and it is generally released into environment as a results of several industrial activities, such as chromium mining electroplating, tannery facilities, metal fishing, and pigment manufacture (Xu et al., 2004).Reduction of Cr (VI) to Cr(III) is desirable as the latter species is an essential nutrient for maintaining a normal physiological function in human organisms and it is also more stable and biocompatible (Gueye et al., 2016). Given the strong dependence of Cr mobility and toxicity on its redox state, the remediation technologies that reduce Cr (VI) to Cr(III) by a ZVI NPs, are a matter of practical interest (Di Palma, et al., 2015). In recent years, a lot of studies demonstrated that zero valent iron (ZVI) is an efficient and inexpensive reducer for Cr(VI) (Alowitz and Scherer, 2002).

The removal mechanisms involved in the treatment of heavy metal with ZVI NPs, depend on the standard redox potential (E°) of the metal contaminant. Metals having more negative E°, or similar to that of Fe^0 (e.g., Zn and Cd) are removed completely by adsorption on the surface of ZVI NPs. Metals with E° more positive than Fe^0 (e.g., As, Cr, Se, U, and Cu) are removed by reduction. Metals with slightly positive E° compared with Fe^0, (e.g.,Ni and Pb) are removed by both reduction and adsorption.

Taking into consideration the above mentioned factors we synthetized zeolite supported ZVI NPs ZE-ZVI and Glass fibre supported GF-ZVI NPs as a membrane component for nitrate and Cr (VI) removal from water.

2. Experimental

2.1 Materials and equipment

The natural zeolite and glass fiber were purchased from St.Cloud Mine in Winston, NM. After washing with hot distillite water, dried raw zeolite was sieved with 200 mesh screen prior to use.Glass fiber was washed with 0.1 M HCl, 0.1 M NaOH and repeatedly with deionised water and dried in the vacuum oven at 70^0 C.

Ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) and sodium borohydride ($NaBH_4$) were purchased from Tianjin Fuchen Agent Manufactory, China. The Ethanol (95%), NaOH (99%), HCl (98%), KNO_3 (98%), PAA (Poly acrylic acid), CTAB (hexadecyl-trimethyl-ammonium bromide) were purchased from Merck (Darmstadt, Germany).K_2CrO_4 was purchased from Fisher Scientific (Pittsburg, PA)

2.2 Synthesis and characterization of ZE-ZVI NPs and GF-ZVI NPs

The synthesis of ZE-ZVI NPs and GF-ZVI NPs was based on the reduction of ferrous sulphate heptahydrate (0.822gr) with potassium borohydride (0.244 gr), at room temperature (Li et al. 2011 b), where zeolite and glass fiber acted as a porous support material. The prepared ZVI NPs were stabilized by PAA and CTAB. The reaction was carried out under vigorous stirring in a nitrogen atmosphere. The reduction of Fe^{2+} to Fe^0 occurred according to the following reaction (Li et al. 2010):

$$Fe^{+2} + BH_4^- + 6H_2O \rightarrow Fe^0 + 2B(OH)_3 + 7H_2 \uparrow \qquad (1)$$

The formed NPs were separated by centrifugation and repeatedly washed with ethanol, in order to remove the interfering ions prior to use (ÜzÜm et al.2009).

SEM and EDS analysis of prepared samples of ZE-ZVI NPs and GF-ZVI NPs were taken on Field Emission Scanning Electron Microscope JEOL JSM-7600F at an accelerating voltage of 15.0 kV, SEI regime.

Ultrasonic processing of materials made in the instrument Sonics Vibramobil VCX 500.

The morphology of samples was studied by means of AFM Integra-Prima (NT-MDT, Russia). Special silica cantilevers, covered by ferromagnetic with curvature radii of 20 nm and a resonance frequency of 40-97 Hz were used for the scanning. The scanning area was 750x750 nm. The measurements were implemented in semi-contact regime on air, and the determination of changes of cantilever amplitude oscillation allowed definition of the surface topography. Scanning rate was 1.969 Hz and the number of scanned lines was 256.

The concentration of ions in solution was analyzed based on the guidelines given in the 20th edition of the standart methods by means UV/Vis spectrophotometer (UV-1800 Series WL=340nm)

Metal concentration was determined by atomic absorption spectrophotometer (AAS) analysis, using an Agilent AA DUO 240 Fs instrument.

2.3 Adsorption/reduction experiments

Batch experiments were first carried out in order to evaluate the removing efficiency of ZVI NPs. The aqueous solutions of nitrate and of dichromate were prepared by dissolving of appropriate amount of KNO_3 and K_2CrO_4 in 100 ml of distilled water. The batch experiments were carried out in 100 ml glass flasks containing 0.05

gram of Ze-ZVI and GF-ZVI NPs. The prepared solutions were stirred at room temperature and sampled at certain time points (30, 90, 120, 180, 240 min) then each sample was filtered and remaining concentrations of pollutants in the solution were analyzed and compared. The removal efficiency (R%) and the adsorption capacity (q_e, mg/g) of sorbents (ZE-ZVI NPs and GF-ZVI NPs) were calculated as follows:

$$R_\% = \frac{C_0 - C_e}{C_0} \times 100 \%$$

$$q_e = \frac{(C_0 - C_e) * V}{m}$$

Where:C_0, C_e = concentrations of ions at initial and equilibrium (mg/l); m = mass of sorbent (g); V = volume of solution (l).

Membrane experiments were then carried out, using ZE-ZVI NPs and GF-ZVI NPs as membranes components for filtration of nitrate and dichromate containing solutions. Membrane experiments were performed in a glass funnel with bottom in which there were holes with diameters of 0.5 mm, as shown in Figure 1.
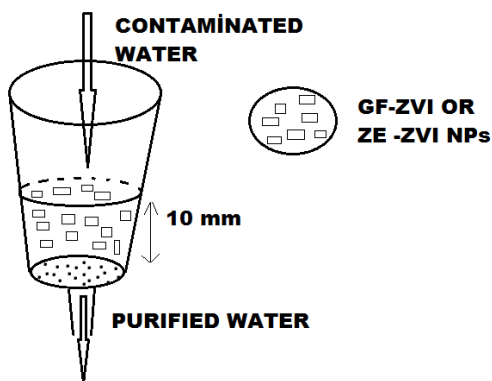

Figure 1:The schema of filtering of contaminated water by means of GF-ZVI NPs and ZE-ZVI NPs as membrane components.

2. Results and discussions

The morphology and structure of ZVI NPs, ZE-ZVI NPs and GF-ZVI NPs were analyzed by SEM, EDS and the results are given in Figure 2.
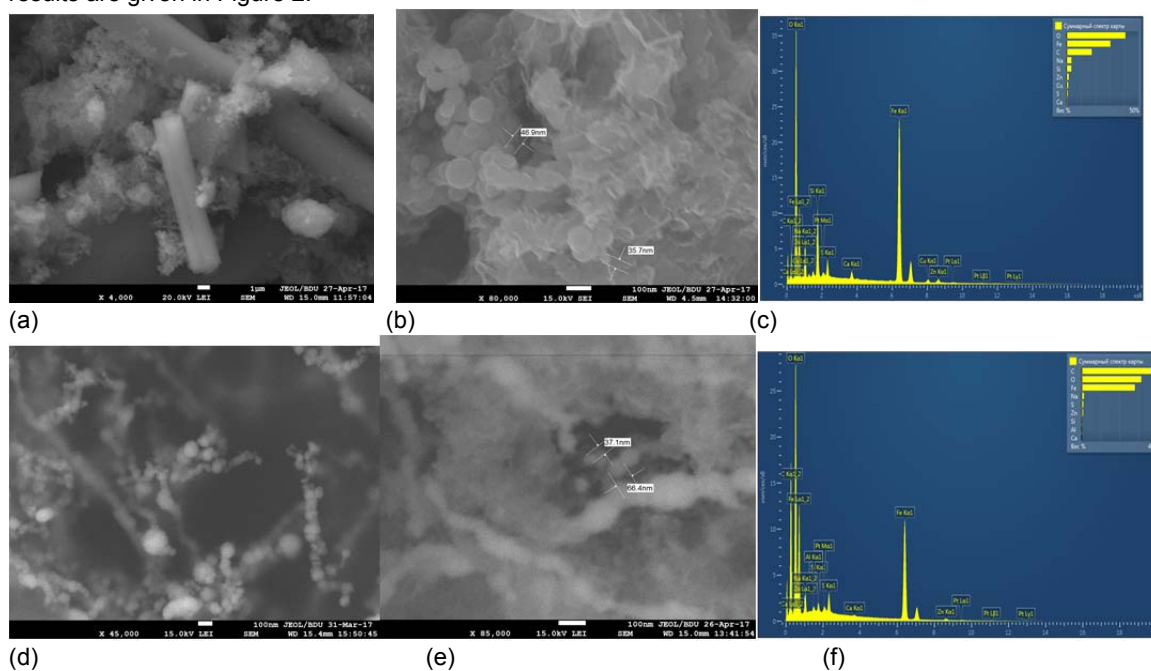

Figure 2. SEM images of CTAB stabilised ZVI NPs (a), GF-ZVI NPs (b), EDS of GF-ZVI NPs (c), PAA stabilised ZVI NPs (d), ZE-ZVI NPs (e), EDS of ZE-ZVI NPs (f)

As it seen from Figure 2 the produced ZVI NPs were evenly distributed and the size of ZVI NPs ranged 35-50 nm. The peaks indicated in the EDS spectra depict the presence of Fe, C, Si (Figure 2c) and Fe, C, Zn, Na (Figure 2f)as the main elements of the GF-ZVI and ZE-ZVI samples respectively. The samples before EDS study were coated by thin layer of Pt in order to avoid their charging and this explains the presence of peak that is characteristic to platinum. The samples also were analyzed by AFM (Figure 3) and the results of AFM scanning showed a very good correlation with the results of SEM analysis. According to the AFM analysis the size of ZVI NPs changes was in the range of 40-50 nm. As it can seen from the Figures 2 and 3, the ZVI NPs resulted evenly distributed in the matrix of supported material without significant agglomeration.
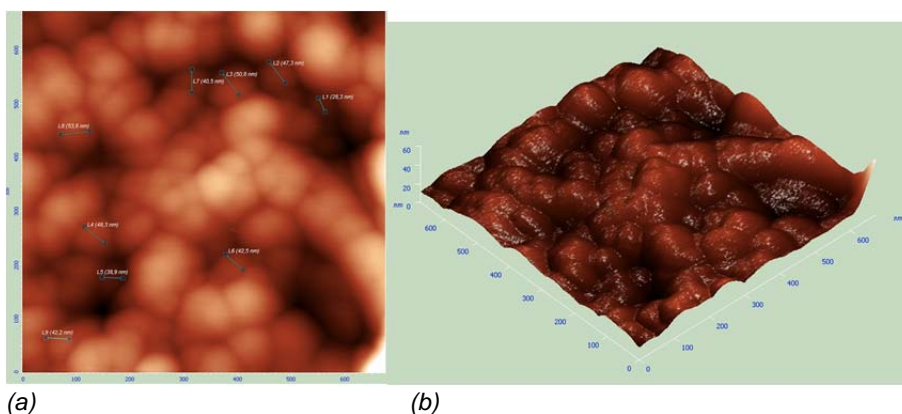

(a)   *(b)*

Figure 3: AFM 2D images of ZE-ZVI NPs (a), 3D image of ZE-ZVI NPs (b)

In order to investigate nanomaterials (ZE-ZVI NPs and GF-ZVI NPs) effectiveness, batch experiments were then carried out. Nitrate removal efficiency (at initial concentration 50 mg/mL)was rapidly increased from 26% to 76% for GF-ZVI NPs at 60-240 min time interval for and from 34% to 90% for ZE-ZVI NPs at the same time interval Figure 4.
The reduction of nitrate ions occurs in accordance to the reaction (2):

$$4Fe^0 + NO_3^- + 10H^+ = 4Fe^{2+} + NH_4^+ + 3H_2O \qquad (2)$$
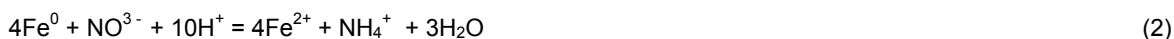
Total decrease of nitrate concentration in the solution were 90% for ZE-ZVI NPs and 76% for GF-ZVI NPs, respectively. The higher efficiency of ZE-ZVI NPs compared with GF-ZVI NPs can be probably addressed to the better adsorption capacity of zeolite, as shown in Figure 5.
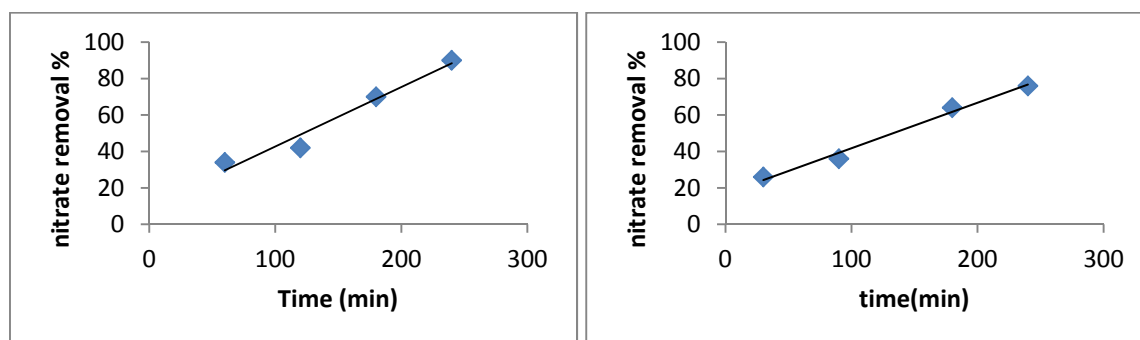

Figure 4: Removal efficiency of nitrate ZE-ZVI NPs (a); GF-ZVI NPs (b)

As it can be seen from Figure 4 the adsorption capacity also increased from 3.4 to 9 mg/g for ZE-ZVI NPs and from 2.6 mg/g to 7.6 mg/g for GF ZVI NPs.
We also studied the removal efficiency of ZE-ZVI NPs and GF-ZVI NPs towards Cr(+6) ions. The reducing of Cr(VI) in accordance of follow reaction (3):

$$3Fe^\circ + Cr_2O_7^{2-} + 7H_2O \rightarrow Fe^{2+} + 2Cr(OH)_3 + 8\,OH^- \qquad (3)$$

The initial concentration of Cr (VI) was 53 mg/l. Figure 5 shows, the reduction rate of Cr (VI) during the treatment of water with a reducing solutions of ZE-ZVI and GF-ZVI NPs, changes to 66% and 56% respectively.
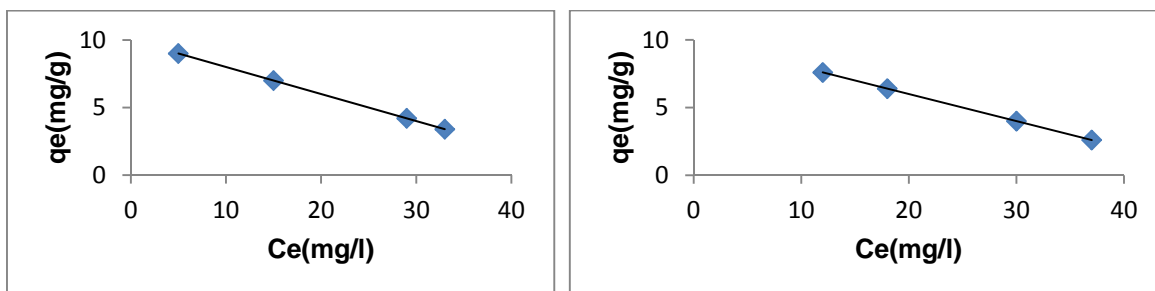

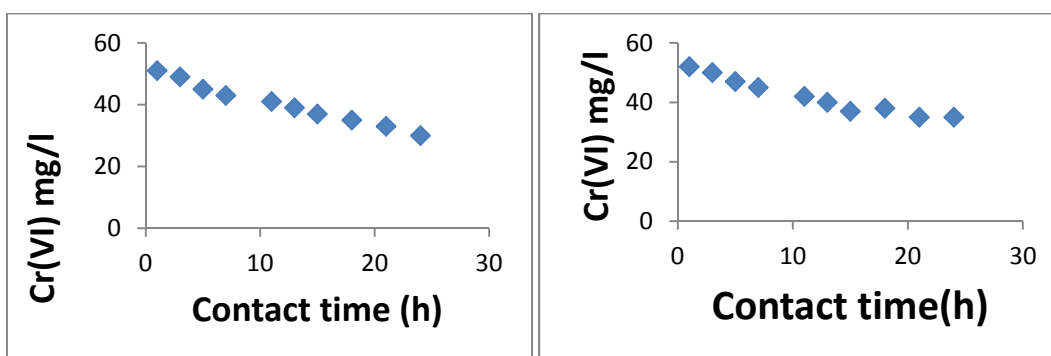Figure 5: Adsorption capacity of ZE-ZVI (a); GF-ZVI NPs (b)

Figure 6: Removal efficiency of ZE-ZVI NPs (a) and GF-ZVI NPs (b) towards Cr(+6) ions.

In order to test the efficiency of ZE-ZVI and ZE-ZVI NPs as membrane component we filtered the contaminated water through prepared materials with 5% of ZVI NPS weight content. The rate of water passage through filter was 0.5 mL/min. The calculated removal efficiency of nitrate was 85% for ZE-ZVI NPs and 76% for GF-ZVI NPs, respectively.

3. Conclusion

In this study ZVI NPs supported by zeolite and glass fiber materials were synthesized and characterized, and applied to the removal of nitrate and Cr(VI) ions from water. The ZVI nanoparticles were evenly dispersed in the supported material without any significant aggregation, and they were characterized by high specific surface area and an average size of 45 nm.

Zeolite and Glass Fiber are inexpensive materials so they can be promisingly used as supporting materials for the preparation of membrane component for removal of contaminated ions from water. Furthermore, the application of GF-ZVI and ZE-ZVI NPs as membrane component allow to prevent the additional pollution of treated solution caused by contamination by unreacted ZVI NPs.

Batch experiments showed that the nitrate removal was 76% and 90% by application of GF-ZVI NPs and ZE-ZVI NPs, respectively.The reduction of hexavalent chromium performed using GF-ZVI NPs and ZE-ZVI NPs proved to be fast and efficient. Cr (VI) reduction rate during the treatment of water with a reducing solutions of ZE-ZVI and GF-ZVI NPs, was 66% and 56% respectively.

Acknowledgements

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