SYNERGISTIC EFFECT OF NANO ZERO-VALENT IRON AND CYCLODEXTRINS: A NANO-STRUCTURE FOR WATER PURIFICATION

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Abstract

Nanoscale zero-valent iron (NZVI) is one of the most important nanostructure for degradative remediation of environmental contaminants. In our research, NZVI was for the first time functionalized with cyclodextrins (CD), recently considered as excellent, environmentally friendly and cheap absorbents of toxic pollutants. Functionalization of the nano zero-valent iron by CD, their derivatives and polymers, can not only improve the ZVI nanoparticles stability and dispersibility, but also can complex toxic contaminants inside the CD cavities that will be further reduced by NZVI to a less toxic products. By this, one of the largest obstacles in the NZVI field i.e. lack of NZVI selectivity could be overcome. Moreover, reactivity towards a recalcitrant non-polar compound, that under standard conditions is not very reactive with the NZVI alone, has been shown herein.

Keywords: Nanoparticles, NZVI, cyclodextrins, water treatment, surface modification

1. INTRODUCTION

The wide range of persistent contaminants including inorganic and organic pollutants [1] in ground and surface waters is becoming more problematic due to, among others, rapid development of industrialization [2]. The constant need for clean water supply urges development of innovative methods for purification and treatment of water and wastewater. On the other hand, advancing technologies based on nanomaterials brought evolution to wide array of technologies in environmental, industrial and domestic applications, including new methods for water remediation [3] and improved drug delivery [4]. Nanoparticles in particular have received a significant attention due to the unique properties such as catalytic, magnetic, chemical and optical capabilities. Their enhanced catalytic activity comes from small size, meaning high specific surface area that improves the tendency to interact, adsorb and react with toxic contaminants [5]. Therefore, their potential use in wastewater treatment has sparked a great deal of interest.

In the last twenty years, nanoscale zero-valent iron particles (NZVI) have been promising topic for groundwater remediation. NZVI was reported to be effective at degradation of contaminants such as: nitrates, heavy metals, phenols, almost all chlorinated solvents, pesticides, azo dyes and pharmaceutical pollutants [6-9] NZVI is also effective in immobilization of inorganic anions like chromium or arsenic and in recovery or removal of dissolved metals from the solution [10-12]. One of the main reasons why NZVI is used for remediation is due to their high specific surface area that allows for better accessibility to the NZVI surface and hence improved catalytic activity [13]. However, there are several key limitations for application of NZVI, such as restricted mobility, stability and selectivity (it tends to react with water instead of contaminants of concern). Moreover, their strong tendency to aggregate in aqueous environment results in lower specific surface area which can result in reduced catalytic reactivity [14]. To overcome these problems, many studies have proposed the modification of NZVI surface by using polymers (e.g. guar gum, gum karaya, chitosan and many others [15-17]), improving their dispersibility, stability and mobility in porous media [18,19].

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β-Cyclodextrins (βCD) are cyclic oligosaccharides with seven glucose units and are biodegradable [20]. Hydrophilic external surface of βCD makes them water-soluble [21], whereas their hydrophobic cavity, allows them to form host-guest inclusion complexes in which an organic guest can be sequestered [22]. In the literature it is reported that cyclodextrins can form moderately stable complexes with some classes of pollutants i.e. phthalic acid esters, chlorinated biphenyls or PAHs [23-25].

In this work, for the first time NZVI particles were synthesized together with βCD. Thus synthesized nanoparticles (βCD-NZVI) were characterized by several techniques by which we have determined their morphology and surface properties. βCD-NZVI composite was further used for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AM). βCD-NZVI has shown enhanced performance in reductive degradation of 4-nitrophenol compared to the NZVI without stabilization.

2. MATERIALS AND METHODS

2.1. Chemicals

Iron (III) chloride hexahydrate (≥98 %, chunks), sodium borohydride (≥99%, granular), 4-nitrophenol (≥ 99 %), β-cyclodextrin (≥97%) were purchased from Sigma-Aldrich, Czech Republic. Sodium hydroxide (≥98 %) was purchased from LACH-NER, s.r.o., Czech Republic. De ionized water (18.2 MΩ·cm-1, ELGA, Veolia Water, Marlow, UK) was used in all experiments.

2.2. Analytical

Scanning electron microscope (UHR FE-SEM Carl Zeiss ULTRA Plus, Germany) was used to study the nanoparticles morphology, operating at acceleration voltage 0.5 - 2.5 kV. Energy-dispersive X-ray spectroscopy analysis was made to evaluate presence of different elements. Zetasizer ZS (Malvern Instruments Ltd, UK) was used for measuring the zeta potential with autocorrelation functions of 10 seconds. Triplicate measurements were taken, prepared in freshly suspension and each result was the average of triplicate.

2.3. Synthesis of iron nanoparticles with βCD

The synthesis of βCD-NZVI was performed in accordance with a modified method previously reported by Wang, et al. [26], who has synthesized iron(II,III) oxide with βCD. Briefly, 100 mL solution of iron (III) chloride hexahydrate (0.02 M) and βCD (0.03 M; i.e. molar ratio of iron (III) chloride hexahydrate: βCD - 1:1.5) was created. First βCD was solubilized by stirring under 60 °C (200 rpm), and then iron (III) chloride hexahydrate solution was added dropwise and the solution was stirred for additional 15 minutes under the nitrogen atmosphere. After that time, 10 mL of NaBH₄ (1 M) was added dropwise and left for additional stirring for 10 minutes. Then synthesized nanoparticles were washed with ethanol 3 times and separated by a strong magnet (MAGSY s.r.o., Czech Republic). Finally, the nanoparticles were freeze-dried and kept for further use. The same procedure was used for other synthesis reported in this work.

2.4. Remediation test

The remediation test for the reduction of 4-nitrophenol (4-NP) was carried out in 10 mL bottle. Based on a procedure of Baruah, et al. [27]. Following conditions were applied: 0.1 mL of NaOH (1 M) was added to 4-NP stock solution (10 mL) then 240 µL of 4-NP (5 mM) was added to reactor and mixed along with a certain amount of βCD-NZVI, rest of the volume was adjusted with DI water. Then, 1 mL of the sample was taken from the solution, filtered (CHS filterpure syringe filters 0.22 μm) and immediately transferred to a 1 cm quartz cuvette. Absorbance measurements were recorded by a UV-Vis spectrophotometer (Hach Lange DR 3900) at the wavelength of 401 nm [28].
3. RESULTS AND DISCUSSION

3.1. Morphology of βCD-NZVI

To study the structure and shape of the synthesized nanoparticles in this work, SEM analysis was made (Figure 1).

Bare NZVI (Figure 1a) exhibits a quasi-spherical shape due to the oxidation of NZVI, and its morphology is in accordance with our previous reports [15]. The synthesized βCD-NZVI (Figure 1b) are also spherical with a visible organic layer at the surface. This has been also further validated by EDX analysis (Figure 1c), which confirmed the presence of carbon and oxygen on the NZVI surface. Presence of both elements could indicate a βCD layer on the NZVI. A 3D model of (as expected) βCD-NZVI was also created herein (Figure 1d). Based on the SEM analysis, particle size distribution was made for both NZVI and βCD-NZVI using ImageJ program. Average particles size distribution was found to be 155 and 86 nm for βCD-NZVI and bare NZVI, respectively.

3.2. Zeta potential analysis

Zeta (ζ) potential is an important parameter by which the stability and aggregation capability of the nanoparticles can be assessed [29]. The zeta potential values of nanoparticles typically range from -100 mV to +100 mV. Moreover, they could indicate the interactions between the nanoparticles also revealing their aggregation. In accordance with literature the ζ-potential above 30 mV produces a good stability [30,31] while around 20 mV gives only a short-term stability and values between +5 mV to -5 mV indicate fast aggregation [32]. Alterations in the pH have a significant effect on zeta potential of the particles and agglomerate size,
changing the pH of the medium in which the nanoparticle is suspended will result in differences in the surface chemistry of a nanoparticle [33]. Not surprisingly, the values of ζ-potential for βCD-NZVI varied depending on the pH value (Figure 2).

![Figure 2](image)

Figure 2 Zeta potential of βCD-NZVI (ratio 1 : 1.5) in different pH conditions

In more acidic conditions, ζ-potential was around +9 mV, +5 mV for pH 3 and 5 respectively. Under more neutral conditions (pH 7, 8) the values oscillated near +1 and 0 mV. The isoelectric point (IEP) for synthesized βCD-NZVI was determined to be at the pH 8. Measured ζ-potential is only negative when pH is higher than IEP since for pH 9 and 11, it was -2.5 mV and -16 mV respectively. Nanoparticles suspended in solutions with neutral pH could aggregate; however, in more acidic and alkaline conditions they could be more stable.

3.3. Remediation tests

4-NP was selected as a model pollutant since it is one of the most used chemicals for leather preservatives, drugs synthesis, pesticides and nitroaromatic compound production [34-37]. Due of its toxicity especially for bacteria, plants and humans [38-41] it is not surprising that 4-NP is commonly used as a model contaminant for catalytic studies [42-44]. 4-NP has the highest absorption peak at ~317 nm, by adding NaOH (1M) the absorption peak shifts to 401 nm, due to the deprotonation and formation of 4-nitrophenolate. Synthesized βCD-NZVI was tested for the hydrogenation of 4-NP to 4-AP (Figure 3).

![Figure 3](image)

Figure 3 a) Comparison of different NZVI types for the hydrogenation of 4-NP (conditions: 0.2 g/L of NZVI and 0.12 mM of 4-NP; T: 25 °C) and b) reduction of 4-NP by βCD-NZVI (ratio 1 : 1.5 conditions: 0.12 mM of 4-NP, T: 25 °C)
For a better comparison of the reduction activity, it was chosen to compare the βCD-NZVI synthesized in three different ratios (1 : 1.5, 1 : 0.75 and 1 : 0.3) with a commercial NZVI-STAR and with the bare NZVI (without stabilization). Under the tested condition a better behavior in this process was shown by βCD-NZVI (ratio 1 : 1.5), at the concentration of 0.2 g/L, the bare NZVI, NZVI-STAR and βCD-NZVI (1 : 0.75, 1 : 0.3) has not shown an appreciable effect. The enhanced catalytic properties shown by βCD-NZVI confirms our suspicions concerning synergistic effect of βCD on the surface of NZVI. The presence of βCD could enhance the accessibility of active sites on the nanoparticles by hosting the organic 4-NP in their cavities. The hypothesis that the βCD can enhance the hydrogenation of 4-NP has been strengthened by the fact that the average particle size of bare NZVI is smaller in comparison to βCD-NZVI (which normally indicates larger available specific surface area and better catalytic properties). However, the presence of βCD on NZVI surface could explain why synthesized βCD-NZVI were more efficient in the degradation process of 4-NP. Nonetheless, further studies are required in order to confirm this hypothesis.

4. CONCLUSION

For the first time NZVI particles were successfully synthesized and functionalized with βCD. Morphology of the particles was studied using SEM and their spherical shape was confirmed. Average particle size of the βCD-NZVI composite was found to be 155 nm. Presence of the organic layer on the nanoparticles surface was confirmed by the EDX test. Zeta potential analysis of synthesized nanoparticles indicated their better stability in more alkaline/acidic conditions (-16 mV, +9 mV). However, further research is needed focusing on better stabilization of these nanoparticles. Their catalytic activity was compared with different NZVI’s during the reduction of 4-NP and synthesized herein nanoparticles were found to be the most effective in the removal of 4-NP. Further studies are required for understanding the degradation kinetics of organic pollutants by βCD-NZVI.

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