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Review

Review on synthesis of NZVI as an effective adsorbent for environmental remediation

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ABSTRACT

Nano Zero Valent Iron (NZVI) is emerging as new selection for the treatment of contaminated soil and groundwater. Due to their small size, the nanoscale particles are more reactive than granular iron which is conventionally applied in reactive barriers and can be applied for in situ treatment. NZVI effectively reduces a large number of organic and inorganic compounds, including halogenated hydrocarbons, organic dyes, antibiotics, heavy metal ions, etc. Its inner core (iron(0)) has exerts a reducing character towards pollutants, whereas the iron oxide (FeO) outer shell acts as a reaction site for chemisorption and the adsorption of contaminants via electrostatic interactions. Generally, NZVI can be produced using physical or chemical methods either by reducing the size of bulk iron to nanoscale (top-down approach) or building up nano iron from atoms generated from ions or molecules (bottom-up approach). Some of These methods include liquid phase-reduction, milling, carbothermal reduction, ultrasound assisted method, electrochemical and green synthesis.

Keywords: NZVI, adsorbent, remediation, synthesis, nanoparticles

Introduction

Nano zero valent iron (NZVI) as a remediation tool has great potential to degrade a broad range of water contaminants, including halogenated compounds, various heavy metal ions, aromatic hydrocarbons, nitrate, phosphate and azo dyes. Due to its small size, high reactivity, sufficient mobility within porous media, low toxicity sufficient reactive longevity has attracted attention compared to its microscale counterpart. Typical NZVI particles have a classic core-shell (Fe(0)-Fe (oxyhydr)oxide) structure which consist of a metallic iron core encapsulated by a thin iron oxide shell of a few nanometers. The metallic iron core serves as an electron source and exerts a reducing character, whereas the oxide shell promotes the adsorption of contaminants via electrostatic interactions and surface complexation [1]. The co-existence of the Fe(0) core and oxidized Fe surface layer enables a unique reactive surface for the initial adsorption of contaminants and their subsequent transformation on the particle surface via reductive or oxidative pathways. At low pH, iron oxide shell is positively charged and attracts anions like phosphates and sulphates, and at high pH it becomes negatively charged and attracts cations like metal ions. Heavy metals are sequestered onto the solid NZVI surface after the reaction. In wastewater treatment and groundwater remediation, NZVI may undergo oxidation (From Fe(0) to Fe(II) and Fe(II) to Fe(III) and in the process reduce other organic as well as inorganic impurities. Nanoscale iron particles are in a process to replace micro-iron particles and have proven to be quite effective reductant and catalyst for a wide variety of common environmental contaminants including chlorinated organic compounds and metal ions [2,3].

1. methods of NZVI synthesis

Synthesis of iron nanoparticles can be done using several chemical and physical methods including grinding, abrasion, milling, etching, lithography, annealing ae elevated temperatures and reacting with reducing agents. These synthesis methods can be done using two approaches: top-down and bottom-up. In top-down approach the bulk particles of iron are converted to fine nano-sized by mechanical methods such as milling, etching and /or machining. Whereas, bottom-up approach involves assembling of nano structures atom-by atom or molecule-by molecule to form nanostructure. Methods which at present are not in common use but which, due to their advantages, may soon become more popular, include precision milling, carbothermal reduction, ultrasound assisted production, electrochemical generation, and green synthesis [4].

1.1 Liquid phase-reduction method

Chemical reduction is the most frequently used method of obtaining NZVI, mainly due to its simplicity. The borohydride solution prepared from concentrated ethanol and $NaBH_4(s)$ is slowly added into the iron (ferric) salt solution under during vigorous stirring under N_2 atmosphere. The resulting black precipitate is vacuum filtered, washed with deionized water or ethanol and subsequently dried. Therefore, by reacting iron compounds with a strong reducing agent such as sodium borohydride ($NaBH_4$) the NZVI can be obtained according to the following reaction [5]:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 (s) + 3H_2BO_3^- (aq) + 12H^+ + 6H_2$$

1.2 Precision milling method

Precision milling method consists of crushing micro iron with steel shot in a high-speed rotary chamber for about 8 h without any toxic reagents to achieve highly reactive nanoparticles of diameter 10–50 nm and surface area 39 $m^2\ g^{-1}$. Upon contact with the steel shot, the particles are deformed and cracked producing nanoparticles with irregular shapes and because of their high surface energy they display a strong tendency of aggregation [6,7].

1.3 Carbothermal reduction

The thermal reduction of iron compounds is another method of obtaining nZVI, that brings interesting effects. In the presence of gaseous reducing agents such as H_2, CO_2 or CO, iron salts or compounds are reduced to nano form (NZVI) using thermal energy at high temperature (> 500 ˚C). Such reactions proceed according to the following equations (1-2):

$$Fe(C_2H_3O_2)_2 (aq) + C (g) \rightarrow Fe^0 (s) + 2CH_2CO + CO + H_2O \quad (1)$$

$$Fe_3O_4 (aq) + 2C (g) \rightarrow 3Fe^0 (s) + 2CO_2 \quad (2)$$

The particles that are produced in these methods have an average particle size ranging from 50 to 300 nm with a specific area of about 7.55 $m^2\ g^{-1}$. The method is friendly to humans and the environment as it does not generate any secondary toxic pollutants. Also, the method leads to a speciation of iron and produce various form of iron nanoparticles at different proportions [8,9].

1.4 Ultrasound assisted method

Ultrasound sonication process can also be used for NZVI production, for the enhancement of both the physical methods of diminution and the chemical methods of synthesis. The usage of ultrasound assisted method for the reduction of particle size was first proposed by Tao et al. [10]. In their study, it was observed that the utilization of ultrasound leads to decreasing particle size of iron with increasing precursor concentration and ultrasonic power. Moreover, the surface area of NZVI was increased using ultrasonic vibration.

$$4Fe^{2+}(aq) + BH_4^-(aq) + 7NH_4OH \rightarrow 4Fe^0(s) + H_3BO_3(aq) + 7\,NH_4^+(aq) + 4H_2O \qquad (3)$$

1.5 Electrochemical method

The next method of producing nZVI is electrochemical method, which employs solution containing Fe^{2+}/Fe^{3+} salts, electrodes (cathode and anode), and electric current [11,12]. In comparison to chemical reduction this method is extremely simple, cheap, and fast. Atoms of iron are gradually deposited on the cathode, but they often display a strong tendency towards aggregation and the formation of clusters. To counteract that phenomenon, cationic surfactants are utilized to act as a stabilizing agent, and ultrasonic waves (20 kHz), which constitute a source of energy necessary for fast removal of iron nanoparticles from the cathode.

Cathode: $Fe^{3+} + 3e^- + \text{stabilizer} \rightarrow nFe^0$

The diameter of NZVI articles produced with applying ultrasonication can be between 1 and 20 nm and have a specific surface area of 25 $m^2\,g^{-1}$ [13].

1.6 Green method

Nanoparticles can also be biosynthesized (green synthesis) using plant extracts which are responsible for the reduction of metal compounds to suitable nanoparticles. The method included the preparation of a polyphenolic solution by heating plant extracts (coffee, green tea, black tea, lemon, balm, sorghum, bran, grape etc.) in water to a temperature close to the boiling point [14,15]. The extracts serve as a reducing agent and then as a capping agent for Fe. Extract prepared in this approach is separated from the plant residue and then mixed with the iron ion solution causing the iron ions to be reduced to NZVI in the presence of polyphenols. This green synthesis procedure is not only eco-friendly, but also inexpensive and is still currently widely used [16].

Conclusion

The insight into the various methods of synthesis of NZVI, its structure and characterization establish its role in the environmental remediation. The usage of nanoparticles in the remediation of the environment not only reduced the concentration of potential toxic substances, but also reduced the costs of large-scale remediation and of the duration of the process. Environmental contamination caused by inorganic compounds is a serious problem affecting soils and surface water. Most remediation techniques are costly and generally lead to incomplete removal and production of secondary waste. Nanotechnology, in this scenario with the zero-valent iron nanoparticle, represents a new generation of environmental remediation technologies. It is non-toxic, abundant, cheap, easy to produce, and its production process is simple.

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