Transport of green synthetic iron nanoparticles in porous media: effect of injecting concentration and flow velocity

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Abstract: Recently iron nanoparticles have become a very promising repair agent in the in-situ remediation of groundwater. However, the mechanism of the transport of green synthetic iron nanoparticles in porous media is less understood. In this paper, iron nanoparticles were synthesized from the Hizikia Fusiforme extracts and ferric chloride solution. Transport and deposition of green synthetic iron nanoparticles in porous media were investigated through sand column experiments and effects of injecting concentration and flow velocity were evaluated on the transport of iron nanoparticles. The results showed that deposition of iron nanoparticles in porous media were due to the irreversible attachment of sand grains and the straining of pore throats. The injecting concentration had a significant effect on the transport of iron nanoparticles, which were negatively correlated. The effluent concentration of iron nanoparticles was unaffected by the flow velocity at low injecting concentrations, however, the flow velocity was proportional to the deposition rate of iron nanoparticles. Moreover, the greater the flow velocity was, the more uniform the spatial distribution of iron nanoparticles in the sand column was.

1. Introduction
In-situ reaction zone (IRZ) plays a key role in the in-situ remediation of soil and groundwater. It is difficult to choose an available repair agent with strong ability of transport and high reactivity so as to form an effective reaction zone after being injected into the subsurface. Studies in recent years have shown that iron nanoparticles can be used to efficiently remove heavy metal pollution in groundwater because of their large specific surface areas and high reactivity[1]. It is a promising repair agent of groundwater, however, aggregation may affect their transport ability due to the large specific surface areas, which limits the practical engineering applications of iron nanoparticles.

Iron nanoparticles are generally performed with the surface modifiers such as polymers with the aim of facilitating transport ability[2-4]. The aggregation is weakened by increasing the particle size of iron nanoparticles[5] and enhancing the electrostatic repulsion between particles[6] through modifying the surface of iron nanoparticles. In recent years, studies has found that the injecting concentration and flow velocity of iron nanoparticles have a great influence on their transport[7, 8]. Esfahani et al.[9] investigated the mobility of polyacrylic acid modified zero-valent iron nanoparticles (PAA-ZVIN) and
polyvinylpyrrolidone modified zero-valent iron nanoparticles (PVP-ZVIN), which showed that two types of polymers enhanced the transport ability of iron nanoparticles. Moreover, PAA had more obvious enhancement effect on the transport. It was also found that the mobility of iron nanoparticles was decreased with increasing the injecting concentration of iron nanoparticles due to aggregation and ripening. Liang et al.\[5\] studied the mobility of polyvinylpyrrolidone modified nano-zero-valent iron (PVP-nZVI) at different flow velocities. The results showed that the effluent concentration increased with the increasing of flow velocity due to the decreasing of contact efficiency between iron nanoparticles and sand grains. Although the electrostatic repulsion between iron nanoparticles can be enhanced by polymer modification, the modified iron nanoparticles may be linked together by organic substances causing aggregation between iron nanoparticles\[10\], and improper polymer may cause secondary pollution to the environment.

The green synthesis of iron nanoparticles by plant extracts and iron salts is also a new means to facilitate the transport of iron nanoparticles. Most of the researches are focused on the green synthesis of iron nanoparticles, however, few researchers have addressed the transport of green synthetic iron nanoparticles in porous media. In this paper, iron nanoparticles were green synthesized from Hizikia Fusiforme extracts and ferric chloride solution. The transport of iron nanoparticles in porous media was investigated by column experiments, and then impact of concentration and flow velocity on the transport of iron nanoparticles was analyzed.

2. Materials and methods

2.1. Chemicals and materials
Hizikia Fusiforme was collected from Dongtou area of Wenzhou City, Zhejiang Province. The algae were yellow-brown with a height of 20 to 50 cm and a fresh/dry weight ratio of 5.14. Ferric chloride (FeCl₃·6H₂O) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Quartz sand (particle size between 0.6 mm and 0.8 mm) used in the column experiments was purchased from Qingdao Deyilin Media Co., Ltd. (Qingdao, China).

2.2. Preparation of iron nanoparticles
The Hizikia Fusiforme was washed with distilled water and then dried. Hizikia Fusiforme was weighed 60 g and placed in a beaker after being crushed. Distilled water was added to the beaker and then put into the water bath at a temperature of 80 °C for 1 h. The supernatant was vacuum filtered to obtain the Hizikia Fusiforme extracts. Ferric chloride solution was prepared by dissolved 27.03 g FeCl₃·6H₂O into 1 L of distilled water. The extracts and 0.1 mol/L FeCl₃ were mixed with a volume ratio of 2:1, and then put in a shaker at 25 °C for 1 h to prepare for iron nanoparticles. The mixed solution was centrifuged and then the precipitate was dried to obtain the powder of iron nanoparticles. The suspension solution of iron nanoparticles was prepared by dissolved the specified mass of iron nanoparticles powder in distilled water, and then ultrasonic treatment was performed to make them fully disperse.

2.3. Column experiments
In the transport experiments, a column with an inner diameter of 5 cm and a length of 22 cm was used as a sand container, and the quartz sand was filled with a thickness of 20 cm. The mass of quartz sand filled in the column was 604 g and the porosity was 0.4. The top of the column was plugged with a rubber stopper with a hose. In order to ensure the stability of the flow field in the column and to maintain the saturated status of the medium, sand column was placed vertically\[12\]. The peristaltic pump was chosen to regulate the flow. Iron nanoparticles were injected from the bottom of the column. The effluent collection device was placed at the outlet.

During the process of experiment, 4 PV (pore volume) distilled water was injected at a specified flow velocity, then 4 PV prepared suspension of iron nanoparticles was injected, and finally 4 PV distilled water was injected to remove the free iron nanoparticles in the pores.
In order to study the effect of injecting concentration on the transport of iron nanoparticles, four different experiments were performed. The injecting concentrations of iron nanoparticles were 175, 312, 506, and 834 mg/L, respectively with the flow velocity of 2.49 m/d. For the purpose of investigating the influence of flow velocity on the transport of iron nanoparticles, four different experiments were carried out with flow velocities of 1.91, 2.49, 3.23, and 3.82 m/d, respectively with the injecting concentration of iron nanoparticles of 170 mg/L. The reasonable intervals of time were taken for sampling and the total iron concentration in the effluent from each experiment was analyzed. The sand column was divided into ten equidistant segments to analyze the total iron concentration in each sections after transport experiment of iron nanoparticles finished. The content and the distribution of iron nanoparticles in porous media were characterized. All of samples were tested by Phenanthroline Spectrophotometry to determine the total iron concentration.

3. Results and discussion

3.1. Effect of injecting concentration on transport of iron nanoparticles

The breakthrough curves were illustrated in Figure 1. It can be seen from the figure that the breakthrough curves at different concentrations were similar. When the injection volume of iron nanoparticles was about 0.73 PV, iron nanoparticles were detected at the outlet of the column. Subsequently, the relative concentration \( \frac{C}{C_0} \) (a ratio of the effluent concentration and influent concentration of iron nanoparticles) dramatically increased, but it remained stable at a value less than 1 after 1.2 PV. It was known that deposition occurred at a certain rate during the transport process\(^{[13]}\). In addition, the increasing of the injecting concentration of iron nanoparticles brought about a decline of \( \frac{C}{C_0} \). When the injecting concentration increased from 175 mg/L to 834 mg/L, \( \frac{C}{C_0} \) decreased from 0.88 to 0.71. Increasing the injecting concentration of iron nanoparticles could enhance deposition, which resulted in the greater amount of iron nanoparticles deposited in the column. When the injection of iron nanoparticles was completed (the injection volume was 4 PV), the concentration of iron nanoparticles in the effluent rapidly decreased and tended to 0 under the displacement of distilled water. It was found that few of the deposited iron nanoparticles in the porous medium was released which indicated that the deposition of iron nanoparticles in porous media was an irreversible process\(^{[6]}\).

Nanoparticles can be deposited in porous media due to attraction, straining, ripening, and blocking\(^{[14]}\). Zhang et al.\(^{[6]}\) studied the mobility of carboxymethyl cellulose stabilized zero-valent iron (CMC-ZVI), which was found that the relative concentration \( \frac{C}{C_0} \) increased with the growing of the injecting concentration and the author attributed it to the blocking of nanoparticles.

During the blocking process, due to the existence of the repulsive force between the iron nanoparticles, the iron nanoparticles deposited on the surface of the medium hindered the deposition of the particles nearby, and the deposition amount and the deposition rate of the iron nanoparticles would be less and less. So under the process of blocking, \( \frac{C}{C_0} \) will increase with the increase of injection concentration, and the breakthrough curve will increase with time.
Bossa et al. [3] investigated the mobility of nano-ZVI stabilized by cellulose nanocrystal (CNC-COOH-nano-ZVI) and found that the breakthrough curves showed a decrease over time, and this phenomenon was attributed to ripening of the iron nanoparticles. There was an attractive relationship between iron nanoparticles due to ripening. The deposited iron nanoparticles would attract the iron nanoparticles in the liquid phase to deposit, and the deposition rate would increase with time, so the breakthrough curves would tend to decrease. According to the breakthrough curves (Figure 1.), the green synthetic iron nanoparticles from the Hizikia Fusiforme did not undergo ripening and blocking during the transport in porous media. The deposition of iron nanoparticles occurred because of irreversible attraction of the sand grains and straining caused by pore throat [3].

Figure 2 demonstrated the spatial distribution of iron nanoparticles in the column. It suggested that there were more deposition of iron nanoparticles at the inlet of the column, and the deposition reduced with the increase of the transport distance. Numerous surveys had indicated that this distribution was caused by the mechanism of straining [15].

3.2. Effect of flow velocity on transport of iron nanoparticles

Breakthrough curves of iron nanoparticles at different flow velocities were represented in Figure 3. It can be observed that the breakthrough curves were basically the same at the different velocities, and the relative concentration $C/C_0$ was all 82%. The results showed that the velocity had no significant effect on the concentration of iron nanoparticles in the effluent at the low velocity of 1.91 m/d ~ 3.82 m/d.
Figure 3. Breakthrough curves of iron nanoparticles at different velocities.

Figure 4. Spatial distribution of iron nanoparticles deposited in the column. Origin of coordinate represents the entrance to the sand column.

Table 1 showed the deposition of iron nanoparticles in the column at different velocities. It can be seen that mass of iron nanoparticles deposited in the column was the same (about 16 mg) when the injecting concentration of iron nanoparticles were the same with the injection volume of 628 ml at the velocity of 1.91, 2.49, 3.23, and 3.82 m/d, respectively. However, the increase of the velocity reduced the injection time of iron nanoparticles, which implied that the iron nanoparticles were captured at a faster rate.

Table 1. Deposition of iron nanoparticles at different velocities.

| Velocity (m/d) | V_e (ml) | C_0 (mg/L) | T (min) | M_r (mg) |
|----------------|----------|-------------|---------|----------|
| 1.91           | 628      | 170         | 240     | 16.8     |
| 2.49           | 628      | 170         | 185     | 16.3     |
| 3.23           | 628      | 170         | 143     | 15.9     |
| 3.82           | 628      | 170         | 120     | 16.6     |

- \(^a\) The volume of iron nanoparticles injected.
- \(^b\) The concentration of iron nanoparticles injected.
- \(^c\) Injection time of iron nanoparticles.
- \(^d\) The mass of iron nanoparticles deposited in the column.

Figure 4 showed the spatial distribution of iron nanoparticles in the column. It can be found that most of iron nanoparticles deposited at the inlet of the column, and the deposition decreased as the transport distance increased. In addition, the distribution of iron nanoparticles in the column was more uniform in cases that the velocity increased. It was confirmed that the flow velocity could change the spatial distribution, which was in good agreement with the finding about the distribution of nanoparticles in the column by Hou et al.\(^8\).

4. Conclusions
Iron nanoparticles can deposit in the porous media owing to the irreversible attachment of the sand grains and the straining caused by pore throats. The injecting concentration of iron nanoparticles had significant impact on their transport. Increasing the injecting concentration of iron nanoparticles brought about decreasing of the relative concentration C/C_0. The velocity had no significant effect on the concentration of iron nanoparticles in the effluent, the relative concentration C/C_0 were all 82% at different velocities. The velocity also did not affect the the deposition mass of iron nanoparticles in the column. With the increase of the flow rate, the distribution of iron nanoparticles in the sand column was more uniform.
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