

Effect of polymer ratio on nZVI loading onto electrospun nanofiber mat for mitigating groundwater contaminants

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ABSTRACT

Nanoscale zero-valent iron (nZVI) has been widely used for the reduction of halogenated organics and heavy metals in the groundwater. However, individual nZVI particles are mobile and prone to aggregate, thereby reducing the reaction sites exposed to contaminants. Electrospun polymer nanofiber mat is an ideal carrier to immobilize and distribute nZVI particles after its merits of high specific area, size-controllable and material-compatible properties. In this study, nZVI particles were loaded onto the polyacrylic acid (PAA)-polyvinyl alcohol (PVA) electrospun nanofiber mats with different PAA/PVA ratios. The results indicate that mat with the PAA/PVA ratio of 3:1 loaded the most nZVI particles (~48 wt%) and had the highest removals to methylene blue at 94% and Cu (II) ions at 84% respectively. The nZVI-loaded electrospun nanofiber mat has promising application for the groundwater contaminants mitigation.

Keywords: nZVI particles, electrospinning, polymer nanofibers, loading

1 INTRODUCTION

Nanoscale zero-valent iron (nZVI) has been widely used for the reduction of chlorinated organics and heavy metals in the soil and groundwater [1]. As an in-situ treatment, nZVI particles were initially coated by stabilizers and directly injected into the soil and groundwater. However, during this process, nZVI particles are prone to agglomerate mutually or adsorbed onto soil grains, thereby reducing the reaction sites with the contaminants in the groundwater. Thus, it is necessary to develop a new method to optimize and immobilize nZVI particles.

An electrospun polymer nanofiber mat is an excellent carrier to immobilize nZVI due to its low cost, large specific area, high porosity and its immobility in liquid phases [2]. Traditional electrospun materials are usually polymers, such as polyvinyl alcohol (PVA), nylon-6 and polyvinylidene fluoride (PVDF) and its copolymers, which exhibit high mechanical strength, stretching capability and chemical resistance. However, in terms of immobilizing nZVI particles, these polymers lack specific functional

groups (like carboxylic group, -COOH) to bond with nZVI particles. Polyacrylic acid (PAA) is widely used as a coating of nZVI for groundwater remediation due to its high ratio of -COOH and its nontoxicity in water. However, it is difficult for PAA itself to be fabricated into nanofibers via electrospinning due to its low solution viscosity. Additionally, neat PAA fibers are not stable in water ambience because of its high solubility. Thus, PVA, whose monomer has hydroxide group (-OH), is usually blended with PAA to increase the solution viscosity to produce nanofibers and after electrospinning, is cross-linked with PAA to make it water-insoluble. Xiao et al. [4] first used the electrospun PAA/PVA nanofibers to immobilize nZVI and the fibers-supported nZVI showed superior capability to decolorize acid fuchsine solution. Also, Ma et al. [5] reported the use of electrospun PAA/PVA nanofiber mats to immobilize Fe/Pd bimetallic nanoparticles, which significantly improved the degradation efficiency of trichloroethylene. However, all of the previous reports prepared the PAA/PVA solution at 1:1 mass ratio, whose mole ratio of their monomers was just at 0.61:1. This indicated that the -COOH groups in the mat are much less than the -OH groups and mostly consumed during esterification. Therefore, for getting more of free -COOH groups to bond with nZVI particles, increasing the PAA/PVA ratio is considered to be a theoretically feasible way.

2 MATERIALS & METHODS

2.1 Materials

Polyacrylic acid (PAA, $M_v = 450,000$), polyvinyl alcohol (PVA, 87-89% hydrolysed, $M_w = 85,000-124,000$), ferrous (II) sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$), sodium borohydride ($NaBH_4$), cupric (II) nitrate ($Cu(NO_3)_2$), methylene blue and ethanol were all purchased from Sigma-Aldrich. Deionized (DI) water from a Millipore Milli-Q water system was used; all the oxygen-free water was prepared by purging nitrogen gas for 10 mins to remove the dissolved oxygen and avoid the oxidation of the nZVI. All chemicals were used as received without any modification.

2.2 Solution preparation

In this study, a large number of electrospinning experiments were conducted to find out well-electrospun PAA/PVA nanofiber mats. Concentration of PVA was prepared at 16% while the neat PAA solution was prepared from 16%, 32% and 48 wt% to make the PAA/PVA ratios at 1:1 (M1), 2:1 (M2) and 3:1 (M3) respectively.

2.3 Electrospinning and cross-linking of PAA/PVA nanofiber mats

The electrospinning set-up is shown in Fig.1. Nanofibers were directly fabricated onto a rotating drum collector covered with baking paper in a sealed chamber. All the fabricated mats were electrospun at an employed voltage of 10-20 kV. The tip-to-collector distance (TCD) was 15 cm and the feed flow rate was controlled at 0.5 ml/hr by a syringe pump.

The polymer solution was supplied by a syringe pump attached with a needle. All the mats were fabricated for 8 hrs. After electrospinning, the as-spun mats were removed from the collector and put into a dry oven at 60°C for 1 day to remove the residual solvent. Then, the dried mats were cross-linked by thermal treatment in an oven at 145°C for 30 min to make them water-insoluble.

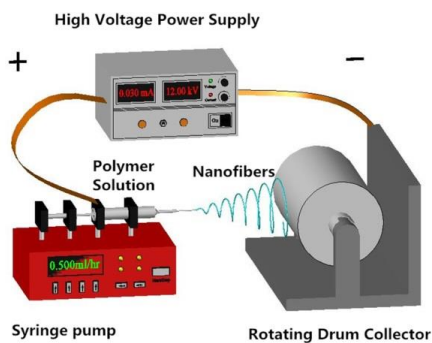
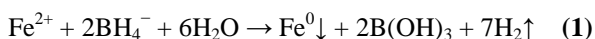


Figure 1. Schematic diagram of the electrospinning configuration

2.4 Synthesis and immobilization of nZVI

As shown in Fig.2, the electrospun mats with different PAA/PVA ratios were soaked into 0.1 mol/L FeSO₄ solution for 6 hrs to allow the complexation of ferrous ions and the rest of free -COOH groups from PAA. Then the mats were rinsed by oxygen-free DI water for the removal of the residual ferrous solution. After that, NaBH₄ solution (0.5 mol/L) was added to the mats drop by drop onto/into the mats in an anaerobic chamber (filled by N₂ gas) to form and immobilize nZVI particles. The reaction is shown below,



The successful formation of nZVI on the electrospun mat is indicated by the change of color of the mat into black, and once the black color was stable, the nZVI-PAA/PVA mats

were rinsed and stored in ethanol in a sealed glass bottle, which was filled with nitrogen gas.

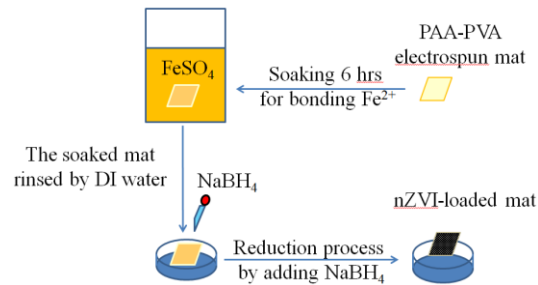


Figure 2. Schematic diagram of nZVI immobilization

2.5 Characterization and measurements

2.5.1 Scanning electron microscopy (SEM)

The surface morphologies of all the mats were observed by scanning electron microscopy (SEM, Zeiss Supra 55VP). Samples taken from each mat were coated by Au/Pd prior to SEM.

2.5.2 Thermo-gravimetric analysis

Thermo-gravimetric analysis (TGA) was carried out on Discovery TGA thermo-gravimetric analyzer (SDT-Q600, United States) from 50°C to 700°C at a heating rate of 10°C/min in N₂ atmosphere.

2.6 Performance of nZVI-PAA/PVA nanofiber mat

2.6.1 Decolorization of Methylene Blue

Methylene blue is a commonly-used chloride dye, selected in this study to test the performance of nZVI-PAA/PVA nanofiber mats. In order to specify the effects of the adsorption of PAA/PVA mats and the reduction of nZVI particles, mats with different PAA/PVA ratios were compared both with and without nZVI. Each mat was soaked in 25 mL of 25 mg/L methylene blue solution and the bare weight of each mat (before soaking in the FeSO₄ solution) in the dye solution was kept at 8 mg. After shaking at 100 rad/min for 6 hrs on a platform mixer, 5 mL supernatant liquid sample was withdrawn for the analysis of decolorization efficiency by an ultraviolet visible spectrophotometer (UV-1700, Shimadzu, Japan) in the wavelength range of 400 to 800 nm. The decolorization efficiency was calculated using the following equation:

$$\text{Decolorization efficiency}(\%) = \frac{C_{\text{int}} - C_{\text{end}}}{C_{\text{int}}} \times 100\% \quad (2)$$

where, C_{int} and C_{end} are the initial and the final methylene blue concentrations, respectively.

2.6.2 Removal of Cu (II)

To further evaluate the contaminants removal capability of nZVI-PAA/PVA mats, Cu(NO₃)₂ solution was also selected in this study to test the performance of nZVI-PAA/PVA nanofiber mats. In order to compare the effect of the adsorption of PAA/PVA mats, electrospun mats with

different PAA/PVA ratios were compared both with and without nZVI. In the similar method as above, each mat (8 mg) was soaked in 25 ml $\text{Cu}(\text{NO}_3)_2$ solution (25 mg/L). The solution was then subjected to shaking using a platform mixer at 100 rad/min for 6 hrs. Supernatant liquid samples (5 ml) were withdrawn for the analysis of Cu (II) concentration via microwave plasma-atomic emission spectrometry (4100 MP-AES, Agilent Technologies, United States). The Cu (II) removal was determined using the following equation:

$$\text{Cu(II) removal efficiency(\%)} = \frac{C_{\text{int}} - C_{\text{end}}}{C_{\text{int}}} \times 100\% \quad (3)$$

where, C_{int} and C_{end} refer to the initial and final Cu (II) concentrations, respectively.

3 RESULTS AND DISCUSSION

3.1 Effect of PAA/PVA ratio on the nZVI loading

the PAA/PVA ratio had a considerable influence on the nZVI loading onto the fibers (Fig. 3). As expected, based from the SEM images, M3 had more nZVI particles loaded on the fiber surface than M2 and M1. Basically, it is observable that there were two types of nZVI particles loaded on the mats. One was on-surface nZVI particles, which were closely attached to the surface of fibers; the other was off-surface nZVI particles, which were off the surface of fibers and attached to other nZVI particles. For M1, the majority of nZVI particles were on-surface and only few nZVI particles were off-surface. In contrast, the majority of nZVI particles on M3 were off-surface and the on-surface nZVI particles were relatively less. The proportion of the two types of nZVI particles in M2 was just between that of M1 and M3.

Possible models were presumed to explain the formation mechanism and morphology of nZVIs on the fiber mats. For M1, most of $-\text{COOH}$ groups on each PAA polymer were esterified with $-\text{OH}$ groups of PVA and formed the backbone of nanofibers. The free $-\text{COOH}$ groups of PAA between $-\text{COO}-$ groups could bond nZVI particles onto the branches of the backbone. Thus, nZVI particles were distributed on the surface of fibers with relatively uniform intervals. For M2, part of $-\text{COOH}$ groups on each PAA polymer were the same as M1 and the nZVI particles were bonded on the branches of the backbone. However, there were still some free $-\text{COOH}$ groups of PAA out of the backbone available to bond nZVI particles. As a result of lack of the interval of $-\text{COO}-$ groups, the $-\text{COOH}$ groups were more compact and hence the nZVI particles were denser. For M3, most of the free $-\text{COOH}$ groups of PAA were out of the backbone and available to bond nZVI particles. Only few $-\text{COOH}$ groups on each PAA polymer were esterified with $-\text{OH}$ groups on the backbone of nanofibers. This resulted in more nZVI particles off the membrane surface.

Meanwhile, the diameter of nZVI particles was found to increase with the increase in PAA/PVA ratio. The

average nZVI particle sizes of the three mats were determined to be 37 ± 18 (M1), 49 ± 28 (M2) and 56 ± 25 nm (M3), respectively. Since the nZVI particles on M1 were more dispersive, they had a lower size. On the contrary, the nZVI particles on M3 were more aggregated therefore leading to a larger size.

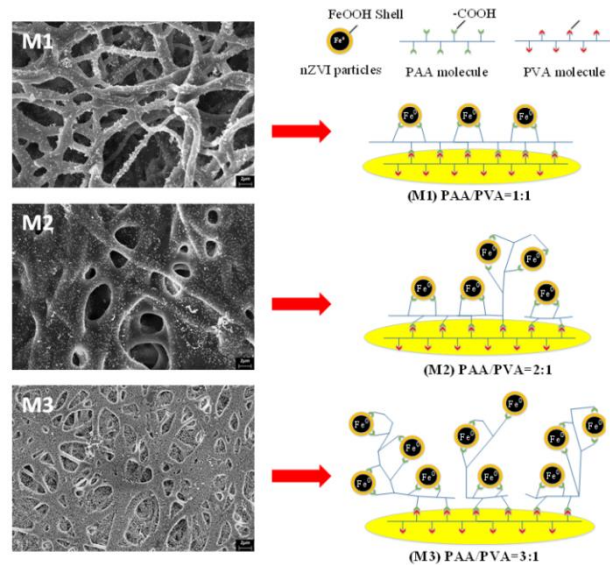


Figure 3. nZVI particle size distributions and SEM-EDS images of nZVI-loaded mats

(a) M1, PAA/PVA=1:1 (b) M2, PAA/PVA=2:1 (c) M3, PAA/PVA=3:1

TGA was used to characterize the loading capacity of immobilized nZVI particles on the cross-linked PAA/PVA nanofiber mats (Fig. 9). There was a slight weight loss on each mat upon heating up to 170°C , which should be due to the evaporation of ethanol and the loss of moisture in the mats.

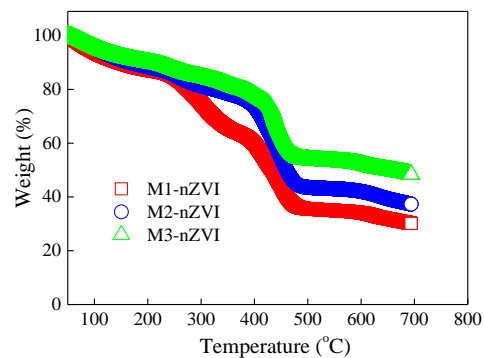


Figure 4. Effect of PAA/PVA ratio on the TGA of nZVI-loaded mats

(M1-nZVI, PAA/PVA = 1:1; M2-nZVI, PAA/PVA = 2:1; M3-nZVI, PAA/PVA = 3:1).

Afterwards, the major weight loss of nZVI-loaded mats at the region from 170 to 500°C is attributed to the decomposition of the PAA/PVA polymers. When it comes

to 700 °C, all the polymeric nanofibers had been burned out, leaving nZVI particles as the residual mass. M3 remained the most nZVI particles at 48% while M2 and M1 obtained 37.3% and 30.2%, respectively. This confirms that more nZVI particles were formed and attached to the fiber mats as also confirmed by other characterization methods explained above.

3.2. Remediation performance of nZVI-decorated cross-linked fiber mats

Methylene blue was selected to test the performance of nZVI–PAA/PVA nanofiber mats with various PAA/PVA ratios. To differentiate the effect of nZVI reduction from mat adsorption, the PAA/PVA mats and the nZVI-PAA/PVA mats were compared in this study. In Fig. 4, it is obvious that all the mats with nZVI had higher removals than those of corresponding mats without nZVI. M3-nZVI had the highest removal of 94% and M2-nZVI was at 84%. Among the nZVI-PAA/PVA mats, M1-nZVI had the minimum removal at 78%, which was even lower than that of M3 at 83%. This could be explained by the significant adsorption effect of PAA/PVA mats. –COOH as well as –OH groups had a strong bonding with methylene blue. As a result, M3 with the highest number of –COOH showed a prominent removal. Meanwhile, M2 had the lowest removal at 49%, even lower than the figure for M1 at 61%. This was probably because the majority of –COOH and –OH groups on the M2 was used to form esters and hence the lowest the groups were left on the mat.

To further check the capability of the present nZVI-loaded mats, Cu (NO₃)₂ was selected to test the performance of nZVI–PAA/PVA nanofiber mats with various PAA/PVA ratios as well. To differentiate the effect of nZVI reduction from mat adsorption, the PAA/PVA mats and the nZVI-PAA/PVA mats were compared in this study. All the mats with nZVI had higher removals than that of corresponding mats without nZVI (Fig.4). M3-nZVI had the highest removal at 83.6%, while the removal of M2-nZVI and M1-nZVI were lower at 70.5% and 59%. These neat mats had a decent effect on the removal on Cu (II) ions as well, particularly M3, whose removal was even higher than that of M1-nZVI and M2-NZVI, at 50.5%.

However, the adsorption effect on Cu (II) ion removal was obviously weaker than that of methylene blue, indicating that the adsorptive capability of –COOH and –OH to Cu (II) ions was lower than to methylene blue. This could be explained by two reasons: One is that the adsorption mechanism of PAA/PVA mats to Cu (II) ion is complexation, which is mainly predominated by –COOH groups rather than –OH groups. Therefore, the adsorption of –OH decreased significantly; the other is that bonding with Cu (II) ion required more –COOH, after the Cu (II) ion is a bivalent heavy metal and methylthionium(I) ion is a monovalent ion. Correspondingly, the adsorption of nZVI-loaded mats to Cu (II) ion were also lower than to methylene blue, thus having a lower removal on Cu (II) ion. Besides, M3 had the highest augment (33.1%) from the neat

mat to the nZVI-loaded mat also because it had the most –COOH groups. In a nutshell, it was effective to boost the removal of Cu (II) ions by increasing the PAA/PVA ratio.

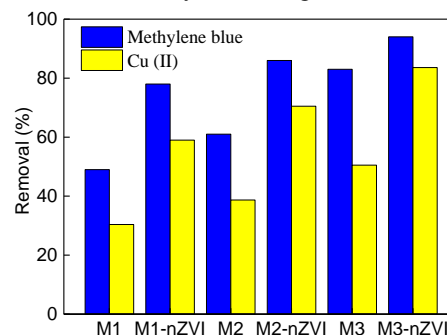


Figure 4. Effect of PAA/PVA ratio on the removal of methylene blue and Cu (II)

4 CONCLUSION

In the present study, we indicate that increasing the PAA/PVA ratio had a great contribution to the loading of nZVI particles and hence improving the decolorization of methylene blue solution and the removal of Cu (II) ions from water. Similarly, it could have great potential in removing other organic contaminants and heavy metals.

Essentially, the increase of PAA/PVA mass ratio is the increase of –COOH/-OH mole ratio. In this study, M3 with the highest –COOH/-OH mole ratio had the most –COOH, which bonded with most nZVI particles (48%). Therefore, M3-nZVI had the highest removals to methylene blue and Cu (II) ions at 94% and 84% respectively. Thus, mat with higher PAA/PVA ratio can immobilize more nZVI particles and had an excellent performance on the application of the groundwater remediation

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