

Nanoscale zero-valent iron/zinc oxide flower-like heterostructure composites: synthesis and removal of selenium in aqueous solution

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In this work, novel flower-like nanoscale zero-valent iron/zinc oxide heterostructure composites were prepared, characterised and used for the enhanced removal of Se(IV) from water. The morphological identification showed that nZVI nanoparticles were uniformly loaded on ZnO nanosheets to minimise their aggregation. Batch experimental results demonstrated that the composites exhibited higher removal efficiency and rate constant on Se(IV) immobilisation than pristine flower-like ZnO and nZVI because of the enhanced dispersion of nZVI nanoparticles. Solution pH, initial Se(IV) concentration as well as interfering ions that affect the removal capacity of Se(IV) were further studied. These results suggested that the composites could be a promising candidate for the potential application in effective remediation of Se-contaminated wastewater.

1. Introduction: Selenium is an essential trace element of the human body and plays an important role in the metabolism. Excessive intake of selenium can lead to poisoning and seriously endanger human health. Selenium usually exists in the form of Se(VI) (selenate, SeO_4^{2-}) or Se(IV) (selenite, SeO_3^{2-}), and is soluble and mobile in water. Since selenium usually enters the human body via drinking water, the removal of selenium from water resources has become an urgent environmental issue [1, 2].

Recently, nanoscale zero-valent iron (nZVI) is widely recognised as one of the most promising adsorbents for the efficient removal of selenium in the subsurface environment [3, 4]. nZVI exhibits a variety of advantages, such as strong reducing power ($E_0 = -0.44$ V), large specific surface area, simple preparation route, and low economic cost. However, there are still some technical challenges in the practical application of nZVI, such as the agglomeration of nZVI due to its high surface energy and magnetic interactions [5–7]. The formation of fractal aggregates or dendrimer will greatly affect the transportation of target ions to the active sites in nZVI particles, which results in the rapid loss of reactivity, durability, and efficiency of nZVI. To solve this problem, immobilisation of the nZVI particles with suitable supporting materials has been proved to be an effective strategy to prevent the aggregation and improve the dispersion of nZVI [4, 8]. Various mechanical supporting materials including natural clay minerals [9], layered double hydroxide [10], mesoporous silica [11], and biochar [12] have been developed in recent studies. The supporting materials with large and stable structure capacity could strongly enhance the immobilisation capability of nZVI in toxic contaminant scavenging and allow nZVI to work under different conditions.

In this study, the flower-like heterostructure composites composed of nZVI and ZnO was facilely synthesised and the Se(IV) removal properties was investigated in aqueous solution. Morphology characterisations show that the nZVI particles are uniformly decorated on the ZnO nanosheets and display typical core-shell structures. It is demonstrated that the stability and dispersity of nZVI particles have been largely improved due to the hierarchical porous structure and the affinity of ZnO. The Se(IV) removal tests confirm that nZVI/ZnO composites exhibit great capability for the adsorption of Se(IV) ions, providing new insights into the

application of nZVI-based heterostructure composites in selenium immobilisation in contaminated wastewater.

2. Experimental details: Flower-like ZnO (f-ZnO) was synthesised according to a previous report [13]. The as-prepared f-ZnO (1.0 g), FeCl_3 (0.4 g), and KH_2PO_4 (0.01 g) were successively added into distilled water (300 ml) and the mixture was reacted at 110°C for 60 h. After reaction, the suspension was centrifuged, washed with ethanol, and dried at 80°C overnight. Then, the collected powder was transferred to a tubular furnace with ultrapure hydrogen flow at 500°C for 2 h to obtain the nZVI/ZnO composites.

Sample characterisation: The powder XRD patterns were recorded on a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54$ Å) with a scanning rate 3°/min. The Brunauer–Emmett–Teller (BET) surface area was tested by a V-Sorb/2800TP nitrogen adsorption–desorption instrument operated at 77 K. The pore size distribution of the sample was determined by assuming cylindrical pore model via Barret–Joyner–Halender (BJH) method. X-ray photoelectron spectroscopy (XPS) data were collected from Shimadzu Amicus X-ray photoelectron spectrometer. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were performed on a JEOL JEM-2100 nanoscope operating at an accelerating voltage of 100 kV.

Batch experiments: Se(IV) removal by different samples was performed by adding the samples (0.5 g l^{-1}) into 100 ml Se(IV) solutions (25.0 mg l^{-1}) at room temperature in glass conical flasks. Then, the flasks were shaken at 200 rpm immediately. The samples were taken out from the solution by filtration, and the concentrations of Se(IV) remaining in the solutions were measured to calculate the removal capacity. The concentrations of Se(IV) in the solution samples were recorded by using Perkin-Elmer Optimal 2100DV inductively coupled plasma-optical emission spectrometry.

3. Results and discussion: The XRD pattern of the f-ZnO and nZVI/ZnO composite are displayed in Fig. 1a. All samples exhibit the intense diffraction peaks at $2\theta = 31.7^\circ$, 34.4° , 36.2° , 47.5° , 56.5° , and 62.8° , which are indexed to the (100), (002), (101), (102), (110), and (103) planes of hexagonal wurtzite ZnO

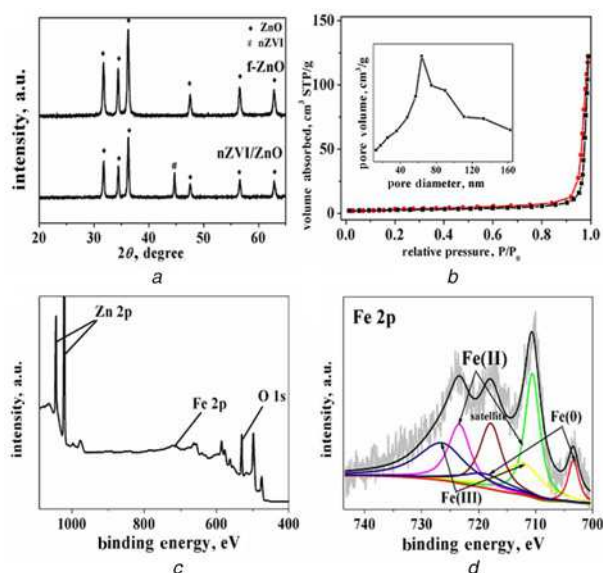


Fig. 1 Characterisations of the nZVI/ZnO composite
a XRD pattern
b N₂ adsorption–desorption isotherm
c XPS spectra
d High-resolution XPS of Fe 2p
Inset of (b): BJH pore size distribution of the composite

(JCPDS No. 36-1451), respectively. For nZVI/ZnO composite, an obvious additional peak at $2\theta = 44.7^\circ$ can be assigned to Fe(0), indicating the formation of nZVI particles on the surface of ZnO. Fig. 1b shows the nitrogen adsorption–desorption isotherms of the nZVI/ZnO composite. The composite exhibits a type III isotherm with an upward deviation in the relative pressure range of 0.8–0.95, implying the presence of macroporous structures in the composite. The inset displays a narrow BJH pore size distribution with macropores mainly around 65 nm and the BET surface area is calculated to be $\sim 11.35 \text{ m}^2 \text{ g}^{-1}$. The unique porous structure and large specific surface area are more favourable for the reduction of Se(IV) and Se(IV) species.

The XPS spectra are used to further prove the formation of nZVI in the heterostructure composite. The survey spectrum in Fig. 1c shows the presence of Zn, Fe, and O elements in the composite. The high-resolution XPS spectrum of Fe 2p region is displayed in Fig. 1d. As can be seen, three iron species with different oxidation state (i.e. Fe(0), Fe(II), and Fe(III)) are simultaneously present in the composite sample. Two peaks centred at binding energies of ~ 710.7 and ~ 723.6 eV demonstrate the existence of Fe(II) species, whereas the peaks centred at binding energies of ~ 712.0 and ~ 726.5 eV with a satellite peak at ~ 718.0 eV are assigned to the Fe(III) species. Besides, the characteristic peaks located at binding energies of ~ 703.4 and ~ 718.8 eV are attributed to metallic Fe(0) species, which indicates the successful fabrication of nZVI particles in the composite.

The size and dispersity of the nZVI particles located on f-ZnO are important for the adsorption and reduction functions for Se(IV) removal, as confirmed in previous reports. The morphology of the nZVI/ZnO composites are characterised by SEM and TEM techniques. In Figs. 2a and b, it is observed that the composites exhibit typical flower-like structures with an average size of 1.5–3 μm which are comprised by numerous nanosheets. Rough globular particles are decorated on the nanosheets which indicates the formation of nZVI nanoparticles. Fig. 2c shows the TEM image of the selected edge area of the nanostructures, confirming the well dispersion of nZVI nanoparticles on ZnO nanosheet. Meanwhile, it can be observed that the nZVI nanoparticles show an average size of ~ 32 nm and exhibit typical core–shell particle architecture. As further characterised by HRTEM in Fig. 2d, the

nZVI nanoparticle has a core composed of Fe(0) and an outer shell composed of Fe(II) and Fe(III) because of the inevitable oxidation of nZVI surface. Owing to the surface oxidation, cavity layer with a thickness of 2–6 nm between the core and shell regions is generated, which may be extremely useful for the adsorption and reduction of Se(IV) ions.

The removal efficiency and rate constant of Se(IV) in aqueous solution using f-ZnO, nZVI, and nZVI/ZnO composite are carried out with an initial concentration of 25.0 mg/l. In Fig. 3a, the removal

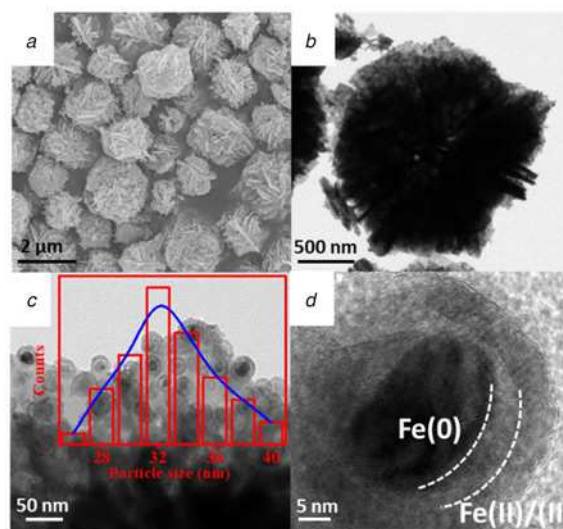


Fig. 2 Morphology of the nZVI/ZnO composite
a SEM image
b, c TEM image
d HRTEM image
Inset of (c): particle size distribution of nZVI loaded on ZnO

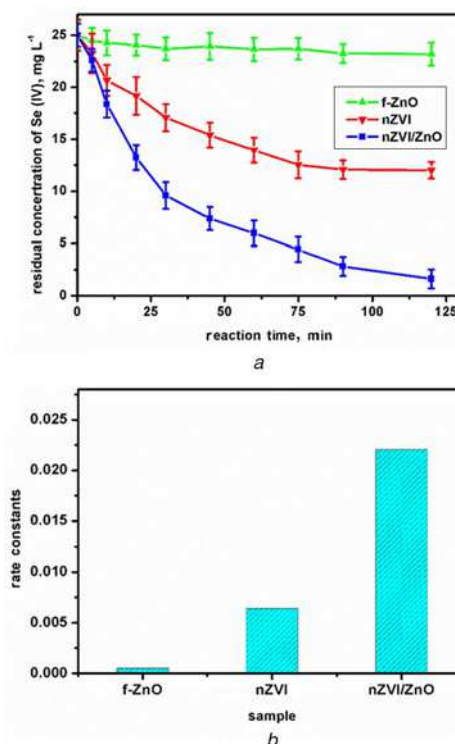


Fig. 3 The Se(IV) removal properties of the samples
a Removal efficiency of Se(IV)
b Rate constant of Se(IV) using f-ZnO, nZVI and nZVI/ZnO composite

efficiencies of Se(IV) were ~ 7.2 , ~ 51.9 , and $\sim 93.5\%$ after contacting for 2 h, when f-ZnO, nZVI, and nZVI/ZnO composite are individually added. The highest Se(IV) removal efficiency of nZVI/ZnO composite demonstrates that the reactivity of nZVI are significantly enhanced when f-ZnO was introduced. The results suggest that f-ZnO can improve the particle dispersity and stability of nZVI nanoparticles to enhance their surface reduction rate. The kinetic process according to the experimental data can be optimally described by a pseudo-first-order model and the equation can be integrated into: $\ln(c/c_0) = -Kt$, where K is called the rate constant (min^{-1}). K is equal to the slope of the line that is obtained by plotting $\ln(c/c_0)$ versus time under certain conditions and is considered as indicative of the reactivity for a given material. The plots of $\ln(c/c_0)$ versus time shows linear plots with correlation coefficients (R^2) higher than 0.9, demonstrating that the removing rates of Se(IV) can be well described by the pseudo-first-order model. The rate constants are observed to be in the order of nZVI/ZnO > nZVI > f-ZnO, which also indicated the improvement in the removal efficiency of nZVI/ZnO is owing to the better dispersion of nZVI nanoparticles located on f-ZnO.

The effect of pH on the removal capacity of nZVI/ZnO composite is investigated in the range of 4–9. It is shown in Fig. 4a that the Se(IV) removal capacity significantly decreased with the increase of solution pH. The sample exhibited a highest Se(IV) removal capacity of 47.66 mg g^{-1} at pH 4, while it reduced to 30.67 mg g^{-1} at pH 9. The remarkable pH-dependent immobilisation of Se(IV) may be owing to the negatively charged surface of nZVI in alkaline environment. It has been reported that the electrostatic repulsion between the Se(IV) and negatively charged surface may decrease the reactive sites for Se(IV) reduction [14]. Besides, the formation of the Fe(II)/Fe(III) hydroxide shell will also occupy the reactive sites on nZVI surface and decrease its reactivity, thus resulting in lower Se(IV) removal capacities.

Fig. 4b displays the effect of initial Se(IV) concentration on Se(IV) removal capacity of the as-prepared composite. It can be seen that the removal capacity first increases and then decreases at an initial Se(IV) concentration of 15–45 mg/l. The decrease of removal capacity is mainly attributed to the reduction of the reactivity of nZVI. Since more Se(IV) ions approach and are reduced at the surface of nZVI, more Fe(0) will be oxidised and the thickness of the Fe(II)/Fe(III) outer shell increases which results in a non-negligible decrease in Se(IV) ion transfer rate.

To determine the influence of the co-anions on Se(IV) removal capacity, SO_4^{2-} , NO_3^- , Cl^- , SiO_3^{2-} , and CO_3^{2-} are added as

competing anions and the results are shown in Fig. 4c. It is clear that the tested anions all show a certain inhibitory effect on Se(IV) immobilisation. The loss of removal capacity of nZVI/ZnO composite in the presence of anions decreases in the following order: $\text{SO}_4^{2-} \approx \text{SiO}_3^{2-} < \text{Cl}^- < \text{NO}_3^- < \text{CO}_3^{2-}$. It is worthy to note that the presence of CO_3^{2-} decreases the removal capacity to 39.03 mg g^{-1} , which shows the greatest negative effect on Se(IV) immobilisation. The high negative charge density of CO_3^{2-} make the anions easier to absorb on the surface of nZVI particles, resulting in fewer active sites for Se(IV) reduction.

4. Conclusion: In summary, we have successfully fabricated nZVI/ZnO flower-like heterostructure composites with high Se(IV) removal performance. Due to the well-dispersion of nZVI on f-ZnO, the composites exhibit good removal efficiency up to $\sim 93.5\%$ and high rate constant. Further batch experiments are conducted by changing reaction conditions such as pH, initial Se(IV) concentration, and interfering ions. This work provides a novel nanomaterials for the immobilisation of Se(IV) from contaminated wastewater. This work will benefit the development of novel heterostructure nanomaterials and may have potential applications in toxic ions removal in water by nZVI-derived materials.

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6 References

- [1] Ling L., Pan B., Zhang W.: ‘Removal of selenium from water with nanoscale zero-valent iron: mechanisms of intraparticle reduction of Se(IV)’, *Water Res.*, 2015, **71**, pp. 274–281
- [2] Song J., Liu Z., Wang X., ET AL.: ‘High-efficiency bubble transportation in an aqueous environment on a serial wedge-shaped wettability pattern’, *J. Mater. Chem. A*, 2019, **7**, pp. 13567–13576
- [3] Xie Y., Dong H., Zeng G., ET AL.: ‘The comparison of Se(IV) and Se(VI) sequestration by nanoscale zero-valent iron in aqueous solutions: the roles of solution chemistry’, *J. Hazard. Mater.*, 2017, **338**, pp. 306–312
- [4] Cao R.S., Fan M.Y., Hu J.W., ET AL.: ‘Artificial intelligence based optimization for the Se(IV) removal from aqueous solution by reduced graphene oxide-supported nanoscale zero-valent iron composites’, *Materials*, 2018, **11**, (3), p. 428
- [5] Liang L.P., Xue Y.Y., Tian G.L., ET AL.: ‘Performance of selenate removal by biochar embedded nano zero-valent iron and the biological toxicity to escherichia coli’, *RSC Adv.*, 2019, **9**, (45), pp. 26136–26141
- [6] Yang Z., Xu H., Shan C., ET AL.: ‘Effects of brining on the corrosion of ZVI and its subsequent As(III/V) and Se(IV/VI) removal from water’, *Chemosphere*, 2017, **170**, pp. 251–259
- [7] Prabu D., Parthiban R., Ponnusamy S.K., ET AL.: ‘Sorption of Cu(II) ions by nano-scale zero valent iron supported on rubber seed shell’, *IET Nanobiotechnol.*, 2017, **11**, (6), pp. 714–724
- [8] Suazo-Hernández J., Sepúlveda P., Manquían-Cerda K., ET AL.: ‘Synthesis and characterization of zeolite-based composites functionalized with nanoscale zero-valent iron for removing arsenic in the presence of selenium from water’, *J. Hazard. Mater.*, 2019, **373**, pp. 810–819
- [9] De León M.A., Sergio M., Bussi J., ET AL.: ‘Application of a montmorillonite clay modified with iron in photo-Fenton process. Comparison with goethite and nZVI’, *Environ. Sci. Pollut. Res.*, 2015, **22**, (2), pp. 864–869
- [10] Sheng G., Hu J., Li H., ET AL.: ‘Enhanced sequestration of Cr(VI) by nanoscale zero-valent iron supported on layered double hydroxide by batch and XAFS study’, *Chemosphere*, 2016, **148**, pp. 227–232

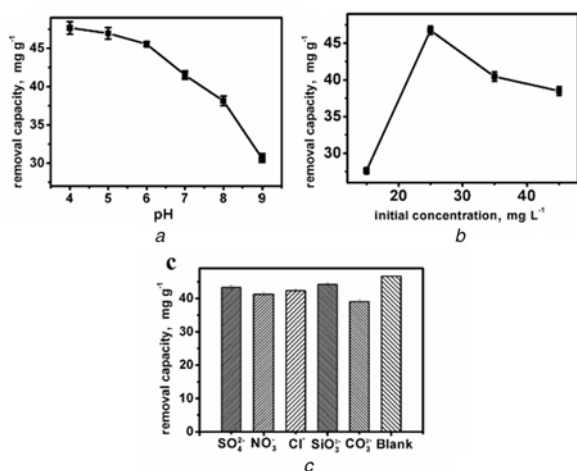


Fig. 4 Effect of
a pH
b Initial concentration
c Co-existing ions on Se(IV) removal capacity of nZVI/ZnO composite

- [11] Petala E., Dimos K., Douvalis A., *ET AL.*: 'Nanoscale zero-valent iron supported on mesoporous silica: characterization and reactivity for Cr (VI) removal from aqueous solution', *J. Hazard. Mater.*, 2013, **261**, pp. 295–306
- [12] Shang J., Zong M., Yu Y., *ET AL.*: 'Removal of chromium (VI) from water using nanoscale zerovalent iron particles supported on herb-residue biochar', *J. Environ. Manage.*, 2017, **197**, pp. 331–337
- [13] Hu B., Ye F., Jin C., *ET AL.*: 'The enhancement roles of layered double hydroxide on the reductive immobilization of selenate by nanoscale zero valent iron: macroscopic and microscopic approaches', *Chemosphere*, 2017, **184**, pp. 408–416
- [14] Yu H., Chu Y., Zhang T., *ET AL.*: 'Recovery of tellurium from aqueous solutions by adsorption with magnetic nanoscale zero-valent iron (NZFe)', *Hydrometallurgy*, 2018, **177**, pp. 1–8