Removal of Hexavalent Chromium Using Nanoscale Zero-Valent Iron Stabilized by Poly (γ-Glutamic Acid)

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Hexavalent chromium (Cr(VI)) is one of the most toxic components in heavy metal pollution. The reduction of highly toxic Cr(VI) into much less toxic trivalent chromium (Cr(III)) is a promising and common method of remediating Cr(VI) contamination. Nanoscale zero-valent iron (nZVI) is an important nanoparticle to facilitate environmental remediation. It was reported on the fabrication of a bionanocomposite (nZVI@PGA), i.e. nZVI stabilized and modified by poly (γ-glutamic acid) (PGA). The bionanocomposite was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The processes of Cr(VI) conversion by nZVI, PGA and nZVI@PGA were investigated and optimized. Compared to unmodified nZVI, nZVI@PGA displayed higher activity in acidic environment. The pH and PGA loading were optimized. The maximum unit removal of Cr(VI) by nZVI@PGA can reach 340 mg/g in acidic environment. The results demonstrated that nZVI@PGA can convert about 97.3 % Cr(VI) (initial concentration was 20 mg/L) in 30 min at pH=3. nZVI@PGA owns high stability and reactivity, and has potential to remove Cr(VI) of sewage in the future.

1. Introduction

Hexavalent chromium pollution has become an increasingly common type of pollution, mainly due to paper, leather, and metallurgical industries (Dong et al., 2016). The main forms of chromium are hexavalent and trivalent, while hexavalent chromium (Cr(VI)) is easier to migrate and approximately 1,000 times more toxic than trivalent chromium (Cr(III)) (Chen et al., 2015). Cr(VI) is not only harmful to human health, but also to plants and microorganisms. It was now an urgent task to remove the Cr(VI) from wastewater.

nZVI owns better adsorption and reduction effect in the field of hexavalent chromium removal from wastewater or contaminated soil (Mouhamadou et al., 2015). As a new type of nanomaterial, nZVI has a lot of advantages, such as large specific surface area, stronger adsorption and reduction capabilities (Dong et al., 2012). nZVI still has some deficiencies in the application of pollutant removal, including the agglomeration and facile oxidation (Guan et al., 2015). Due to the van der Waals and attractive magnetic forces, nZVI aggregates easily to form large particles, which caused the reactivity of nZVI to decrease severely (Xie et al., 2017). To solve this problem, many researchers have applied various carriers to stabilize nZVI and disperse nanoscale iron particles, such as carboxymethyl cellulose, bentonite, sodium alginate, resin, and biochar. As a macromolecular polymer, PGA was widely used in industrial fields due to its excellent adsorption performance (Elizabeth et al., 1999). PGA has been applied as an adsorbent to study the adsorption effect of divalent copper ions (Hu et al., 2017). To remove the divalent cobalt, the adsorption effect of PGA had been investigated (Zakariyah et al., 2017). The complexation of PGA with lead ions was carried out to remove the lead pollution (Magdolna et al., 2008). In the lab, the previous work had proved that nZVI modified by PGA had excellent performance of stability and dispersion, degrading p-chlorophenol more than 90 % in 30 min (Zhang et al., 2018). When the composite material includes PGA–dopamine and Fe-Pd nanoparticles, the degradation rate of p-chlorophenol almost reached 100 % in 60 min (Zhang et al., 2018). PGA has many carboxyl groups, which can provide static and

spatial repulsion to disperse nano-scale iron particles (Elizabeth et al., 1999). nZVI modified by PGA is a stable system, which has potential to remove the pollution of Cr(VI) from water.

To our knowledge, there is no report on nZVI@PGA application on the reduction of Cr(VI) to Cr(III). The major work of this paper includes preparation of PGA-modified nZVI materials (nZVI@PGA), characterization of nZVI@PGA, and application and optimization of nZVI@PGA for Cr(VI) removal.

2. Materials and methods

Poly (γ-glutamic acid) (PGA, MW 100,000–50,000 kDa) was purchased from Yuanye Bio-Technology (Shanghai, China). Ferrous sulfate heptahydrate ($FeSO_4·7H_2O$, > 99.0 %), potassium borohydride (KBH_4, 97 %), potassium dichromate ($K_2Cr_2O_7$, ≥ 99.8 %), diphenyl semicarbazide ($C_{13}H_{14}N_4O$) and sodium hydroxide (NaOH, 96 %) were supplied by Aladdin Reagent Company (Shanghai, China). Hydrochloric acid (HCl, 36-38 %), sulfuric acid (H_2SO_4, 95-98 %) were purchased from Jiangtian Chemical Technology (Tianjin, China). All chemicals were used without further purification. All water was purified by a water purification system (arium pro VF, Sartorius Germany).

2.1 Preparation of nZVI@PGA

The nZVI@PGA was prepared by the method of borohydride reduction. The total reaction volume was 50 mL. Then, 25 mg $FeSO_4·7H_2O$ was added into PGA solution which included different amounts of PGA (0.1, 0.5, 1 and 2 mg), and always under the protection of nitrogen to create an anaerobic environment. Next, 15 mg KBH_4 were dissolved in 3 mL deionized water to form a solution that dropped to the mixing system. When the Fe^{2+} reacted with BH_4^- to give Fe^0, it was necessary to purge nitrogen for 20 min to eliminate the excess of hydrogen (Abel et al., 2017). pH was kept constant in the nZVI@PGA solution by addition of hydrochloric acid or sodium hydroxide. The preparation of nZVI@PGA was carried out in a water bath with constant temperature at 25 °C. The synthesized system was poured into a conical flask containing hexavalent chromium solution.

2.2 Characterizations

The morphology of nZVI@PGA was studied by scanning electron microscopy (S-4800, Hitachi, Japan). The composition and stability of nZVI@PGA were characterized by X-ray diffraction (D8-Focus, Bruker, Germany) and settlement experiment (Zhang et al., 2018).

2.3 Batch experiments of Cr(VI) removal

1 g/L stock solution of Cr(VI) was prepared by dissolving potassium dichromate in water at 25 °C. Then, the prepared nZVI@PGA system was poured into four 150 mL conical flasks containing the stock solution of Cr(VI) (1, 2, 2.5, 4 mL), so that the initial Cr(VI) concentration was 20, 40, 50, 80 mg/L. In these mixed systems, different mass ratio Fe:Cr(VI) (5:1, 2.5:1, 2:1, 1.25:1) were obtained to explore the effect of initial hexavalent chromium concentration on Cr(VI) removal. At the same time, it is also necessary to consider the effect on the removal of Cr(VI) at different pH (3, 6, 9) and temperature (15, 25, 35, 45 °C) values. According to the time node of the experimental design, 1 mL of sample solution was took out from the mixed systems each time. The absorbance of Cr(VI) was measured with a spectrophotometer at a wavelength of 540 nm. The Cr(VI) concentration was calculated according to the calibration curve, designed in the 0.02 mg/L-5 mg/L concentration range, and having a coefficient of determination of 0.9996. All experimental measurements were repeated twice.

3. Results and discussion

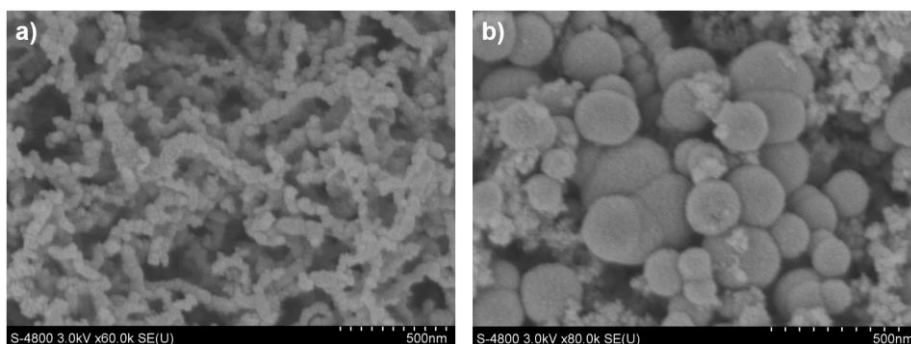### 3.1 Characterization of nZVI@PGA

Figure 1: SEM micrographs of the (a) nZVI and (b) nZVI@PGA

The morphologies and size of nZVI and nZVI@PGA were characterized by SEM. As shown in Figure 1a, in the absence of PGA in synthesis process, the resulted nZVI formed chain aggregations. Figure 1b shows that the majority of nZVI@PGA had relatively spherical shapes and smooth surfaces in the size range of 50−150 nm. In general, the results proved that nZVI was easily oxidized and PGA could inhibit the aggregation and restrain oxidation.

3.2 Cr(VI) removal by nZVI@PGA

Under acidic conditions (pH=3), the removal of Cr(VI) with nZVI@PGA was studied through batch tests. Figure 3a shows the amount of Cr(VI) (20 mg/L) removed followed the order PGA<nZVI<nZVI@PGA. Compared with nZVI and PGA, nZVI@PGA was the most effective for Cr(VI) removal, and the amount removed in 30 min was twice compared to that obtained with nZVI. Bare PGA had little effect on the removal of Cr(VI) with approximately 3 % removal in 150 min. According to the theory of surface-mediated reactions, the reactivity was directly proportional to the effective surface area (Choe et al., 2001). nZVI@PGA presents better dispersion and a large specific surface area, indicating that the removal of Cr(VI) was more efficient and the removal amount can reach 97 % in 30 min. As shown in Figure 3a, nZVI@PGA was much more efficient and faster on the removal of Cr(VI). In this study, when the mass ratio Fe:Cr(VI) was 5:1 and pH=3, nZVI@PGA exhibited high activity on the removal of Cr(VI), which shows that nZVI@PGA is a promising nanomaterial. The sketch of Cr(VI) removal was shown in Figure 2.
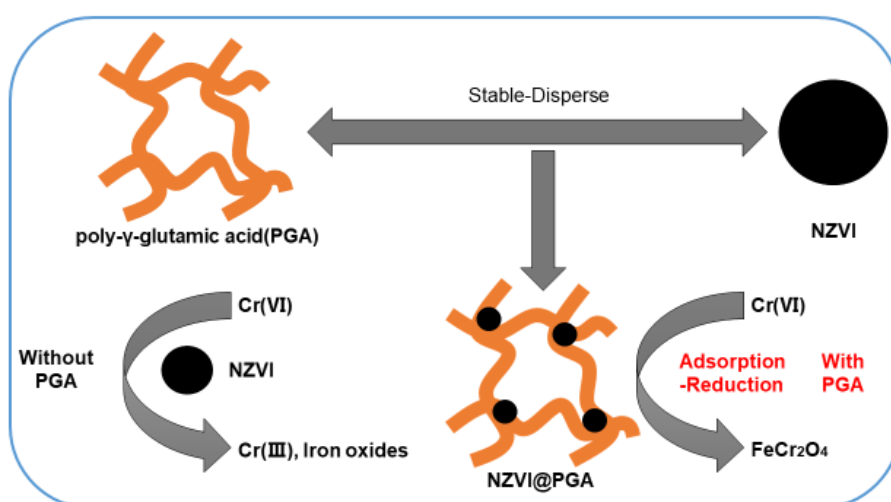

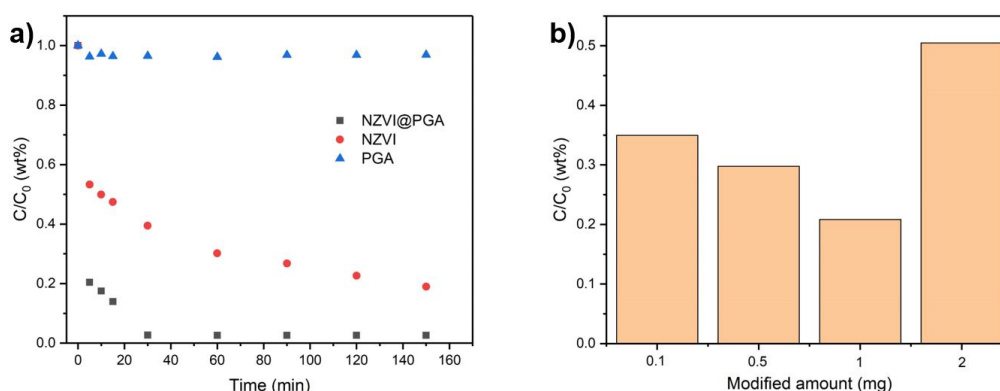Figure 2: Schematic diagram for the synthesis of nZVI@PGA and the removal of Cr(VI)

Figure 3: (a) Time curve of Cr(VI) (20 mg/L) removal using PGA, nZVI and nZVI@PGA (pH=3.0, T=25 °C); (b) Effect of Cr(VI) (40 mg/L) removal under different PGA loadings (pH=3.0, T=25 °C)

3.3 Effect of nZVI to PGA mass ratio on the removal of Cr(VI) by nZVI@PGA

As shown in Figure 3b, the effects of Cr(VI) removal was studied by changing the nZVI:PGA mass ratio (50:1, 10:1, 5:1 and 2.5:1). The result shows that the maximum removal amount was 79.15 % when the mass ratio nZVI:PGA was 5:1. Known from the characterized SEM image, nZVI particles were easier to gather when the proportion of PGA was small. When the PGA mass ratio increased, the nZVI particle was present better dispersion, which provided more active sites for Cr(VI) removal. Excessive PGA loading prevented nZVI from reacting with Cr(VI), indicating that active sites and specific surface area of nZVI were reduced. Many studies had proven this phenomenon, for example, nZVI supported by biochar to remove the methyl orange (Han et al., 2015). The best mass ratio nZVI:PGA was 5:1, which showed efficient removal effect for the Cr(VI).

3.4 Effect of pH on the removal of Cr(VI) by nZVI@PGA

Figure 4 shows that the initial pH of nZVI@PGA had a significant effect on the removal of Cr(VI). When the initial pH increased, the amount of Cr(VI) removed was severely reduced, which can only reach 18.6 % at pH=9 and 28.6 % at pH=6 in 150 min. The reduction rate of nZVI@PGA decreased significantly with the increased initial pH, indicating that lower pH was beneficial for the removal of Cr(VI). According to previous literature reports, $HCrO_4^-$ was the main form of Cr(VI) in the acidic solution and CrO_4^{2-} in the alkaline solution (Dinesh et al., 2006). Under acidic conditions, the main reaction was shown in Eq 1.

$$2HCrO_4^- + 3Fe^0 + 14H^+ \rightarrow 2Cr^{3+} + 3Fe^{2+} + 8H_2O \tag{1}$$

In acidic environment, H^+ ions speed up the reaction with $HCrO_4^-$, and the electrostatic interactions between nZVI@PGA and Cr(VI) increased the adsorption of Cr(VI) onto the surface for removal (Shi et al., 2011). The electrostatic repulsion between nZVI@PGA and CrO_4^{2-} might inhibit the Cr(VI) absorption onto the composite material in alkaline environment. Cr(III) and Fe(III) produced during the reactions were easily accumulated on the surface of nZVI@PGA, which prevented further reduction (Fang et al., 2011).
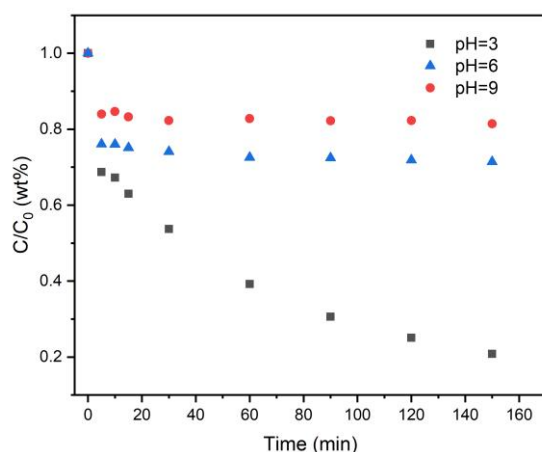

Figure 4: Cr(VI) (40 mg/L) removal by nZVI@PGA at different initial pH (T=25 °C)

3.5 Effect of initial Cr(VI) concentration on the removal of Cr(VI) by nZVI@PGA

Figure 5a shows the effect of initial Cr(VI) concentration for the removal of Cr(VI) at pH=3. When the initial Cr(VI) concentration was 40, 50, and 80 mg/L, the amount of Cr(VI) removed was about 79.2 %, 68.8 %, 51.1 % in 150 min. Besides, nZVI@PGA removed Cr(VI) faster, which can achieve 97.3 % in 30 min when initial Cr(VI) concentration was 20 mg/L. When the initial Cr(VI) concentration was raised from 20 to 80 mg/L in acidic environment, the unit removal capacity of nZVI@PGA increased from 160 to 340 mg/g. Compared with other composite materials, such as activated carbon supported nZVI (AC/nZVI) (Soroosh et al., 2018), biochar supported nZVI (nZVI-BC) (Fan et al., 2019), and silicon rich biochar supported nZVI (nZVI-RS700) (Qian et al., 2019), nZVI@PGA was more efficient for the removal of Cr(VI) as shown in Table 1. The unit remova (U_r, mg/g) of nZVI@PGA was calculated by Eq 2,.where M_{Cr} was the mass of Cr(VI) removed, and M_{Fe} was the total mass of nZVI@PGA in the reaction. The unit removal capacity could decrease when nZVI was overloaded (Zhang et al., 2018). When the initial concentration of Cr(VI) was excessive, nZVI will be oxidized quickly so that the

Cr(III)/Fe(III) oxides/hydroxides stacked on the surface of nZVI@PGA, making it unavailable for further reduction (Liu et al., 2010).

$$Ur = M_{Cr} / M_{Fe} \tag{2}$$

Table 1: The unit removal of nZVI@PGA compared with other composite material (pH=3.0)

Composite material	AC/nZVI	nZVI-BC	nZVI-RS700	CMC-nZVI	nZVI@PGA
Unit removal (mg/g)	3.3	14.5	111.9	136.0	162.2
Time (h)	48	5	24	0.5	0.5

3.6 Effect of temperature on the removal of Cr(VI) by nZVI@PGA

As shown in Figure 5b, when the initial temperature increased, nZVI@PGA removed Cr(VI) more efficiently. When the initial temperature increased from 15 to 45 °C, the removal amount was from 71.6 % to 89.7 % in 150 min. The ion diffusion became more intense as temperature was raised, giving nZVI@PGA more chance to react with Cr(VI) (Shi et al., 2011). Consequently, when the temperature increased, the reaction rate was also raised, which significantly reduced the time for the removal of Cr(VI) (Manning et al., 2007).
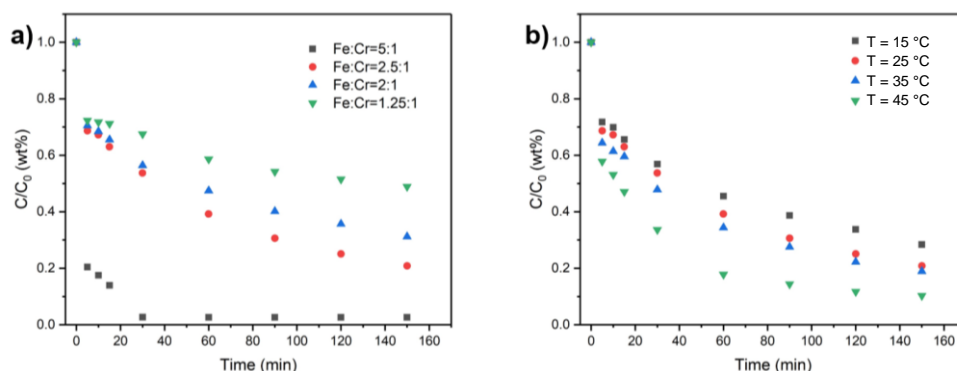

Figure 5: Degradation curves of Cr(VI) removal at (a) different initial concentrations (20, 40, 50, 80 mg/L) and (b) different temperatures (pH=3.0)

4. Conclusions

The main work was to investigate the feasibility of the Cr(VI) removal with nZVI on support of PGA. The results show that nZVI@PGA was better than nZVI, having excellent reduction effect for Cr(VI). When the mass ratio nZVI:PGA was 5:1, nZVI@PGA showed a better stability and dispersion. Cr(VI) removal by nZVI@PGA can reach 97.3 % in acidic solution, indicating that low pH can promote the reaction. The maximum unit removal of nZVI@PGA was 340 mg/g, which was more efficient than AC/nZVI, nZVI-BC and nZVI-RS700. The higher temperature facilitates the diffusion of ions, which is beneficial for the removal of Cr(VI). Besides, the Cr(III)/Fe(III) hydroxides produced precipitation, eliminating potential secondary pollution issues to the environment. The results indicate that nZVI@PGA is an efficient composite material for the removal of Cr(VI), especially in acidic environment.

Acknowledgments

References

Abel M.M., Gunel R.A., Ulviyya A.H., Mahammadali A.R., Luca D.P., 2017, Synthesis and application of zeolite and glass fiber supported zero valent iron nanoparticles as membrane component for removal nitrate and Cr (+6) ions, Chemical Engineering Transactions, 60, 163–168.
Chen T., Zhou Z.Y., Xu S., Wang H.Y., Lu W.J.,2015, Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge, Bioresource Technology, 190, 388–394.
Choe S., Lee S.H., Chang Y.Y., Hwang K.Y., Khim J., 2001, Rapid reductive destruction of hazardous organic compoundsby nanoscale Fe^0, Chemosphere, 42(4), 367-372.

Dinesh M., Charles U.P., 2006, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, Journal of Hazardous Materials, 137, 762-811.

Dong H.R., Guan X.H., Irene M.C.L., 2012, Fate of As(V)-treated nano zero-valent iron: determination of arsenic desorption potential under varying environmental conditions by phosphate extraction, Water Research, 46(13), 4071–4080.

Dong H.R., He Q., Zeng G.M., Tang L., Zhang C., Xie Y.K., Zeng Y.L., Zhao L., Wu Y.N., 2016, Chromate removal by surface-modified nanoscale zero-valent iron: Effect of different surface coatings and water chemistry, Journal of Colloid and Interface Science, 471, 7–13.

Elizabeth G., Thomasin C.M., Jose R.G., James A.H., 1999, Characterization of immobilized poly-L-aspartate as a metal chelator, Environmental Science Technology, 33, 1664–1670.

Fan Z.X., Zhang Q., Gao B., Li M., Liu C.Y., Qiu Y., 2019, Removal of hexavalent chromium by biochar supported NZVI composite: Batch and fixed-bed column evaluations, mechanisms, and secondary contamination prevention, Chemosphere, 217, 85-94.

Fang Z.Q., Qiu X.Q., Huang R.X., Qiu X.H., Li M.Y., 2011, Removal of chromium in electroplating wastewater by nanoscale zero-valent metal with synergistic effect of reduction and immobilization, Desalination, 280(1-3), 224-231.

Guan X.H., Sun Y.K., Qin H.J., Li J.X., Irene M.C L., He D., Dong H.R., 2015, The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: the development in zero-valent iron technology in the last two decades (1994–2014), Water Research, 75, 224–248.

Han L., Xue S., Zhao S.C., Yan J.C., Qian L.B., Chen M.F., 2015, Biochar supported nanoscale iron particles for the efficient removal of methyl orange dye in aqueous solutions, Plos One, 10(7), e0132067.

Hu P.G., Zhang F.S., Shen F., Yu X., Li M.S., Ni H., Li L., 2017, Poly-g-glutamic acid coupled pseudomonas putida cells surface-displaying metallothioneins: composited copper(II) biosorption and inducible flocculation in aqueous solution, RSC Advances, 7, 18578–18587.

Liu T.Y., Zhao L., Sun D.S., Tan X., 2010, Entrapment of nanoscale zero-valent iron in chitosan beads for hexavalent chromium removal from wastewater, Journal of Hazardous Materials, 184(1-3), 724-730.

Magdolna B., Anna-Lena K., Reka M.M., John F.H., Lajos D., Bo N., Janos B., 2008, Nanoparticles formed by complexation of poly-gamma-glutamic acid with lead ions, Journal of Hazardous Materials, 153, 1185-1192.

Manning B.A., Kiser J.R., Kwon H., Kanels S.R., 2007, Spectroscopic investigation of Cr (III)-and Cr (VI)-treated nanoscale zerovalent iron, Environmental Science Technology, 41, 86-592.

Mouhamadou T.G., Elisabetta P., Luca D.P., 2015, Chemical reduction of hexavalent chromium (VI) in soil slurry by nano zero valent iron, Chemical Engineering Transactions, 43, 655–660.

Qian L.B., Shang X., Zhang B., Zhang W.Y., Su A.Q., Chen Y., Da O., Lu H., 2019, Enhanced removal of Cr(VI) by silicon rich biochar-supported nanoscale zero-valent iron, Chemosphere, 215, 739-745.

Shi L.N., Zhang X., Chen Z.L., 2011, Removal of chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron, Water Research, 45(2), 886-892.

Soroosh M., Hyeunhwan A., Dongwon C., Jaeyun M., 2018, Activated carbon impregnated by zero-valent iron nanoparticles (AC/NZVI) optimized for simultaneous adsorption and reduction of aqueous hexavalent chromium: Material characterizations and kinetic studies, Chemical Engineering Journal, 353, 781-795.

Xie Y.K., Dong H.R., Zeng G.M., Tang L., Jiang Z., Zhang C., Deng J.M., Zhang L.H., Zhang Y., 2017, The interactions between nanoscale zero-valent iron and microbes in the subsurface environment: A review, Journal of Hazardous Materials, 321, 390–407.

Zakariyah A.J., Tawfik A.S., Shaikh A.A., 2017, Biogenic glutamic acid-based resin: its synthesis and application in the removal of cobalt(II), Journal of Hazardous Materials, 327, 44–54.

Zhang S.Y., Zhang C., Liu M.Y., Huang R.L., Su R.X., Qi W., He Z.M., 2018, Poly (γ-Glutamic Acid) Promotes Enhanced Dechlorination of p-Chlorophenol by Fe-Pd Nanoparticles, Nanoscale Research Letters, 13(1), 219.

Zhang S.Y., Zhang C., Liu M.Y., Huang R.L., Su R.X., Qi W., He Z.M., 2018, Dechlorination of p-chlorophenol by Fe-Pd nanoparticles promoted by poly (γ-glutamic acid)–dopamine composite, Chemical Engineering Transactions, 70, 2095–2100.