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Original Research Article

# HEAVY METAL REMOVAL FROM SYNTHETIC WASTE WATER BY USING ZERO VALENT IRON NANOPARTICLES

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**Abstract:** Heavy metals ions such as Chromium (Cr (VI)), Nickel (Ni(II)), Copper(Cu(II)) are highly toxic. Various methods have been attempted to remove these heavy metals from water including filtration, chemical precipitation, electrodeposition etc., but these methods suffer from disposal of metal residual sludge, membrane clogging, intensive energy consumption, and high cost. Zero Valent Iron nanoparticles (ZVINPs) possess high capacity for remediating heavy metal ions in water owing to their large surface area, high reactivity, non-toxicity, and ease of production. In this research, Zero Valent Iron nanoparticles were synthesized by liquid phase reduction method , and the remediation of multi heavy metal (in its solutions) in synthetic acidic waste water by using ZVINPs with different concentrations of the metal solution, sonication times, loadings of ZVINP's and pH levels of the acidic water as constraints has been studied and investigated. The results show that Cr, Ni, and Cu ions could be removed effectively from waster water by using ZVINPs with sonication in a weak acidic (pH ~5.5) environment.

Key word: Zero-valent iron nanoparticles, Heavy metals, Waster water, Sonication

**Introduction*:*** Water is the most important compound on the earth for living beings. The water is continuously polluted due to rapid industrialization and commercialization, which leads to harmful effects on human beings. Out of all the contaminations in water heavy metals are the one that leads to toxic and harmful effects on the human beings. Among all pollutants, hexavalent chromium (Cr (VI)) has become a major concern for human health and environment owing to its wide range of sources such as metal plating, leather tanning, metal corrosion inhibition, pigment production, mining and wood-preserving industries as well as its high toxicity and carcinogenicity in aquatic system [1]. Cr (VI) is on the list of top toxic pollutants by the United States Environmental Protection Agency and the maximum

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contaminant level (MCL) for Cr (VI) is 0.1 mg/L for drinking water.

Common methods for removing Cr (VI) from contaminated water include chemical precipitation, electrodeposition, ion exchange, and filtration/adsorption [2], but investigations on more economic and effective Cr (VI) remediation in ground and waste water as well as Cr(VI) elimination in drinking water are still under way [3-4]. Zero valent iron (ZVI) particles have been used as a versatile remediation agent in groundwater treatment since early 1990s [5] because they are excellent electron donor under ambient conditions and thus very reactive in water treatment. With the development of nanotechnology, ZVI nanoparticles (ZVINPs or nZVI) have attracted intensive attention to address Cr(VI) contamination because of their higher remediation capability due to high specific surface area and high reactivity. ZVINPs now have become a new class of remediation technique for water treatment.

In this project, we synthesized ZVINPs, and tested and studied the remediation of multi heavy metals in synthetic acidic waste water solutions prepared under different conditions.

**Materials and Methods**

**Zero Valent Iron Nanoparticle synthesis:** ZVINPs can be synthesized through both chemical and physical processes. Chemical methods include liquid phase reduction [6], gas phase reduction, and micro-emulsion, etc. Physical methods include high-energy ball milling [7], and inert gas condensation, etc. In this project, we used liquid phase reduction method because this method is simple, where no sophisticated equipment or chemicals are necessary, and nanoparticles produced have uniform size (R.Yuvakumar et al, 2011). ZVINPs were synthesized by reacting iron salt (Iron (III) chloride hexahydrate, from Alfa Aesar, MA USA) with sodium borohydride ($NaBH_4$, from Fisher Scientific, NJ, USA) which is strong reducing agent under constant stirring. This whole process was carried out under anaerobic condition, the experimental set-up is as shown in Figure 1

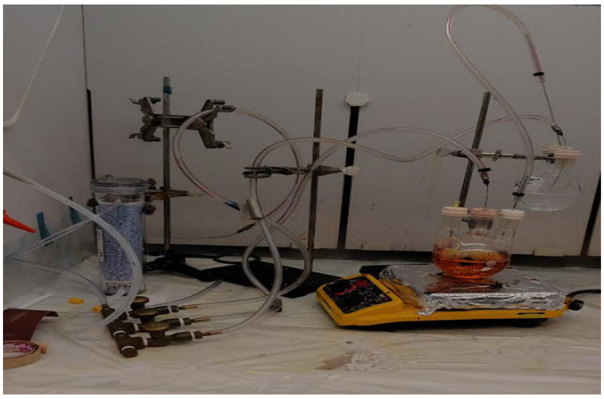

Fig. 1. ZVINP synthesis set up.

In the process, 10.81227g of iron precursor was weighed and placed into 500ml three-neck flask with magnetic stirrer, which was purged with nitrogen gas. In another 500ml three-neck flask approximately 4.53978 g of $NaBH_4$ was added, which was also purged with nitrogen gas. 250ml of deoxygenated DI water was added into these two flasks to form solutions respectively. $NaBH_4$ solution was slowly added into the iron salt solution in a drop wise manner. Once the chemical reaction process was done, ZVINPs were centrifuged and washed with ethanol until no residue was observed. Then these nanoparticles were vacuumed dried and were ready for use.

**Metal solution preparations:** Heavy metal solutions combining of three (Cr, Ni, Cu) were prepared by dissolving $K_2Cr_2O_7$, $CuSO_4$, and Ni $(NO_3)_2$ into DI water with appropriate ratios to form 10, 25,50ppm respectively. pH levels (4.5 and 5.5) in the solutions were adjusted by using nitric acid. Then certain amounts of ZVINPs were added to the solutions to make the solutions at three different ZVINPs concertation levels, 0.025g/L, 0.1 g/L, and 0.4 g/L respectively.

These heavy metal solutions with ZVINPs were sonicated for 5, 30, 60 minutes respectively, and then ZVINPs were separated from the heavy metal solutions by using syringe filter. The rest of solutions were stored and tested by using Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES).

The conditions of these heavy metal solutions for the remediation are listed in table 1.

Table 1. Factors for the remediation.

| Concentration of ZVINP (g/lit) | Concentration of heavy metal solution (ppm) (Cr,Cu,Ni) | Time of sonication (mins) | pH of the solution |
|---|---|---|---|
| 0.4 | 10,25,50 | 5,30,60 | 4.5,5.5 |
| 0.1 | 10,25,50 | 5,30,60 | 4.5,5.5 |
| 0.025 | 10,25,50 | 5,30,60 | 4.5,5.5 |

**Results and Discussions:** Figure 2 shows SEM Morphologies of the ZVINPs before and after the remediation respectively. Heavy metal particles adsorbed on ZVINP particles were observed in the figure in comparison each other, which was also clearly demonstrated in the EDX images of ZVINPs in Figure 3 by comparing the image after the remediation with the image before the remediation.

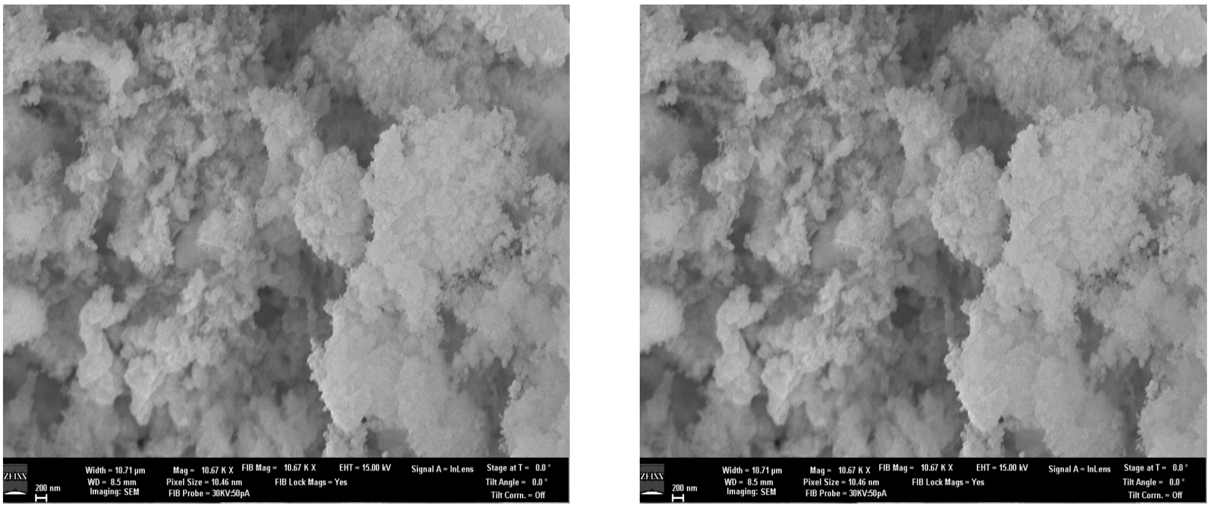

FIG. 2. SEM Morphologies of ZVINP particles before and after remediation.

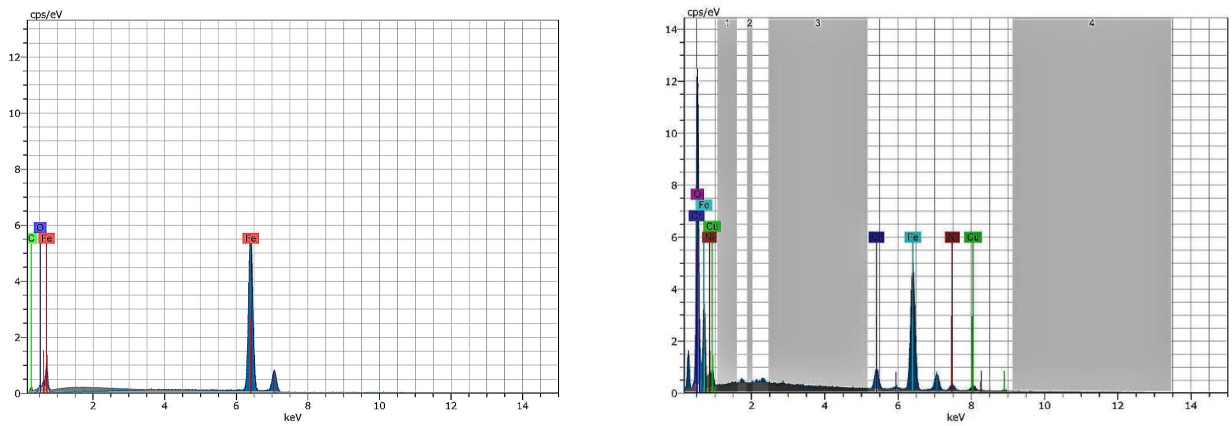


FIG.3. EDX images of ZVINP particles before and after remediation.

For 0.4 g/l concentration of ZVINPs at pH 4.5, 5.5, the results show 100% heavy metal ions removal rate at all their three concentration of 50, 25 and 10ppm with both pH levels (4.5 and 5.5) in as less as 5 minutes sonication. Because larger concentration ZVINPs and well dispersion of ZVINPs in the metal solutions via sonication provided more sorbents which enlarged the absorption surface area, and thus to improve remediation efficiency.

Table 2 shows the remediation results with 0.1 g/l concentration of ZVINPs at pH 4.5. The data indicates that sonication could help in remediation performance especially in lower concentration of chromium and copper ions. In higher concentrations, the performances were not as good as in lower concentrations, it is because higher acidic environment might help ZVINPs re-agglomeration, which leaded to lower absorptions overall. Obviously the remediation performances of nickel ions were not good, it might be because of 4.5 pH acidic environment. The data also shows that longer sonication time might not always contribute the removal efficacy. As sonication time increased particles became smaller and smaller and thus enhanced the performances of the remediation but in the meanwhile the sonication might free the absorbed ion particles and might help ZVINPs re-agglomeration in lower ion concentrations, which reduced the removal performance overall.

Table 2. Remediation results for ZVINP particles with 0.1g/L concertation at pH 4.5.

| Initial concentrations (ppm) | % Removal | | |
|---|---|---|---|
| Cr | 5mins | 30mins | 60mins |
| 10 | 98.0 | 100.0 | 100.0 |
| 25 | 97.0 | 98.4 | 99.8 |
| 50 | 69.7 | 84.4 | 84.1 |
| Cu | 5mins | 30mins | 60mins |
| 10 | 89.6 | 79.4 | 100.0 |
| 25 | 56.8 | 54.7 | 48.8 |
| 50 | 28.4 | 51.0 | 47.0 |
| Ni | 5mins | 30mins | 60mins |
| 10 | 31.8 | 32.8 | 48.5 |
| 25 | 25.8 | 27.5 | 8.6 |
| 50 | 21.9 | 27.7 | 11.6 |

Table 3 shows the remediation results with 0.1 g/l concentration of ZVINPs at pH 5.5. The data shows lowing acidic level could enhance the performances especially for nickel ions, because lower acidic environment might increase the absorption rate and reduce chance for ZVINP re-agglomeration. 0.025g/L concentration of ZVINPs is too low, which makes the sorbent tend to saturate itself (larger concentration of metals for minimal quantity of sorbent) and reduces chance to collide and thus to absorb the ion particles as indicated in table 4 and 5.

Table 3. Remediation results for ZVINP particles with 0.1g/L concertation at pH 5.5.

| Initial concentrations (ppm) | % Removal | | |
|---|---|---|---|
| Cr | 5mins | 30mins | 60mins |
| 10 | 100.0 | 100.0 | 100.0 |
| 25 | 100.0 | 100.0 | 100.0 |
| 50 | 98.0 | 100.0 | 100.0 |
| Cu | 5mins | 30mins | 60mins |
| 10 | 100.0 | 100.0 | 100.0 |
| 25 | 99.0 | 100.0 | 100.0 |
| 50 | 87.0 | 100.0 | 100.0 |
| Ni | 5mins | 30mins | 60mins |
| 10 | 62.0 | 100.0 | 100.0 |
| 25 | 87.0 | 88.0 | 100.0 |
| 50 | 21.0 | 65.0 | 44.0 |

Table 4. Remediation results for ZVINP particles with 0.025g/L concertation at pH 4.5

| Initial metal concentrations (ppm) | % Removal | | |
|---|---|---|---|
| Cr | 5mins | 30mins | 60mins |
| 10 | 28.4 | 66.3 | 43.5 |
| 25 | 30.3 | 29.7 | 31.4 |
| 50 | 18.4 | 25.3 | 27.3 |
| Cu | | | |
| 10 | 6.3 | 18.3 | 11.4 |
| 25 | 8.7 | 9.8 | 8.1 |
| 50 | 6.5 | 8.7 | 8.3 |
| Ni | | | |
| 10 | 1.0 | 7.4 | 5.7 |
| 25 | 3.0 | 6.6 | 5.7 |
| 50 | 4.9 | 7.1 | 6.0 |

Table 5. Remediation results for ZVINP particles with 0.025g/L concertation at pH 5.5

| Initial concentrations (ppm) | % Removal | | |
|---|---|---|---|
| Cr | 5min | 30min | 60min |
| 10 | 22.7 | 64.4 | 47.4 |
| 25 | 15.4 | 44.3 | 67.7 |
| 50 | 10.7 | 14.5 | 17.6 |
| Cu | | | |
| 10 | 41.3 | 69.0 | 68.1 |
| 25 | 37.0 | 36.6 | 58.8 |
| 50 | 19.7 | 15.9 | 20.2 |
| Ni | | | |
| 10 | 3.3 | 13.1 | 20.4 |
| 25 | 3.3 | 2.7 | 8.6 |
| 50 | 1.9 | 3.5 | 4.4 |

Conclusions: In this project, the effects of Iron nanoparticles (ZVINPs) on removal of combination of three (Cr, Ni, Cu) in synthetic acidic waste water by using ZVINPs with different concentrations of the metal solution, sonication times, loadings of ZVINP's and pH levels of the acidic water as constraints were evaluated and reported. The results show certain concertation (larger than 0.1g/L) of ZVINPs could remove Cr, Ni, and Cu ions effectively from weak acidic waster water solutions with certain amount of time of sonication.

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