USE OF IRON NANOPARTICLES FOR POST-TREATMENT OF METAL FINISHING WASTEWATER

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Abstract

Our research is targeted on treatment and post – treatment of metal finishing wastewater. This wastewater contains specific, hardly degradable pollutants, especially heavy metals and cyanides. Required outlet concentrations of these substances in the discharged stream are usually very low and difficult to reach. We have developed new treatment method using nanoscale zerovalent iron particles (nZVI) for heavy metal removal.

nZVI is characterized by nanosize, high reactivity and large surface area. Because of a high reduction potential, nZVI is often applied for the remediation of wastewater or groundwater polluted by heavy metals. We started to apply nZVI for treatment of industrial wastewaters containing heavy metals based on those experiences. This environmentally friendly technology has great potential to combine redox processes with sorption and coagulation effect in one technological step. Reaction products are non-toxic iron compounds. The combination of more treatment effects enables removal of very resistant pollutants in cases where conventional technologies were not successful.

Tests performed with pretreated metal finishing wastewater and nZVI revealed good efficiency of the removal of residual concentrations of nickel and copper. Pilot - scale reactor was designed for nZVI application, based on SBR (Sequential Batch Reactor) configuration. The system is not continuously operated and long reaction times can be set for required removal of pollutants. The reactor is equipped with the automatic control of the process phases and dosing of the nZVI under inert atmosphere. Testing and verification of the reactor on real wastewater is in the progress and the results will be presented.

Keywords: Zerovalent iron nanoparticles, metal finishing wastewater, post – treatment, copper and nickel removal

1.   INTRODUCTION

Wide range of applications and big potential is represented by evolving branch: nanotechnology. Materials of "nano" dimensions offer applications from treatment, remediation, sensing and detection to pollution prevention, according to Cloete *et. al* [1]. Nanoscale zerovalent iron (nZVI) is part of the nanotechnology branch and pertain to section treatment and remediation. With average particle size 10-100 nm and a specific surface area of 20-25 m^2/g nZVI has become a valuable material for its environmental remediation abilities. [1, 2, 3]. Nanoscale zerovalent iron is composed of iron in oxidation state 0 which is very unstable, thus reactive. This feature makes from nZVI one of the strongest reducers [2, 4]. High reactivity and relatively large surface area facilitate to combine processes reduction, sorption and coagulation into one technological step. Reaction products are ferrous and ferric oxides and hydroxides, commonly found in nature. Thanks to those advantages we can call this technology environmentally friendly.

It was proved that nZVI is an efficient tool for the treatment of various contaminants in aqueous systems [2, 4, 5, 6]. Number of studies deals with removal of chlorinated hydrocarbons, dioxines, polychlorinated

biphenyls, DDT and heavy metals (As, Cd, Cr, Cu, Pb, Hg, Ni, Se). nZVI oxidative state and high surface/volume ratio lead in adsorption of the pollutant to the iron surface. The reaction mechanism is dependent on the difference between redox potential of nZVI and pollutant. There are three possible reaction mechanisms: i) sorption or complex formation, ii) reduction and precipitation and iii) reduction and adsorption systems [7]. However, the adsorption of impurities is also pH dependent, as well as the formation of iron (hydr)oxides onto the surface [8].

nZVI has been successfully applied for decontamination of groundwater containing pollutants listed above. There are a lot of full-scale applications in Czech Republic and all over the world [9]. We focused on treatment of wastewater containing heavy metals, based on good experiences with groundwater remediation. This article deals with use of nanoscale zerovalent iron (nZVI) for post – treatment of industrial metal finishing waste water with residual heavy metals content. Industrial waste water used in our test was characterized by low concentration of heavy metals - copper, nickel and zinc. The removal mechanisms of Ni and Cu include both reduction and surface complex formation [7] with the result that the reduction and/or adsorption of heavy metals depends on the redox potential of each of them. Hence, when the reduction potential of the cation is more negative than that of ZVI the main mechanisms of removal is achieved by sorption or complex formation; when the reduction potential of the cation is more positive the mechanism of removal is mainly by reduction and precipitation; and when the reduction potential is slightly more positive than that of ZVI the removal mechanism include reduction and adsorption [8]. When Ni and Cu are presented, both reduction and surface complex formation occurs [10,11].

Wastewater from metal finishing industry is usually treated by traditional chemical precipitation. This technology is characterized by simplicity and low capital cost. The biggest advantage is conversion of pollutants into well separated insoluble compounds. Nevertheless this technique is ineffective at low heavy metals concentration and produces high amounts of sludge which needs to be treated. Another methods applicable for heavy metals removal are ion-exchange, adsorption by activated carbon, carbon nanotubes or bioadsorbents, membrane filtration or electrochemical processes [12]. Each method has its limitations, from high investment or operational costs to low removal efficiency and big volume of produced sludge. In regards to apply both economical and efficient solution, another technological step is usually necessary to treat low concentrations. nZVI seems to be very promising. nZVI is an efficient method for heavy metal removal with great advantage in production of non-harmful compounds. Volume of the produced sludge is minimal compare to conventional technologies.

In our study we investigated the effect of nZVI applied for removal of residual Cu, Ni and Zn. Residual concentrations are the most difficult to remove and pose a significant problem in the industry. The aim of our testing was to reveal the efficiency of the nZVI method, setting of the optimal conditions (dosing, pH) of nZVI application in lab-scale and nZVI testing in pilot-scale reactor.

2   MATERIALS AND METHODS

2.1   Wastewater

Real processing wastewater from metal finishing industry was used for laboratory and pilot plant testing. Rinsing wastewater from degreasing of metals after chemical precipitation contained relatively low concentrations of copper, nickel and zinc (

Table). Outlet limits for Cu and Ni in our case are 0.5 mg/L, and 0.1 mg/L, respectively.

Table 1 Rinsing water characteristics

Parameter	Unit	Non-filtered sample	Filtered sample	Limit according GD 23/2011, Annex 1)
COD	mg/L	593	540	300
Cu	mg/L	3.16	1.08	0.5
Ni	mg/L	0.38	0.27	0.8*
Zn	mg/L	0.56	0.45	2
CN^-	mg/L	0.19	0.08	1
pH	-	9.56	9.46	6-7

*Ni limit in locality is 0.1 mg/L according to the sewerage operational manual.

2.2 nZVI

Aquatic dispersion of nZVI made from pyrophoric iron was used for testing. Sample was supplied by NANOIRON, s.r.o., characterized by 18.4 % of nZVI. Average diameter of nZVI particles was 50 nm. Thanks to the narrow size distribution of nZVI and stabilization process, the product is characterized by high reactivity and very low degree of agglomeration. Suspension must be stored in cold and the contact with the air should be minimized once applied. The suspension must be homogenized using a laboratory shaker to achieve accurate iron dose before application. Optimal nZVI dose was revealed through lab test.

2.3 Methods

Copper, nickel and zinc concentrations were analyzed and reaction conditions like pH, temperature and conductivity were characterized. Preparation of samples for analysis were performed by Crack Set LCW 902 from HACH Lange. All metals presented in wastewater are assessed as a sum of free and bounded ions by using this technique. Analyses were provided by HACH tests LCK 329 for copper, LCK 337 for nickel and LCK 360 for zinc with spectrophotometric detection by Spectrophotometer HACH DR 3900.

2.4 Pilot scale reactor

Pilot-scale reactor is specifically designed for nZVI application. It is constructed as SBR (Sequential Batch Reactor). The system is discontinuously operated and long reaction times can be set for required removal of pollutants. The reactor is equipped with pH adjustment of the sample, automatic mixing and dosing of nZVI, coagulation and flocculation step, safety control units, continual mixing of the reactor, remote control and GSM module. The whole system including the nZVI dosing is working under the inert nitrogen atmosphere and is fully automatized.

2.5 Metal ions removal

2.5.1 Lab test

Lab test was performed to set the optimal dose of nZVI. nZVI slurry was added while quick manual mixing to 250 mL Erlenmeyer´s flasks containing 100 mL of real wastewater. Seven flasks with wastewater were prepared with nZVI dosage ranging from 0 to 800 mg/L. Erlenmeyer´s flasks were closed and slowly mixed on the shaking device in 200 rpm. The samples were collected and filtered through glass fibers filter (pore size 1.1 µm) after 3 hours of reaction. The reaction time of 3 hours was based on our previous experiences from laboratory kinetic tests. The samples were analyzed for copper, zinc and nickel concentrations. The test was performed with access of atmospheric air. The results were assessed and the optimal dose of nZVI was chosen. Additional test was performed, investigating the optimal pH value for Cu and Ni removal.
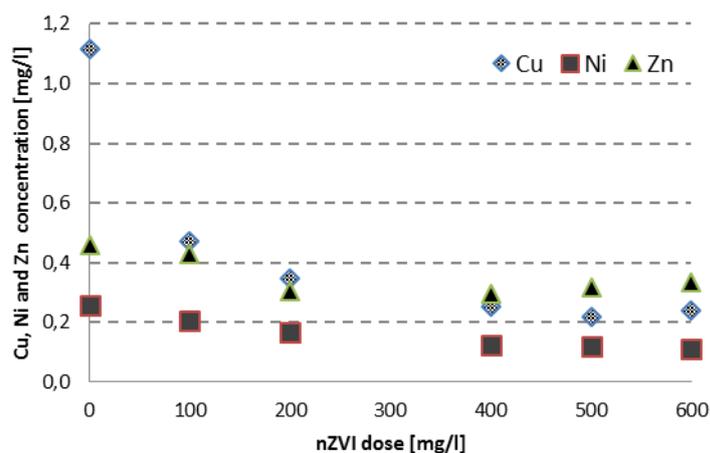
2.5.2 Pilot test

Pilot testing was performed in SBR. Optimal dosage of nZVI corresponding to 400 mg/L (resp. 300 mg/L) was applied into the reactor. pH was adjusted at pH 9 before the nZVI dosing. Wastewater was continuously mixed at a speed of 250 rpm in SBR for 3 hours. Dosing of nZVI and reaction were performed in inert nitrogen atmosphere. The dissolved oxygen concentration was lowered below 0.1 mg/L before nZVI dosing by stripping with nitrogen gas. Samples of raw water, treated water after magnetic separation and treated water after magnetic separation followed by filtration on PTFE cross – flow microfiltration membrane were collected. Filtrates were analyzed for copper, nickel and zinc concentrations. Reaction conditions including pH, temperature and conductivity were monitored.

3   RESULTS AND DISCUSSIONS

3.1   Lab test

Results show the significant decrease of nickel, copper and zinc concentration with increasing dosing of nZVI. The optimal dose of 400 mg nZVI/L was chosen based on required outlet parameters and test results. The effluent limit for Ni was not achieved even for the nZVI dose of 600 mg/L. Decrease of Ni under limit concentration was not successful. The reason is probably inappropriate mixing of nZVI particles in the liquor in lab conditions. Increasing of nZVI dose above 400 mg nZVI/L did not cause the adequate increase of removal efficiencies (Figure 1).

Copper concentration was decreased under effluent limit (0.5 mg/L) at the dose of 100 mg/L in lab conditions with the removal efficiency 57.7%. Copper removal efficiency 77.2% was achieved at the dose of 400 mg nZVI/L. Concentration of the nickel in the treated water was 0.125 mg/L after dosing of 400 mg nZVI/L, corresponding to the removal efficiency of 51%. According to Li et al. [8], Common removal of Ni and Cu shows lower efficeincy (61% and 36%, respectively) contrary to the experiments with separate metal removal (above 80%).This may be explained by possible competition among the metal ions when they are found in the same solution. Concentration of zinc in the raw water has already fulfilled the effluent limit 2 mg/L therefore the Zn concentration was monitored only for evaluation of removal efficiency. Decrease of zinc concentration (35.4%) was less significant in comparison with nickel and copper.


Figure 1: Removal of Cu, Ni and Zn by increasing nZVI doses in lab conditions.

3.2   Pilot test

Test in SBR with nZVI dose 400 mg nZVI/L revealed significantly better results compared to laboratory conditions. The concentration of copper, nickel and zinc was reduced by 85.2%, 85.2 % and 40%, respectively in the inert atmosphere of SBR (Fig.). Effluent limits for nickel and copper were met. Higher

efficiencies obtained during pilot testing in comparison with laboratory results was probably caused by the inert atmosphere in the reactor. pH adjustment before nZVI dosing, proper stirring of the sample and separation of reaction products by PTFE membrane was also important for successful removal of pollutants.

Second pilot test was performed with the nZVI dose of 300 mg/L. The aim was to investigate the efficiency of the process at SBR with lower doses. All effluent limits were met as well. Efficiency of Cu and Ni removal was slightly lower compared to the previous case (dose of 400 mg nZVI/L), reaching 70% and 70.1 % respectively. Zinc removal efficiency increased to 60.5% (Fig). Higher efficiency of zinc removal at lower dose of nZVI can be caused by inappropriate sampling and analytical error.
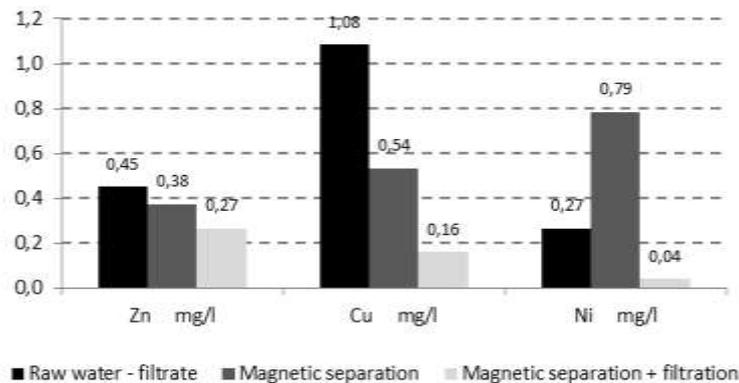
Fig. 2 Removal of Cu, Ni and Zn in SBR at nZVI dose 400 mg/L nZVI
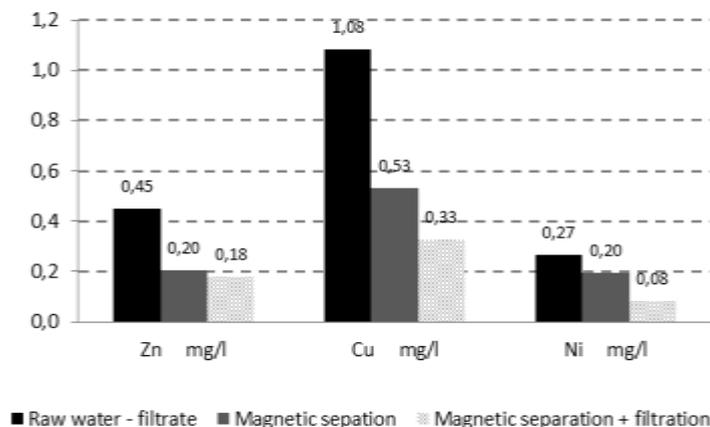
Fig. 3 Removal of Cu, Ni and Zn in SBR at nZVI dose 300 mg/L nZVI

CONCLUSIONS

This study evaluated the efficiency of copper, nickel and zinc removal from industrial metal finishing wastewater using nZVI material in lab and pilot scale conditions. Initial concentrations of Cu, Ni and Zn in raw wastewater were 3.16 mg/L, 0.38 mg/L and 0.56 mg/L, respectively. All metals were presented in residual concentrations and difficult to remove. Copper concentration was lowered by 77.2% in lab scale and 85.2% in pilot scale test for nZVI dose of 400 mg/L after 3 hours of reaction. Removal efficiency of nickel was 51% in the lab scale and 85.2 % at the pilot scale. Decrease of zinc concentration was less significant and reached 35.4% and 40% in lab and pilot scale experiment, respectively. Increase of efficiency in pilot scale testing was caused by the application of nZVI under inert atmosphere which ensured the preservation of high iron reactivity. pH adjustment before the nZVI dosing had also significant influence for efficiency of reaction.

No changes and fluctuations of temperature and conductivity were observed. Pilot-scale test with lower dose of nZVI was performed to reveal the surpluses of previous dose of iron. The dose of 300 mg nZVI/L was applied into the reactor under inert atmosphere with pH adjustment before iron dosing. Efficiency of metals removal dropped to the 70% and 70.1% for copper and nickel. Efficiency of zinc removal increased to the 60.5%. nZVI dose of 300 mg/L was sufficient for reaching of limits for wastewater discharge.

nZVI applied in SBR showed the desired efficiency for residual heavy metals removal from industrial wastewater in environmentally friendly way. More individual and long-term tests has to be performed to prove the reliability of the technology. High price of reactive iron material is a remaining barrier which makes the introduction of nZVI to the wastewater treatment applications difficult.

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