Application of electrochemical peroxidation with nanoscale zero-valent iron particles (nZVI) for selenium removal from oil refinery wastewater

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Abstract This study uses the electrochemical peroxidation process to remove selenium in combination with nanoscale zero-valent iron particles (nZVI) as the iron source. Also, experiments with just the addition of the nZVI doses without current application were carried out. The nanoparticles were synthesized by the chemical reduction of iron chloride hexahydrate with sodium borohydride obtaining particles with an average size of 78 nm. The initial percentage of oxygen was in the range of 4.57% - 6.25% with no measurable increase after 15 days. 1 L of oil refinery wastewater was used in each experiment and the treatment time for all of them was 1 hour. The nZVI doses were: 950, 3800 and 11400 molFe/MolSe and the current density values were: 100 and 200 A/m^2, all combinations were tested. The initial concentration of total Se in the wastewater was 0.16 mg/L. After the treatment, in the case of electrochemical peroxidation, a removal of 21.4 to 28.4% was achieved, depending on the nZVI dose and current density. In the case of treatment with just nZVI and no application of current, a removal of 54.1 to 94.5% was obtained, with the highest removal efficiency reached at a nanoparticle dose of 11400 molFe/MolSe.

Keywords: Selenium removal, electrochemical peroxidation, nanoparticles

1. Introduction

Selenium is a non-metallic element that can have the oxidation states of -2, 0, +4 and +6, with its most common chemical species being selenite (SeO_3^{2-}) with an oxidation state of +4 and selenate (SeO_4^{2-}) with an oxidation state of +6. This element is toxic at doses higher than 400 μg/day (dos Reis et al., 2017), leading to diseases like selenosis, carcinomas and pulmonary oedemas. The environmental protection norm for the discharge of wastewater in Chile is the Decreto Supremo N°90. This Decree establishes the maximum selenium limit of 0.01 mg/L for wastewater discharged in water bodies with littoral protection. However, in Chilean oil refineries, there have been events where the concentration of selenium in their wastewater has surpassed the norm. The selenium in this type of wastewater comes from organoselenides that are present in crude oil.

The removal of selenium from wastewater is a current challenge, this means that the existing techniques are few and, in general, can remove efficiently only one of the selenium species: selenite or selenate. One of the proposed techniques for its solution is electrochemical peroxidation because it is effective in the removal of both selenium species (Baek et al., 2013). This process requires zero-valent iron (Fe^0), which can come from an iron electrode that consumes or from the addition of materials that act as an iron source such as nanoparticles.

An investigation carried out by Hansen et al. in 2019 used electrochemical peroxidation to remove selenium from oil refinery wastewater with zero-valent iron nanoparticles (nZVI) purchased from Nanoiron. Inert graphite electrodes were used and removal efficiencies of 93% and 73% were obtained for 240 min and 60 min of treatment, respectively. However, due to prolonged storage periods since the nanoparticles were sent by the supplier Nanoiron, these showed a high percentage of oxidation, meaning they were not as Fe^0 entirely (Hansen et al., 2019).

The objectives of this research are to study the electrochemical peroxidation process with nZVI synthesised in a laboratory with a low oxygen percentage and to evaluate its effectiveness in removing selenium from wastewater originating from an oil refinery.

2. Experimental

### 2.1 Synthesis of zero-valent iron nanoparticles (nZVI)

The synthesis of nZVI was performed by the method of reduction of iron chloride hexahydrate (FeCl$_3$x6H$_2$O) with sodium borohydride (NaBH$_4$) as a reducing agent. The reaction was carried out under a nitrogen inert atmosphere and in an ethanol medium to prevent rapid oxidation of the nanoparticles (Yuvakkumar, 2011), according to (Pasinszki and Krebsz, 2020):

$$4Fe^{3+} + 3BH_4^- + 9OH^- \rightarrow 4Fe^0 \downarrow + 3H_3BO_3 + 6H_2$$
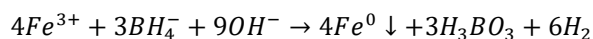
The chemical reagents used (FeCl$_3$x6H$_2$O and NaBH$_4$) were of analytical grade and obtained from Merck. A FeCl$_3$x6H$_2$O 0.33 M solution was prepared with 48 mL of ethanol and 12 mL of deionised water and a NaBH$_4$ 0.5 M solution with 200 mL of deionised water, which is in excess to accelerate the formation of nZVI.

The synthesis was conducted in a three-neck flask, which contained the FeCl$_3$x6H$_2$O solution. A mechanical stirrer

was inserted into the central neck and rotated at 200 rpm. In the left neck, a burette was positioned to add the NaBH$_4$ solution at a rate of 0.18 – 0.22 mL/s and, in the right neck, nitrogen was injected, as shown in Figure 1. After the addition of NaBH$_4$ was complete, the mixture was stirred for an additional 15 min. The product obtained was then vacuum filtered using Adventec MFS filters (diameter 7 cm, pore size 3 μm) and washed three times with deionized water to eliminate subproduct salts, followed by three washes with ethanol. The synthesized nZVI were dried in an oven for 24 h at 50 ºC until a constant mass was reached to dose them. For their storage, the nZVI were maintained under refrigeration with a layer of ethanol and nitrogen atmosphere.
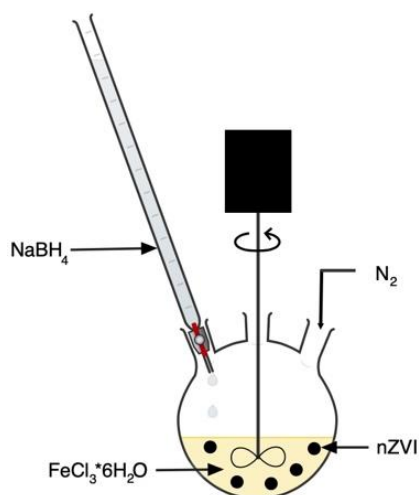
**Figure 1**: nZVI synthesis setup

2.2 nZVI elemental characterization

The characterization of the nZVI was carried out in the Scanning Electron Microscopy and Microanalysis Laboratory of the Physics Department at Universidad Técnica Federico Santa María. Elemental analysis was conducted with a scanning electron microscope (SEM) (Zeiss, EVO MA 10) coupled with dispersive energy spectroscopy (EDS) (Oxford Instruments, X-act), to obtain the mass percentages of iron and oxygen in the nZVI and determine their oxidation level. The analysis was performed five times: at 1, 4, 8, 11 and 15 days after the nZVI synthesis to track their oxidation over time.

2.3 Electrochemical peroxidation

The wastewater was obtained from the Phenol Plant of ENAP Refinería Aconcagua, V Región, Chile. Solutions for pH adjustment were prepared using analytical grade sodium hydroxide lentils 97.0% (NaOH) and sulfuric acid 95-98% (H$_2$SO$_4$) from Winkler. Analytical grade hydrogen peroxide 30% p/p (H$_2$O$_2$) from Merck was used. The selenium content was analysed according to the Chilean Norm NCh 2313/30 Of 99 at the Chemical and Instrumental Analysis Laboratory in Universidad Técnica Federico Santa María.

1.0 L of wastewater previously filtered using Adventec MFS filter paper (diameter 7 cm, pore size 3 μm) and with its pH adjusted to 5 was loaded to a reactor, along with the established dose of nZVI. Two concentrical graphite electrodes (EK20) were used, which were connected to a power supply (Extech, Model 382285) and a polarity inverter, as shown in Figure 2. Air was injected with a cylindrical bubbler at a rate of 5 L/min and H$_2$O$_2$ was added with a burette at 0.1 mL/min.
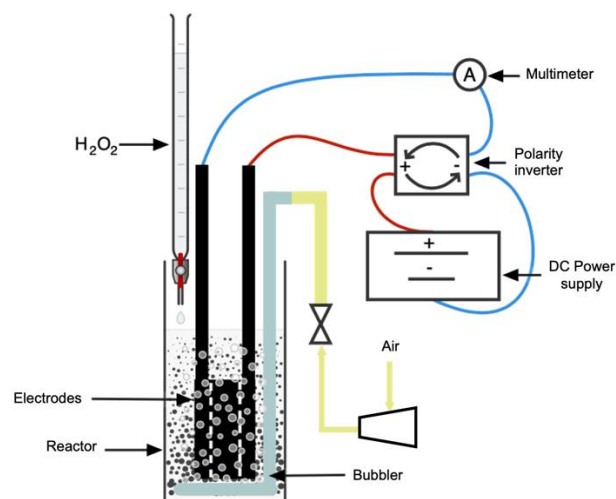
Figure 2: Electrochemical peroxidation setup

A treatment time of 60 min was used in all experiments, and after this time, the wastewater was vacuum filtered. The manipulated variables were the nZVI dose at 950, 3800 and 11400 mol Fe/ mol Se and the current density at 100 and 200 A/m^2.

Also, selenium removal experiments were carried out using only nZVI and mechanical stirring, without the addition of hydrogen peroxide, electrical current or air, to compare with the electrochemical peroxidation process. The same conditions and variables as those used for the electrochemical peroxidation case were maintained.

3. Results and discussion

3.1 nZVI synthesis and elemental characterization

A yield of 1.14 ± 0.04 g of nZVI per synthesis was obtained, this result agrees with the reported chemical reaction (Pasinszki and Krebsz, 2020).

SEM images of the synthesized nZVI are shown in Figures 3 and 4, the nanoparticles comply with the particle size indicated by the references (<100 nm) (Cook, 2009). Additionally, in Figure 4, it can be noted that the nZVI have a spherical shape and are connected to each other, forming chains (Yuvakkumar, 2011).

Table 1 and Figure 5 present the results of the elemental characterization of the nZVI with EDS. The analysis showed a minimum iron mass percentage of 93.75% and a maximum of 95.43%, indicating that the oxygen content in the nZVI is below 6.25%. Therefore, it can be concluded that the nZVI do not exhibit considerable oxidation and are mainly composed of Fe^0. It has been reported that the

dominant species formed by the oxidation of nZVI is magnetite (Fe_3O_4) (Mackenzie and Georgi, 2019). Thus, it is suggested to perform FRX and DRX analysis to determine the speciation of the synthesized nZVI and obtain the percentage of Fe^0 specifically.
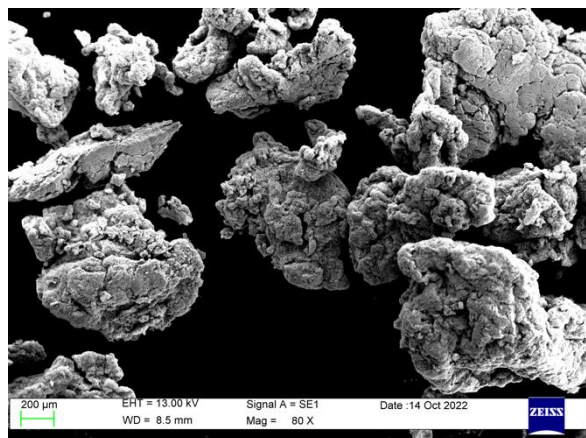


Figure 3: SEM nZVI Mag 80 X
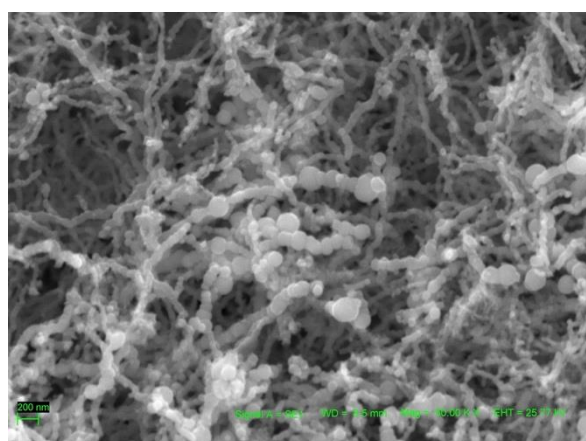
Figure 4: SEM nZVI Mag 50 kX

Furthermore, Figure 5 shows that during the 15 days since their synthesis, the mass percentage of oxygen in the nZVI did not increase, indicating that the nanoparticles did not continue to oxidize. This validates the storage conditions used and allows establishing that the nZVI comply with the necessary conditions to be used in the selenium removal experiments.

Table 1: Mass percentage of O and Fe in the nZVI, obtained by EDS.

Element	Oxygen (O), %	Iron (Fe), %
Day 1	6.25 ± 1.18	93.75 ± 1.18
Day 4	6.24 ± 2.05	93.76 ± 2.05
Day 8	5.46 ± 0.54	94.54 ± 0.54
Day 11	4.44 ± 1.37	95.36 ± 1.37
Day 15	4.57 ± 1.04	95.43 ± 1.04
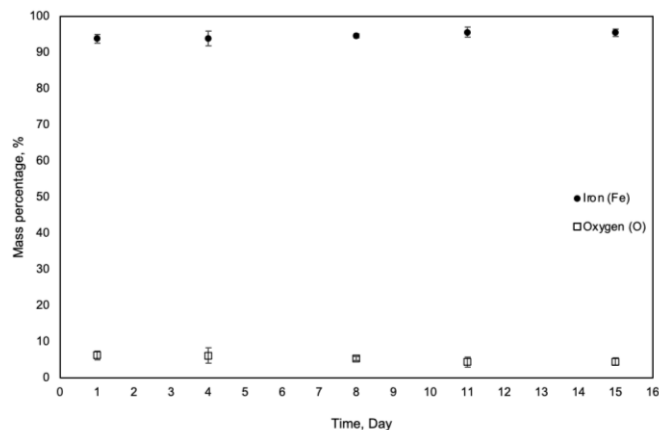


Figure 5: Mass percentage of O and Fe over time in the nZVI, obtained by EDS.

3.2 Selenium removal

The oil refinery wastewater used presents an initial selenium concentration of 0.16 mg/L, which is 16 times higher than the Chilean normative limit.

Figure 6 shows the selenium removal results for the wastewater treatment with nZVI, both with electrochemical peroxidation and without the application of electrical current.
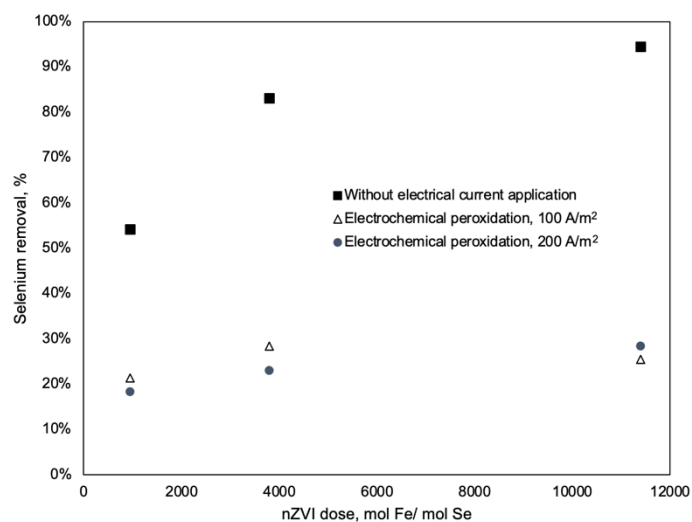
Figure 6: Selenium removal results for one hour of treatment with nZVI, both with electrochemical peroxidation and without the application of electrical current.

With electrochemical peroxidation, the maximum removal of 28.4% was obtained for a nZVI dose of 3800 mol Fe/mol Se and current density of 100 A/m², as well as for a dose of 11400 mol Fe/mol Se and current density of 200 A/m². The minimum removal obtained was 18.4% for a dose of 950 mol Fe/mol Se and current density of 200 A/m².

In the case of nZVI without the application of current as wastewater treatment, the maximum removal of 94.5% was obtained at a nZVI dose of 11400 mol Fe/mol Se, while the minimum removal was 54.1% for a dose of 950 mol Fe/mol Se. Unlike electrochemical peroxidation, using

only nZVI with stirring showed a clear relationship between the nZVI dose and the selenium removal, where a higher nZVI dose resulted in higher removal rates. With respect to the environmental regulation (DS N° 90), a nZVI dose of 11400 mol Fe/mol Se without the application of electrical current complied with the maximum limit of 0.01 mg/L of selenium, reaching a concentration of 0.0086 mg/L.

The results indicate that the most effective technology for selenium removal from the type of wastewater studied is the use of nZVI with stirring rather than electrochemical peroxidation. The main reason for the difference between the two studied cases may be the inorganic selenium species present in the wastewater. Selenate removal is more complex and difficult than selenite (Klas and Kirk, 2013). On one hand, high content of selenate in the wastewater can slow down the electrochemical peroxidation process (Klas and Kirk, 2013) and, on the other hand, an elevated concentration of hydrogen peroxide can oxidize the selenite to selenate (Arienzo et al., 2001).

Moreover, while not incorporating hydrogen peroxide, the nZVI act as a reducing agent, because the Fe^0 allows the reduction of selenite and selenate to elemental selenium (Tang et al., 2014), forming a thin layer of Se^0 and Se^{2-} between the Fe^0 core of the nZVI and their iron oxide surface, thereby the selenium is encapsulated within the nanoparticles (Ling et al., 2015). This mechanism of selenium removal is promising in cases where the selenium adsorbed in the nZVI needs to be recovered.

4.   Conclusions

From the obtained results it is possible to evaluate the removal of selenium from a petroleum refinery using nanoparticles of iron and electrochemical peroxidation.

The nZVI manufactured in the laboratory showed very low initial oxidation, which was promising for selenium removal since selenium could be reduced chemically and adsorbed on the particle surface.

Because of the selenium speciation, the removal was found to be better when only applying nanoparticles and not the electrochemical peroxidation for this specific wastewater. The low removal efficiency for the electrochemical peroxidation could be contributed to the rapid oxidation of selenite to selenate by hydrogen peroxide. Selenate is more difficult to remove.

When only using nZVI the Se removal was found to be around 95%, therefore it is recommended to follow this approach for future work on Se removal. In addition, electricity and reagent costs would be lower.

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