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Surface-Modified Zero-Valent Iron Nanoparticles (nZVI) for Removal of Total Chromium and Chemical Oxygen Demand in Wastewater from Tanning Processes.

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Abstract

The present study evaluated the performance of five different iron-based nanomaterials (nZVI, Biochar@nZVI, nZVI-S, nZVI-Al, and Fe_x-N) for the removal of chemical oxygen demand (COD) in four different types of water (tannery wastewater, water with BSA simulating COD value, Water with Cr, and water with both BSA and Cr). The results showed that all five materials had a significant effect on COD removal, with the highest removal efficiency achieved by Biochar@nZVI in water with both BSA and Cr (97.9%). Biochar@nZVI also showed better performance than nZVI, nZVI-S, and nZVI-Al in most cases. Additionally, the results suggested that the presence of chromium in the system may have contributed to improved efficiency in some materials, while high chloride content

in tannery wastewater may have inhibited the action of the nanomaterials. These findings highlight the potential of iron-based nanomaterials for the treatment of tannery wastewater, with Biochar@nZVI showing promising results.

1. Introduction

The leather tanning industry is known for producing large volumes of wastewater that are heavily polluted with organic and inorganic contaminants. These pollutants, such as COD and Cr, pose a significant threat to the environment and human health. Traditional treatment methods for this wastewater have shown limited success in removing these contaminants, which has led to increased interest in the use of nanoparticles for improved treatment.

Recent studies have shown the effectiveness of using iron zero-valent nanoparticles (nZVI) in the treatment of tannery wastewater. However, the surface modification of nZVI is critical as it affects the way in which the iron is released into the system, producing free radicals that play a crucial role in the treatment process. Studies have shown that modifications such as biochar, aluminum, sulfur, and nitride can enhance the performance of nZVI by increasing its coagulation, corrosion resistance, and organic matter retention capabilities.

For example, biochar has been shown to have high adsorption capacity for heavy metals. On the other hand, nitride of iron has high resistance to corrosion and has shown promising results in the removal of Cl from effluents (Kas et al., 2022).

In addition, the modification of nZVI with aluminum has been shown to enhance its coagulation properties, leading to improved removal efficiency for COD and Cr in tannery wastewater. Similarly, modifications with sulfur have shown increased retention of organic matter, resulting in more effective treatment of tannery effluent (Hallberg et al., 2011; Wang et al., 2022)

Therefore, this study aims to answer the following question: How can the wastewater treatment processes in the tanning industry be optimized to achieve efficient removal of COD and Cr contaminants present in the water, through modification of the surface of zero-valent iron nanoparticles?

2. Materials And Methods

2.1. Materials and Chemicals:

Stable zero-valent iron nanoparticles (nZVI) in air, Biochar-immobilized nZVI, and iron nitride were obtained from NANOFER (Olomouc, Czech Republic). Sodium sulfide (Na_2S) and aluminum sulfate ($Al_2(SO_4)_3$) were acquired from Merck (Darmstadt, Germany). Chromium (III) sulfate ($Cr_2(SO_4)_3$.x and Bovine Serum Albumin (BSA) were acquired from Sigma. Wastewater samples from tanning processes (TTW) were obtained from Colombo-Italiana de Curtidos, a tanning company in Villapinzón, Colombia.

2.2. Wastewater Characterization and control solutions

The tannery wastewater (TWW) was characterized by AAS to determine the total Chromium content. For the TWW, Chlorine was considered as a relevant parameter; therefore, it was determined through the titring method. On the other hand, the chemical oxygen demand (COD) was determined using the Spectrophotometric method in a certified external laboratory. The samples were diluted ten times to avoid interferences duo to high salinity. Other parameters such as pH and salinity were determined using a multiparameter probe. TWW was also characterized using SEM-EDS analysis, in order to determine elemental traces. **Table 1**. Shows main characteristics of TWW.

Table 1. Tanning wastewaster characteristics.

Parameter	**Units**	**Value**
COD	mg L^{-1}	6160 ± 14
Total Chromium	mg L^{-1}	2367 ± 63.6
Chlorine	mg L^{-1}	15500 ± 0.1
pH	-	3.45 ± 0.01
Salinity	PSU	10.47 ± 0.01

Subsequently, in order to identify possible interferences in the remediation reaction between nZVI and wastewater, the following control solutions were prepared in distilled water: i) A BSA solution to simulate a COD value of 6 g/L (Solution A), (ii) a solution of chromium (III) sulfate (2 g/L) (Solution B) and (iii) a solution of BSA and Chromium (III) Sulfate to simulate COD and Chromium (III) values of 6 g/L and 2 g /L respectively (Solution AB).

2.3. Surface modifications of nZVI:

Among the five surface modifications of nZVI compared in this study, three of them (stable nZVI in air, iron nitride and nZVI in Biochar) were purchased directly from the supplier and only underwent an activation process, which consisted of disperse them with ultraturrax (one minute on and one minute off, for 10 minutes) with distilled water in a ratio of 1:4. Subsequently, each activated material was left in a passivation process for 48 hours.

The surface of stable nZVI in air was modified with sulfide, for which the nZVI underwent a similar prior activation process as described, except in the presence of sodium sulfide.

Additionally, the surface of stable nZVI in air was modified with aluminium using the same activation process in the presence of aluminum sulfate. Each material was analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction, and Mössbauer spectroscopy.

2.4. Batch experiments for contaminant removal

Each of the five previously described materials was mixed with (i) 5 mL of TWW setting a ratio of nZVI/COD as 3,2 w/w. Then, the same quantity of material was mixed with (ii) 5 mL of Solution A, (iii) 5 mL of Solution B, and (iv) 5 mL of Solution AB,

For all samples, mixing (reaction) was carried out for 24 h with mechanical stirring at 60 rpm under ambient temperature and pressure conditions. Subsequently, the samples were centrifuged at 13500 rpm. The supernatant was analyzed by AAS and the COD was determined. On the other hand, the solid was analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Mössbauer spectroscopy.

Statistical analysis was performed on the data obtained from the experiments using an analysis of variance (ANOVA) to determine if there were significant differences between the different materials and types of treated water. Tukey's post hoc tests were also performed to identify differences between groups. All statistical analysis were performed using Minitab.

3. Results

3.1. Batch experiments for contaminant removal

EDS-SEM analysis was conducted on the tanning wastewater, revealing the presence of crystals of sodium chloride, as well as crystals containing chromium, sulfur, and traces of organic matter, as seen in Figure 2. No specific or distinguishable nanoparticulate material was found.

When comparing the COD removal between the TWW, Solution A, and Solution AB, significant differences were observed between the results for all three samples. The highest COD removal was achieved in Solution AB, with efficiencies consistently above 97%, followed by TWW, which showed efficiencies above 90% except in the case of iron nitride treatment, which yielded approximately 88% reduction. The lowest COD reduction efficiencies were observed in Solution A, where the use of nZVI or nZVI with aluminum resulted in efficiencies of 89%, while the use of other materials (which can be listed if desired) yielded efficiencies of only 80%. Initially, it was thought that the high removal rates in TWW and Solution AB were due to the presence of trivalent chromium, which could interfere with COD measurement.

However, as shown in Figure 2, chromium removal efficiencies in TWW were consistently above 98% and close to 100% in Solution AB. Therefore, it could be considered that the COD removal efficiencies are due to the reduction of organics regarding to total chromium remotion in the samples. Besides, taking into account the chromium removal percentage shown in figure 2, it can be observed that there are no significant differences in chromium removal among TWW, Solution B, and Solution AB. For TWW, chromium removal is slightly lower (around 98% or higher for all materials), but the ANOVA analysis indicates that there are no significant differences between treatments. In fact, it appears that the presence of chromium in the different solutions enhances the removal of organic matter, as can be observed in the TWW and Solution AB compared to Solution A. The increased removal of organic matter may be attributed to the ability of chromium to produce reactive oxygen species (ROS) in the presence of hydrogen peroxide, which can further contribute to the degradation of organic matter.

This fact can be explained by the well-known fact that transition metals (including Cr) in the presence of hydrogen peroxide are capable of producing free radicals that oxidize organic matter (Das &

Roychoudhury, 2014; Mazivila et al., 2019; Wen et al., 2022). For example, it has been demonstrated that chromium is capable of producing free radicals by the oxidation of Cr (III) to Cr (VI) with hydrogen peroxide (Liu et al., 2022; Lu et al., 2022). Lu et al. in a study case achieved removal efficiencies of Cr and Total Organic Carbon (TOC) of 81.2% and 41.4% respectively (Lu et al., 2022). In addition, numerous studies have shown the ability of nZVI to produce hydrogen peroxide by themselves upon contact with an aqueous (specially acidic) medium (Babuponnusami & Muthukumar, 2014; He et al., 2016), fact that can explain the presence of H_2O_2 in TWW and Solution AB during the treatment.

On the other hand, it has also been widely demonstrated that nZVI has the ability to remove both Cr(VI) through mechanisms such as reduction or adsorption (Ponder et al., 2000; Vilardi et al., 2017; Yin et al., 2020) and Cr(III) mainly by adsorption (Wang et al., 2022). For example in the research of Qiu et al, Cr(III) (1 g/L) was removed with a yield of 28% approximately using nZVI supported on Biochar (1 g/L) (Qiu et al., 2020). This can explain the fact that, although Chromium is completely removed at the end of the process, in some intermediate processes it can contribute to the degradation of organic contaminants, which can result in increased yields when Chromium is present.

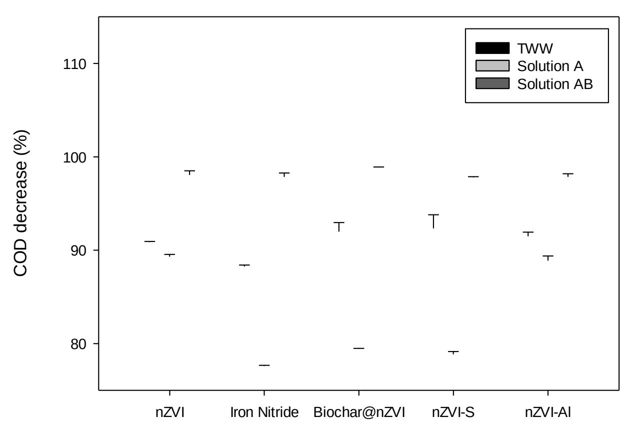

Figure 1. COD removal efficiencies for all materials used in this study.

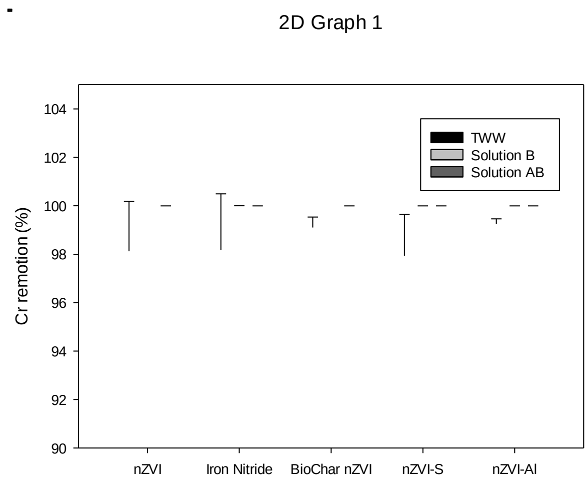

Figure 2. Cr removal efficiencies for all materials used in this study

Following the ANOVA and the Figure 1, also there was a clear difference in the removal of COD between the TWW and the AB solution for all five materials. One potential explanation for this difference is the high chloride content in the TWW, which could inhibit the action of the nZVI. Chloride ions have been reported to form a complex with iron that can interfere with the production of ROS, thus reducing the efficiency of the nZVI (Laat & Le, 2006; Rommozzi et al., 2020).

Comparing the materials, it was observed that the iron nitride material had a lower efficiency in the removal of COD in all types of water. It has been demonstrated that the nitrided material is more surface-resistant to the action of oxygen compared to the non-nitrided form, which suggests that a lower amount of Fe(II) and Fe(III) may have interacted in the system, leading to lower removal efficiencies (Kas et al., 2022; Spies, 2015). Iron nitride achieved removal efficiencies of 88.2%, 77.6%, and 97.9% in TWW, Solution A, and Solution AB, respectively. As mentioned before, the presence of chromium may have contributed to the improved efficiency in TWW and Solution AB. Additionally, the presence of chloride ions may have caused a decrease in efficiency in TWW. It has been demonstrated that iron nitride nanoparticles have the ability to react significantly with chlorine, and this may affect the dissolution of iron from the nanoparticle into the medium (Kas et al., 2022).

Based on the results, there were no significant differences in the average performance among nZVI, Biochar@nZVI, and nZVI-Al for any type of water, with higher means observed. nZVI-S showed higher performance than Fe_x-N but lower than the other three materials. In TWW, all treatments except Fe_x-N did not show statistically significant differences. This can be seen in the means obtained, which are 90.9% ± 0.1, 92.0 ± 1.0, 92.3 ± 1.4, and 91.5 ± 0.5 for nZVI, Biochar@nZVI, nZVI-S and nZVI-Al, respectively. In Solution A, significant differences were observed where nZVI and nZVI-Al with removal efficiencies of 89.2% ± 0.2 and 88.9% ± 0.5, respectively, had a clear difference over treatments using Biochar@nZVI (79.4% ± 0.0) and nZVI-S (78.9% ± 0.3). For Solution AB, no significant differences were found among treatments for any material, with removal efficiencies of 98.1% ± 0.4, 97.9% ± 0.4, 98.9% ± 0.0, 97.9% ± 0.1, and 97.9% ± 0.3% for materials 1, 2, 3, 4, and 5, respectively. However, taking into account the interaction between the type of material and the type of water, a significant difference can be observed in the combination referring to Biochar@nZVI in Solution AB. Additionally, it can be seen that Biochar@nZVI is generally in the group of materials that provide better removal efficiencies (except for Solution A). This suggests that Biochar@nZVI may provide better removal of COD when the system contains chromium and low chloride content.

Conclusions

In conclusion, the study showed that the performance of nZVI-based materials in the removal of COD from water is influenced by the presence of different contaminants and water quality parameters. The results showed that Biochar@nZVI, nZVI, nZVI-S, and nZVI-Al materials performed similarly in all tested waters, while Fe_x-N and iron nitride had lower removal efficiencies. The highest removal efficiencies were observed in water with BSA simulating COD and Cr, followed by Tannery wastewater and Solution with only BSA. The study suggest that the presence of chromium improved the efficiency of the materials over the treatment, while the high chloride content could decrease the efficiency of the nZVI-based materials.

Among the five materials tested, Biochar@nZVI was generally in the group of materials that provided better removal efficiencies, especially in water with BSA and Cr. These findings suggest that Biochar@nZVI may be a promising material for the treatment of industrial wastewater containing chromium.

Overall, the study highlights the importance of considering water quality parameters and the presence of contaminants when evaluating the performance of nZVI-based materials in the removal of COD. Further research is needed to investigate the long-term stability and potential environmental impacts of using these materials in water treatment applications.

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