

# Assessing the performance of green nano Zero Valent Iron in column experiments for the removal of NSAIDs from water

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**Abstract** The existence of emerging contaminants in the aquatic environment is globally a major concern. Among them, non-steroidal anti-inflammatory drugs (NSAIDs) are a vast category of pharmaceuticals that are widely consumed and cannot be completely removed in typical wastewater treatment systems, thus entering the environment and causing adverse effects on living organisms and human health. Nano Zero Valent Iron (nZVI) has been proved capable of removing a wide range of recalcitrant pollutants from contaminated water and soil. Its reactivity, and large specific surface area, in combination with the ability to be produced via 'green' low-cost methods make it a promising material for the reclamation of wastewater from persistent micropollutants. In this study, nZVI made of green tea extracts, was incorporated in a cationic resin and was used in continuous flow pilot experiments to investigate the removal efficiency of two nonsteroidal anti-inflammatory drugs NSAIDs from wastewater, namely Naproxen and Ketoprofen. Results indicated that the nZVI columns exhibited improved performance to the removal of these pharmaceuticals for the lowest initial concentration of pollutants and for the largest bed height investigated, but pH also played a key role on the overall process performance.

**Keywords:** nano zero valent iron, green synthesis, continuous flow experiments, NSAIDs, emerging contaminants

## 1. Introduction

Nonsteroidal anti-inflammatory drugs are pharmaceutical compounds, which are widely consumed to relieve from pain and reduce inflammation and fever. During the last decades, their production has been increased and is expected to become even bigger (Fortune Business Insights, 2020). Among them, Naproxen (NPX) is commonly used for pain relief and inflammations as both prescribed and non-prescribed medicine (Kyeremateng et al.2019) and Ketoprofen is widely used to treat arthritis-related symptoms. It is reported that Ketoprofen is consumed world widely to the same or even bigger extent than Diclofenac (Wang et al. 2018). After their disposal, usage or excretion, residues of these substances are

transferred through the sewage systems to wastewater treatment facilities. Conventional WWTPs have not been designed to remove completely these compounds from wastewater, and as a result they enter the environment polluting water bodies. According to (Tyumina et al. 2020), Naproxen and Ketoprofen belong to the most detected NSAIDs around the world, after Diclofenac and Ibuprofen. Due to their frequent appearance at low concentration levels and their toxic effects on aquatic living organisms and in human health, NSAIDs are classified as Emerging Contaminants.

Various processes for efficient removal of emerging contaminants are currently under the scope of the scientific community. Nanomaterials, Advanced Oxidation Processes (AOPs), such as ozonation, Fenton and Fenton-like processes, sonocatalysis and others are investigated as promising techniques for removing these micropollutants from wastewater. These processes could be integrated in WWTPs as post-treatment methods, enhancing the quality of the effluent stream before its disposal into the environment. However, issues on performance, the maturity of the technology and the treatment costs are arising. To begin with, some technologies may result to partial degradation of the substances, leading to even more toxic intermediate products and metabolites, than the parent compound. Furthermore, the addition of required drastic chemical reagents may increase the treatment costs. As the majority of studies focusing on the removal of NSAIDs from wastewater regard batch and laboratory experiments, the research is still at infantry level. Therefore, the need to explore the performance of technologies aiming to eliminate emerging contaminants from wastewater in continuous flow experiments, at low cost and using environmentally friendly materials, is nowadays urgent.

Nano Zero Valent Iron is a promising material for the removal of NSAIDs from wastewater, as it has been proved capable of removing a wide range of refractory substances from wastewater and soil. Its small particle size, and large specific area, are considered to be the major advantages of processes utilize nZVI. In addition, 'green' methods for producing nZVI has come to light in the recent years (Machado et al. 2013), which could limit the use of

chemical compounds that could also have a negative impact on the environment and aquatic life. On the other hand, the most major limitations of the method are the requirement for a host porous supportive material to protect ZVI nanoparticles from corrosion and agglomeration, increasing also the stability and dispersity, the partial reduction of trivalent iron to nZVI which may lead to iron loss, and the uncertainty for the possibility of undesirable effects when nZVI processes are incorporated as post-treatment steps in larger wastewater treatment trains.

Several studies are examining the performance of nZVI in the removal of pharmaceuticals, heavy metals, dyes, herbicides, etc. However, to our best knowledge no prior work evaluates the performance of nZVI material in continuous flow experiments for the removal of NSAIDs.

In the present study, the performance of nZVI produced by green tea extracts, and supported onto a cationic resin to remove selected emerging compounds from water has been investigated through continuous flow experiments. The selected NSAIDs were Naproxen (NPX) and Ketoprofen (KTP). Two experimental runs took place, investigating the effect of the bed height of the column and the initial concentration of the pollutants in the process performance.

## 2. Materials & Methods

### 2.1. Materials

The two tested NSAIDs (NPX and KTP), as well as MCF (Meclofenamic acid sodium salt), used as surrogate during the analysis were purchased from Sigma Aldrich (purity grade  $\geq 93\%$ ). Methanol (MeOH) and ethyl acetate (ETH) with high-performance liquid chromatography (HPLC) grade were purchased from Merck, Germany and from Fluka, Germany, respectively. For silylation, pyridine and Bis(trimethylsilyl)trifluoroacetamide (BSTFA) +1% trimethylchlorosilane (TMCS) were acquired from Sigma Aldrich. Stock solutions for NPX, KTP and MCF with a concentration of 1000ppm were prepared and stored at  $-18^{\circ}\text{C}$ , as in (Koumaki et al., 2017). Furthermore, the cartridges C18 6ml for solid phase extraction (SPE) were acquired from Isolute, Biotage. Ultra-pure water was prepared in the laboratory using a MilliQ/Milli-RO Millipore system (Millipore, Billerica, Massachusetts USA). Ultra-pure HCl (32%) was used for acidification of the samples (Sigma Aldrich, Germany). Sodium chloride (NaCl), iron chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) was purchased from Fluka, USA. Resin Amberlyst 15 hydrogen form wet was purchased from Sigma Aldrich. For the green tea extracts utilized in the synthesis process of ZVI nanoparticles, a commercial product was used from Twinings of London.

### 2.2. Analytical Methods

The analysis of the NPX and KTP was based on an already developed analytical protocol (Samaras et al., 2011). Briefly, the basic steps of the method include the pre-concentration of the acidified wastewater samples at pH

2.5 to ETH solutions of 6ml through SPE, the evaporation to dryness of the ETH solutions by nitrogen purge and the addition of  $50\mu\text{L}$  BSTFA + 1% TMCS along with  $10\mu\text{L}$  of pyridine for derivatization of the targeted compounds in bath device at  $70^{\circ}\text{C}$  for 20 min. The final extracts were analyzed by Gas Chromatography (Agilent 7890A) coupled with a Mass Selective Detector (Agilent, 5975C). Water characteristics were determined according to Standard Methods ((APHA), 2005).

### 2.3. R-nFe synthesis

The synthesis of the cationic resin containing ZVI nanoparticles, was performed according to (Toli et al., 2018) was followed. More specifically, the beads of the resin were treated for 2h with NaCl 1M solution at 200rpm and then the material was agitated for 4h with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution of 0.05M concentration at 200rpm in order sodium ions  $\text{Na}^+$  to be replaced by trivalent iron cations  $\text{Fe}^{+3}$ . Finally, an agitation for 20h took place, after the addition of green tea extracts in order the contained polyphenols to reduce the adsorbed  $\text{Fe}^{+3}$  to nano zero valent iron (nZVI). Then, the resin containing the nZVI (denoted hereafter as R-nFe) was ready for application.

For the preparation of the green tea extracts, tea bags were added in distilled water and the liquid was boiled for 5 min in  $80^{\circ}\text{C}$ . After this step, the extracts were cooled to room temperature, and they were filtered using a membrane filter with pore size of  $0.45\mu\text{m}$ .

### 2.4. Column experiments

The pilot system set up consisted of an inlet tank, a peristaltic pump, two identical PE columns connected in series with intermediate plastic pipes and an outlet tank. Each column was equipped with a valve at the bottom to enable sampling. After the assembly of the pilot system, each column was filled with R-nFe 200g which corresponded to a height of approximately 20cm. Furthermore, glass fiber was placed at the bottom of each column, to avoid material loss. The inlet tank had a capacity of 75L and was filled with tertiary treated wastewater. The targeted compounds were spiked and mixed with the liquid matrix at a concentration of  $1\mu\text{g L}^{-1}$  and  $5\mu\text{g L}^{-1}$  for the first and the second experimental run, respectively. Sampling was taken every day of operation from the inlet tank and the outlet of the first and second column. The peristaltic pump was adjusted to achieve a downward flow of  $26\text{L d}^{-1}$ . pH, DO, and T were monitored every day of the columns' operation.

It should be noted that before the experimental runs, the nZVI material was pre-treated with solution of NaCl 1N, as preliminary batch experiments indicated the beneficial effect of NaCl to the performance of nZVI on the removal of NSAIDs. The design calculations for the nZVI columns are presented synoptically below:

The bed volume (BV) of each column with specific height (h) and diameter (d) was calculated, as follows:

$$BV = h \cdot \pi d^2 / 4$$

For a certain mass of the material (M) the bulk density was given by the following equation:

$$\rho_{bulk} = M/BV$$

The external porosity  $\theta$  was calculated as:

$$\theta = 1 - \rho_{bulk}/\rho_p$$

where  $\rho_{bulk}$ , and  $\rho_p$  the bulk and particle density, respectively.

The Pore volume size VPV was calculated by the following equation:

$$VPV = BV \cdot \theta$$

The normalized pore volume was calculated for each column, with the following equation:

$$Norm.Pore Volume = V_t/VPV$$

where  $V_t$  the volume of the treated wastewater in a given time period.

Furthermore, prior to experimental runs, the porosity of the filling material was experimentally found 18%, close to the theoretical value which was used in the design phase which was 20%. The breakthrough of the column was considered to happen when the concentration (C) of the target compounds at the effluent of each column was above (80%) of the initial concentration ( $C_0$ ). The experimental runs were completed at the normalized pore volume of 2000, at which the breakthrough of the targeted compounds had been accomplished in all cases. The column containing R-nFe with 20cm height is denoted hereafter as Column A and the other one with twice the height of the first column (40cm height) is denoted as Column B.

### 3. Results and Discussion

#### 3.1. Effect of initial concentration of pollutants

For investigating the effect of the initial concentration of the pollutants, two experimental runs were implemented, one with the initial concentration of the targeted compounds in the inlet tank to be  $1 \mu\text{g L}^{-1}$  and the second one with  $5 \mu\text{g L}^{-1}$ . As illustrated in Fig. 1 indicatively for the case of NPX and Column A, the increased initial concentration of the pollutants led to decreased removal efficiency; the R-nFe material lost sooner the ability of removing the polluting. The breakthrough for NPX in Column A occurred at a value of normalized pore volume 310 for the higher initial concentration, whereas for the lowest it occurs at 550. Similar results were obtained for KTP in Column A for the highest and lowest initial concentration, respectively. It seems that the initial concentration of the target compound significantly affected the performance of the material for both NSAIDs, leading to material's saturation and no further removal could be observed after that point.

#### 3.2. Effect of bed height

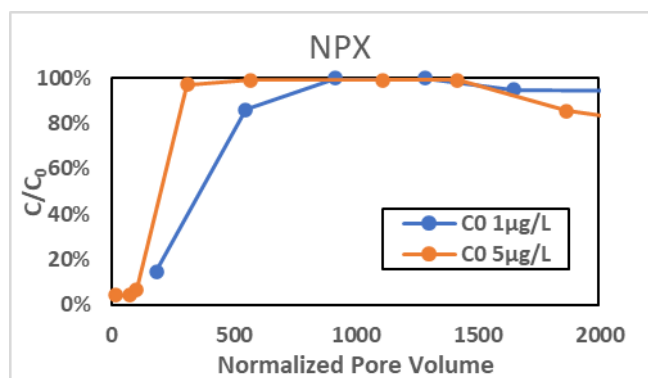
The effect of bed height was evaluated in Column A and B for both experimental runs. As indicated in Fig. 2 for KTP indicatively in case of the lowest initial concentration of the selected compounds, Column B exhibits better performance compared to Column A which has the half bed height. More specifically, for KTP and NPX breakthrough occurred at 642 for  $C_0 1 \mu\text{g L}^{-1}$  in Column B. This was consistent also for the second experimental run with the higher initial concentration of  $5 \mu\text{g L}^{-1}$ . In this case, breakthrough occurring at 416 normalized pore volumes in Column B for both selected NSAIDs. The larger bed height increases the contact time between nZVI material and targeted pollutants, offering more active sites of R-nFe to react with the targeted pollutants.

#### 3.2. Effect of pH

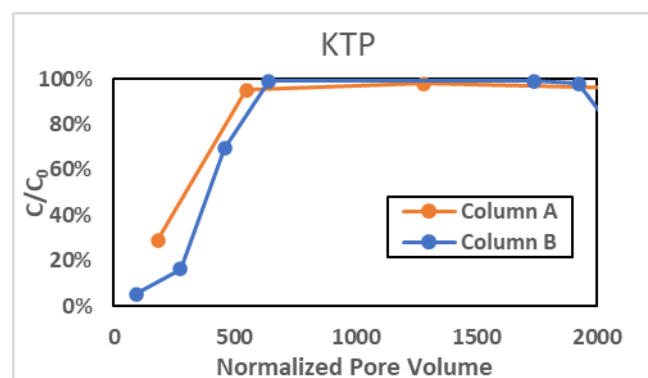
It was observed that breakthrough occurred simultaneously for both pharmaceuticals under the same conditions, i.e. bed height of the column and initial concentration. This may be attributed to the effect of pH. In both experimental runs, the pH value was increased in each column gradually, from acidic to alkaline values till the breakthrough point. More specifically, due to the acidic nature of nZVI and the cationic resin, the pH values of the liquid samples taken from Column A and B were at the range of 2.1-3.8 at the beginning of the experiments and elevated initially in Column A and later in Column B, till the equalization with the pH value of the influent tertiary treated wastewater took place which was at 7.3. As this pH increase in each column, occurred almost simultaneously with the breakthrough of the targeted compounds, pH seems to play a major role to the removal of these compounds with the nZVI process.

### 4. Conclusions

In this study, two NSAIDs were selected for investigating the process performance of nZVI produced by green tea extracts supported into a porous matrix, namely a cationic exchange resin, in continuous flow experiments. The results indicate that the initial concentration of pollutants, and the column's bed height affect the process performance of nZVI, with increased initial concentration of pollutants and smaller bed height leading to reduced removal efficiency of the nZVI columns, however pH may be the most dominant parameter for the removal of these NSAIDs in continuous flow processes with nZVI. As the obtained results are limited for the selected NSAIDs in this study, further research is still needed to evaluate the process performance of nZVI in removing NSAIDs using a representative mix of these compounds.



**Figure 1.** Comparison of the two experimental runs in column A, for NPX and different initial concentrations  $C_0$   $1 \mu\text{g L}^{-1}$  and  $5 \mu\text{g L}^{-1}$



**Figure 2.** Comparison of the process performance of ZVI for different bed heights, 20cm (Column A) and 40cm (Column B), for the initial concentration of  $C_0$   $1 \mu\text{g L}^{-1}$

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