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Investigation of the performance of green nano Zero Valent Iron for the removal of emerging contaminants from water

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Abstract Nano Zero Valent Iron (nZVI) is considered as a promising nanomaterial for the removal of a wide range of recalcitrant pollutants from contaminated water and soil. Due to its high reactivity, large surface area, its catalytic and reductive properties along with the ability to be produced at low cost using herbal extracts, technologies incorporating nZVI are recently receiving a lot of attention. This study focuses on the utilization of nZVI made of green tea extracts which is supported in a cationic exchange resin, to remove selected emerging contaminants, classified as non-steroidal anti-inflammatory drugs and endocrine disrupting chemicals from water. The effectiveness of the nZVI resin (R-nFe) and the effect of crucial parameters, as the contact time, initial pH, nZVI resin's dose, and the pre-treatment of the nZVI resin with NaCl was evaluated through batch experiments. The effect of the resin was also investigated in the removal performance. Results indicate that most of the selected compounds can be removed efficiently in acidic pH values, and the pre-treatment of the nZVI resin with NaCl is optimal for achieving higher removal efficiencies. However, the adsorption capacity of the resin seems to play also an important role in the removal of some targeted compounds.

Keywords: nano zero valent iron, green synthesis, endocrine disrupting chemicals, pharmaceuticals, emerging contaminants

1. Introduction

Emerging contaminants (ECs) are one of the most significant topics of 21st century, regarding water and soil pollution. The term 'Emerging contaminants' refers to a wide range of recalcitrant chemical compounds, including pharmaceuticals and personal care products (PCPPs), pesticides, herbicides, surfactants, illicit drugs and others, (Jones-Lepp, 2012; Teodosiu, et al., 2018) that are frequently detected in the environment and in water bodies, usually at trace levels (ng/L-μg/L). However, even at these small concentrations, ECs may have adverse effects on living organisms, posing a great risk to aquatic life, and human health (Wilkinson et al., 2017). Their elimination is subjected to several challenges. Some of the main ones are related to the increasing number of ECs as a result of the release of new chemical products in the global market and their massive consumption for everyday uses, the requirement of advanced analytical techniques for their identification and qualification (Geissen, et al., 2015) and the limited knowledge about their fate in WWTPs and in the environment. Furthermore, conventional activated sludge systems are not designed to remove completely these micropollutants from water (González et al., 2016). Therefore, alternative processes, that may serve as an additional post-treatment step towards the elimination of ECs, have recently stimulated the interest of the scientific community.

Nano Zero Valent Iron (nZVI) has been successfully employed in various treatment processes for the removal of a wide range of organic and inorganic pollutants, such as TCEs, heavy metals, antibiotics, dyes, pesticides, etc. (Pasinszki & Krebsz, 2020). Due to the small particle size and large specific area, its high reactivity, and its reductive, catalytic, and adsorptive properties, it is considered as a promising material for the removal of ECs from water. Recently, nZVI has also gathered a lot of attention, as it can be synthesized via 'green' methods, i.e. utilizing polyphenols contained in herbal extracts, as reducing agents for trivalent iron (Fe^{+3}), thus offering a low-cost, and environmentally friendly option for wastewater treatment (Machado, et al., 2013). However, ZVI nanoparticles tend to agglomerate and become less reactive in the presence of electron acceptors, minimizing their beneficial properties. In order to overcome this limitation, and also to provide stability and dispersity, nZVI is usually incorporated into porous matrices, like biochar, organic polymers, zeolites and others (Fu et al., 2014; Li et al. 2019).

In this study, the efficiency of nZVI produced by green tea extracts, and supported onto a cationic resin to remove selected emerging compounds from water has been investigated through batch experiments. The selected ECs regard two commonly used non-steroidal anti-inflammatory drugs (NSAIDs), namely Ibuprofen (IBU) and Naproxen (NPX) and Bisphenol-A (BPA), as representative of endocrine disrupting chemicals. Furthermore, the effect of the contact time, nZVI-material dosage, pre-treatment with NaCl, the effect of different pH values and the role of the porous supportive material are investigated.

2. Materials & Methods

2.1. Materials

IBU, NPX, BPA, MCF (Meclofenamic acid sodium salt), and deuterated BPA (BPA-d16) compounds with high purity grade (≥93%) were purchased from Sigma Aldrich. Methanol (MeOH) and ethyl acetate (ETH) of high-performance liquid chromatography (HPLC) grade were purchased from Merck, Germany and from Fluka, Germany, respectively. Pyridine and Bis(trimethylsilyl)trifluoroacetamide (BSTFA) +1% trimethylchlorosilane (TMCS) for silylation were purchased from Sigma Aldrich. Stock solutions for each compound with a concentration of 1000ppm were prepared and stored at -18°C, as in (Koumaki et al., 2017). Cartridges C18 6ml for solid phase extraction (SPE) were purchased 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 carbonate (Na_2CO_3) was purchased from Merck, Germany, and sodium chloride (NaCl), iron chloride hexahydrate ($FeCl_36H_2O$) was purchased from Fluka, USA. Resin Amberlyst 15 hydrogen form wet was purchased from Sigma Aldrich. For the green tea extracts, a commercial product was used from Twinings of London.

2.2. Analytical Methods

For the quantification of the selected ECs, the analytical method developed by (Samaras et al., 2011) was used. In summary, the basic steps of the method include the pre-concentration of the acidified liquid 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 50μL BSTFA + 1% TMCS along with 10 μL of pyridine for derivatization of the targeted compounds in bath device at 70°C for 20 min. The analyses were performed via an Agilent Gas Chromatograph (7890A) connected with an Agilent Mass Selective Detector (MSD) (5975C). MCF and BPA-d16 were used as surrogates for the NSAIDs and EDCs, respectively. Water characteristics were determined according to Standard Methods ((APHA), 2005).

2.3. R-nFe synthesis

For the synthesis of nZVI resin, the methodology proposed by (Toli et al., 2018) was followed. Synoptically, the beads of the resin were treated for 2h with NaCl 1M solution at 200rpm (denoted hereafter as R-Na). Then, the R-Na was agitated for 4h with $FeCl_36H_2O$ solution of 0.05M concentration at 200rpm in order sodium ions Na^+ to be replaced by trivalent iron cations Fe^{+3} (denoted as R-Fe). Finally, R-Fe was agitated for 20h with the green tea extracts in order the contained polyphenols to reduce the adsorbed Fe^{+3} to nano zero valent iron (nZVI). Then, the resin containing the nZVI (denoted hereafter as R-nFe) was ready for use. It should be noted that the nZVI content in the resin was considered to be 0.35mmol g^{-1} resin, and that the resin was not sieved before use as (Toli et al., 2018) obtained that for the removal of hexavalent chromium, the particle size of the resin did not play a major role.

The green tea extracts were prepared, by adding tea bags in distilled water and boiling the liquid for 5 min in 80°C. After this step, the extracts were cooled to room temperature and they were filtered using a membrane filter with pore size of 0.45μm.

2.4. Batch experiments

All experiments were performed in 1L conical glass flask, where the targeted compounds were spiked at an initial concentration of 1μg L^{-1}. The flasks were agitated for 15 minutes to ensure the homogeneity of the solution. After this step, the batch experiments were performed in 1L glass bottles adding the desirable nZVI-resin dose. During the experiments, the bottles were protected against light and they were placed in an agitation plate adjusted to 200 rpm. Control experiments were performed to ensure that the selected investigated compounds remain stable without the addition of the R-nFe resin. Also, background tests with R-nFe, and R-Na were conducted without spiking the compounds. The results indicated that none of the resin materials could have a negative effect on the removal of NPX, IBU, and BPA.

3. Results and Discussion

3.1. Effect of Contact Time and R-nFe dosage

The effect of the contact time was evaluated for two different R-nFe doses of 15g L^{-1} and 30g L^{-1}, respectively. The maximum removal efficiencies were achieved at the end of the experiment (2 days) for both R-nFe doses. The rate of the removal seemed to be faster at the beginning of the experiments, and decreased significantly after 6 hours, even though this was more profound for the larger R-nFe dose. This effect could be attributed to the initially higher reactivity of nZVI, which gradually diminishes with the increase of contact time due to nZVI consumption or corrosion under aerobic conditions.

After 2 days of contact time with the smaller R-nFe dosage, IBU had medium removal efficiency (of approximately 32%), whereas for NPX and BPA higher removal efficiencies were obtained, (75% and 69% respectively). With the increase of R-nFe dosage from 15 to 30g L^{-1}, the removal efficiencies increased to 56%, 87% and 74% for IBU, NPX and BPA respectively. It could be assumed that as R-nFe dose increases, more active sites are available for adsorption and reactions to take place, leading to improved removal efficiencies of the target compounds. Indicatively, the effect of contact time and R-nFe dosage is illustrated in Figure 1 for IBU.

3.2. *Effect of NaCl pre-treatment.*

The effect of R-nFe pre-treatment with NaCl 1M solution was investigated through batch experiments. The R-nFe resin was treated for 1 day at 200 rpm with NaCl 1M solution before employed in batch tests and compared with R-nFe of the same dosage without the pre-treatment with NaCl solution. As illustrated in Figure 2 indicatively for NPX, this pre-treatment achieved higher removal efficiencies independently of the investigated contact time. The maximum removal efficiencies were achieved at the larger contact time of 2 days and were 50%, 85% and 70% for IBU, NPX and BPA respectively. However, the beneficial effect of NaCl pre-treatment was maximized at 6 hours, with an increase in the removal efficiencies up to 33% for the small dosage of R-nFe, whereas at 3 hours of treatment this increase was also significant (up to 29%). This finding was in agreement with (Ghauch et al., 2009) who reported that the addition of NaCl may trigger the iron corrosion, thus increasing the reactivity of nZVI. Furthermore, the use of an electrolyte before treatment may equalize the pressures in the liquid medium with the pressures inside the pores of the resin, enhancing the transportation of the pollutant into more active sites in the pores of the resin. Therefore, the pre-treatment of R-nFe with NaCl 1M was adopted for the rest experiments.

3.3. *Effect of pH*

For investigating the effect of pH, two experiments were conducted for the same dosage, at pH 3 and at pH 7. For the pH 3, no addition of an initial buffer was needed, while for the experiments performed at pH 7, the initial solution was adjusted with $NaHCO_3$ at a concentration of 1.5g L^{-1}, namely a ratio $NaHCO_3$ to R-nFe equal to 1:10, and during the experiments with drops of NaOH 1N or HCl 1N when necessary. It was observed that at pH 7 the removal of the target compounds was minor. On the other hand, at pH 3, the removal was significantly higher for NSAIDs but for BPA this was not the case. As both resin's and nZVI's surface charge is negative at pH 3, and also the selected target compounds are not ionized at their most part in pH values lower of their pKa, these increased removals cannot be attributed to adsorption due to electrostatic attractions. One explanation could be that Fenton reactions may occur in the presence of oxygen and Fe^{+2}/Fe^{+3} at pH 3 although a major drop at dissolved oxygen level was not observed during the experiments. On the other hand, at pH values greater than 3, the adsorbed trivalent iron into the resin may precipitate which could negatively affect the removal of the targeted compounds by blocking active sites for adsorption and diminishing the available iron source.

3.4. *Effect of the resin*

The adsorption capacity of the resin may play important role on the removal efficiencies of some compounds. Although the resin is cationic namely it adsorbs positive charged ions, maybe other adsorption mechanisms are responsible for the removals obtained such as π-π interactions and hydrogen bonds. For IBU and NPX, the positive effect of nZVI was apparent. However, for the removal of BPA almost the same removal was observed for R and R-nFe.

4. Conclusions

nZVI is a promising material for the removal of ECs from water. 2 representatives of NSAIDs and 1 of EDCs were selected for investigating the performance of nZVI produced by green tea extracts supported in a porous matrix, i.e., a cationic exchange resin. The results indicate that nZVI may have a positive effect on the selected target compounds, and this is depending on the R-nFe dosage, the pH value, the contact time and the pre-treatment with NaCl. Also, the resin may offer additional removal mechanisms for the elimination of some emerging compounds.

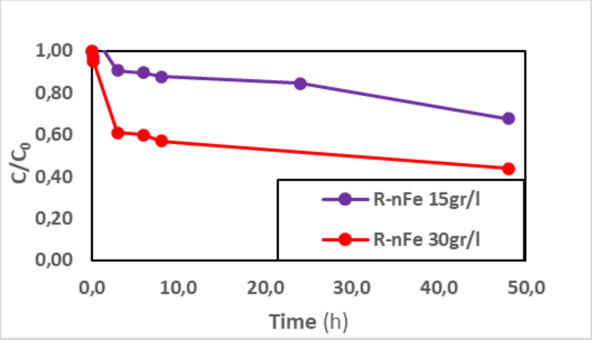

Figure 1. a) Effect of Contact Time and R-nFe dosage in the removal of Ibuprofen (IBU). R-nFe 15g L^{-1}, 30g L^{-1} , pH 4,5 -5, C_0 1μg L^{-1}, DO 8mg L^{-1}

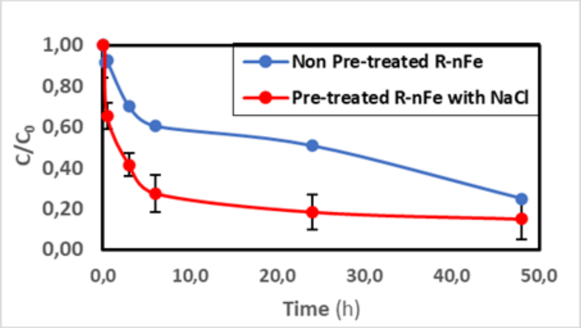

Figure 2. Effect of R-nFe Pre-treatment with NaCl 1M on the removal of Naproxen (NPX). R-nFe 15g L^{-1}, C_0 1 μg L^{-1}, pH 4, DO 8mg L^{-1}

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