Heterogeneous Fenton process for natural organic matter removal: steel nails as zero-valent iron source

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EXTENDED ABSTRACT

Introduction

Natural organic matter (NOM) may be responsible for drinking-water quality issues regarding colour, odour, taste, and formation of disinfection by-products (DBPs, which can be formed in the reaction of chlorine with NOM during the production of drinking water in treatment plants (WTPs)). Drinking water containing such DBPs has been associated with an increased risk of cancer in human beings especially in the bladder, and adverse reproductive outcomes [1][2]. *In this way, NOM removal before the chlorination step is essential to minimize the risk of formation of the DBPs. Advanced Oxidation Processes (AOPs) are recognized as possible NOM removers during water treatment* [3]. *However, some applications require the use of special equipment such as UV lamps or ozone generators* [4], *which increases the treatment costs. In this context, seeking both operational simplicity and low cost, the AOP Fenton is an alternative to removing NOM. The conventional Fenton reaction uses hydrogen peroxide (H_2O_2) and iron (II) salts to produce a highly reactive radical (HO•) capable of oxidizing organic compounds* [5]. *However, none of these investigations reported the Fenton process for the removal of NOM in drinking water treatment using comercial iron-nails as iron source. Thus, in this study, a Heterogeneous Fenton process was investigated to remove the NOM present in natural water (water from the Regent's Park lake - London, UK), using commercial carbon steel nails as a source of zero valent iron (ZVI). Here the application of carbon steel nails is proposed due to their lower associated cost, commercial accessibility, and easier separation from the water compared to commercial particulate iron powder. The investigated process may be especially interesting for WTPs in regions that may lack sufficient infrastructure and/or finance.*

Methods and Materials

A factorial design in three variables and two levels (2^3) was used for the evaluation of the effect of the pH, dosage of H_2O_2 and amount of ZVI on the Heterogeneous Fenton process. Statistical analysis was performed using software Statistica 8.0, StatSoft (Inc., USA). All experiments were carried out as batch runs, with 1 L of test water, under agitation at 250 rpm, in Jar-test equipment, at room temperature. The chemical reagents used were of analytical grade and the solutions prepared with ultrapure water (Milipore Mili-Q, resistivity > 18.2 M_cm). The average values of the compositional characteristics of the study water were (n=5): pH = 8.0 ± 0.26; DOC (mg L^{-1}) = 6.5 ± 2.5; Conductivity (µs m^{-1}) = 1007 ± 39.6; Turbidity (NTU) = 1.13 ± 0.19; Chlorine (free) (mg L^{-1}) = 0.03 ± 0.01. The NOM content was determined from samples previously filtered through a 0.45 µm (characterized as dissolved organic matter). Small low-carbon steel nails (AISI 1010) with total trace elements amount of 1% [3] were applied as ZVI source in the process.

Results and Discussion

Table 1 indicates the effect of pH on the efficiency of the Fenton Heterogeneous process. The significant decay of $SUVA_{254}$ at pH 4.5 indicates possible changes in the structure of NOM, such as loss of aromatic structures, reported as reactive to chlorine for the formation of DBPs [3].

Table 1 - Removal of MON and residual concentration of ferrous ions and solid precipitates at the end of the Heterogeneous Fenton (ZVI = 50 g L^{-1} and [H_2O_2] dose = 100% of excess of the stoichiometric dosage, and pH = 4.5 and 6.5) applied in Regent's Park water.

pH	DOC removal (%)	$SUVA_{254}$ removal (%)	[Fe^{2+}] (mg L^{-1})	Sludge formed (mg L^{-1})
4.5	51	77.2	1.05	29
6.5	8	44.9	0.05	49.6

Figure 1 shows the response surface to the interaction between the variables that responded significantly ($p < 0.05$) to the DOC removal effects of the present study by the AOP Fenton Heterogeneous: pH (p = 0.0001) and H_2O_2 dosage (p =

0.0248) (R^2= 0.956). Results indicate significantly removal of DOC when there was a shift to the minimum values of pH (4.5) and maximum values of H_2O_2 dose (100% excess).

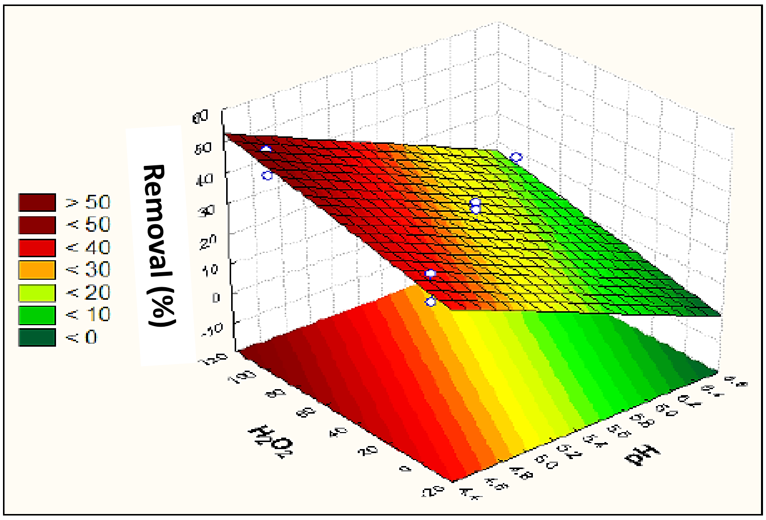

Figure 1 - Surface chart of interaction between pH and H_2O_2 dosage by Heterogeneous Fenton (amount of ZVI = 50 g L^{-1}).

In this investigation, DOC removal was described as an empirical model (Equation 1). The adjustment of experimental values to the model indicated satisfactory linear regression (R^2 = 0.7813) and positive linear relationship (Pearson value = 0.884). Based on the model, one can propose that the Heterogeneous Fenton process may be governed by (1) the initial pH of the medium and (2) the dose of H_2O_2. It is important to highlight that interferents such as organic/inorganic ions in water can influence the kinetics of the process. Thus, the derived empirical model is considered satisfactory to explain the removal of DOC present in natural water by the Heterogeneous Fenton using nails as ZVI source.

$$Z = 42.09 - 5.148 * x + 0.198 * y + 0.004 * x * y - 0.307 * K1 * x - 0.0026 * K1 * y + 69.8 \qquad \text{(Equation 1)}$$

where: Z = DOC removal (%); y = excess of dosage of H_2O_2 (%); K1 = constant value (ZVI = 37.5 g L^{-1}, according to the central point of statistical planning)

Conclusions

ZVI-nails showed potential as source of iron for application in the heterogeneous AOP Fenton. The AOP presented satisfactory removal of organic compounds with favourable characteristics of operational simplicity and low cost, indicating the possibility of its application as a pre-oxidation step in a conventional drinking water treatment process. In addition, it is expected that the consequent removal of the remaining fractions may still occur in the ensuing treatment steps after the Heterogeneous Fenton. Future studies are proposed to confirm this possibility.

REFERENCES

[1] M. Kitis, T. Karanfil, J. E. Kilduff, and A. Wigton, "The reactivity of natural organic matter to disinfection by-products formation and its relation to specific ultraviolet absorbance," *Water Sci. Technol.*, vol. 43, no. 2, pp. 9–16, Jan. 2001, doi: 10.2166/wst.2001.0067.

[2] S. D. Richardson, M. J. Plewa, E. D. Wagner, R. Schoeny, and D. M. DeMarini, "Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research," *Mutat. Res. - Rev. Mutat. Res.*, vol. 636, no. 1–3, pp. 178–242, 2007, doi: 10.1016/j.mrrev.2007.09.001.

[3] N. de O. dos Santos, L. A. Teixeira, Q. Zhou, G. Burke, and L. C. Campos, "Fenton pre-oxidation of natural organic matter in drinking water treatment through the application of iron nails," *Environ. Technol.*, pp. 1–14, Mar. 2021, doi: 10.1080/09593330.2021.1890838.

[4] M. Sillanpää, *Natural Organic Matter in Water: Characterization and Treatment Methods*, First Edit. Finland: Elsevier, 2015.

[5] D. H. Bremner, A. E. Burgess, D. Houllemare, and K.-C. Namkung, "Phenol degradation using hydroxyl radicals generated from zero-valent iron and hydrogen peroxide," *Appl. Catal. B Environ.*, vol. 63, no. 1–2, pp. 15–19, 2006.