Zero-valent iron from iron wastes for environmental applications

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Keywords: iron waste, zero-valent iron, waste valorisation, green tea.

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The European environmental policies have been enforcing the "end-of-waste" strategy by promoting recycling and valorisation of waste (Directive 2008/98/EC). Different chemical, metallurgical and mining industries, among others, yield high amounts of Fe-based by-products and wastes. Some of these wastes may not be recycled into subsequent industrial processes due to some possible contaminations, thus being dumped in landfills.

Iron, either in Fe^0, Fe^{2+} or Fe^{3+} form, is often used for environmental remediation purposes both for soil and wastewater treatments. Zero-valent iron (ZVI, Fe^0) has been used during the last decades due to its high reactivity in reducing chlorinated compounds such as PCBs and TCE, nitrate and metals including Cr, Zn, Pb, Cd or Ni (Crane and Scott, 2012). Moreover, ZVI can be used to oxidise organic matter when combined with, for example, H_2O_2, allowing the depuration of wastewaters (Martins *et al*, 2012). Though ZVI can be synthesized by several approaches, like electrochemical or sonochemical methods, the most used for research purposes involves chemical reduction of iron salts, such as $FeSO_4$ or $FeCl_3$ using $NaBH_4$ (Wang and Zhang, 1997). More recent studies proposed biodegradable natural substances such as polyphenols present in tea extracts (Hoag *et al*, 2009) as an alternative reducing agent to obtain ZVI from iron salts.

The main goal of this research is to synthesize ZVI from iron wastes, as alternative precursors to the traditional iron salts, using $NaBH_4$ or green tea extracts as reducing agents. A waste from the Fenton's Process for wastewater treatment, Iron Fenton Sludges (IFS), and two wastes from a Portuguese metallurgical industry, Cast Iron Shot (CIS) and Grind Precipitate Dust (GPD), were chosen to be tested as iron sources. The wastes were characterised regarding their moisture (M), volatile solids (VS), iron content, elemental analysis (C, N, H and S), besides Brunauer–Emmett–Teller (BET) specific surface area (Table 1). Moisture content and VS results were found to be high for IFS, which indicates the presence of organic matter in this sample.

The potential for releasing pollutants in water was determined by leaching at the natural pH of the materials, according to the standard EN 12457-2, with a liquid/solid ratio of 10 L/kg (L/S=10) for 24 hours. The results obtained are shown in Table 2. The three leaching solutions appear to have a near neutral pH and low metals content (Fe, Cd, Pb and Zn). However, significant values for electric conductivity (EC), chemical oxygen demand (COD) and dissolved organic carbon (DOC) were found only on IFS sample. Eco-toxicity analysis were performed by the LUMIStox test (DIN/EN/ISO 11348-2), based on the inhibition of luminescent bacteria (*Vibrio fischeri)*. IFS seems to be eco-toxic possibly due to the high organic load content showed by COD and DOC.

Table 1. Physico-chemical characterisation of the iron wastes (IFS, CIS and GPD).

	IFS	CIS	GPD
M (%)	52.3±0.7	0.1±0	0.6±0
VS (%)	52.8±0.1	1.3±0.4	0±0.1
Fe (g/kg)	283.7±58.6	37.4±19.2	232.6±38.9
C (%)	30.60	5.29	0.82
N (%)	1.56	0.33	0.25
H (%)	5.51	0.19	0.09
S (%)	2.64	1.88	1.86
BET (m^2/g)	0.58±0.03	-	5.30±0.05

The results for IFS and GDP appear to be promising, since the iron content is significant and thus both are good candidates for the ZVI production. Nevertheless, before iron reduction to ZVI, the organic contents present in IFS should be eliminated in a first step by calcination at 550 ºC. CIS and GPD, as non eco-toxic wastes, are able to be directly reduced to ZVI form.

Next steps of this study consisted in the comparison of iron wastes reduction to ZVI with $NaBH_4$ and with green tea extracts. The applicability of the ZVI produced was tested to remove the colour from a simulated textile effluent produced by an azo-dye. The reactivity of ZVI particles was ascertained by H_2 production according to Quina *et al* (2015).

Table 2. Characterisation of the leaching solutions (L/S = 10).

	IFS	CISW	GPD
pH	6.7±0.1	7.2±0.3	7.0±0.3
EC (mS/cm)	3.98±0	0.05±0	0.16±0
Fe (mg/kg)	1.43±0.55	0.15±0.21	< DL
Pb (mg/kg)	0.30±0.42	< DL	1.05±0.78
Cd (mg/kg)	0.18±0.04	0.14±0.01	0.06±0.08
Zn (mg/kg)	0.15±0.15	0.04±0.05	0.06±0.08
Cu (mg/kg)	1.00±0.13	< DL	< DL
Cr (mg/kg)	0.03±0.01	< DL	< DL
COD (mgO_2/L)	2404±13.1	< DL	< DL
DOC (ppm)	1781±189.5	0.97±2.9	25.11±2.6
Eco-toxicity	EC_{20}= NC	EC_{20}= NC	EC_{20}= 21.08%
	EC_{50}=15.45%	EC_{50}=NC	EC_{50}=NC

DL - Detection Limit; NC - Non Calculated.

Acknowledgements

The authors gratefully acknowledges the Portuguese National funds through the FCT, Fundação para a Ciência e a Tecnologia, under the Project PD/BD/114106/2015 (D.V. Lopes) and the FCT investigator 2014 programme (IF/00215/2014) with financing from the European Social Fund and the Human Potential Operational Programme.

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