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Zero-valent iron from iron wastes for environmental applications

Daniela V. Lopes, Rui C. Martins, Rosa M. Quinta-Ferreira, Jorge R. Frade, Margarida J. Quina

CIEPQPF – Chemical Processes and Forest Products Research Center

CICECO – Centro de Investigação em Materiais Cerâmicos e Compósitos

Chemical Engineering Department, **University of Coimbra**, **Portugal**

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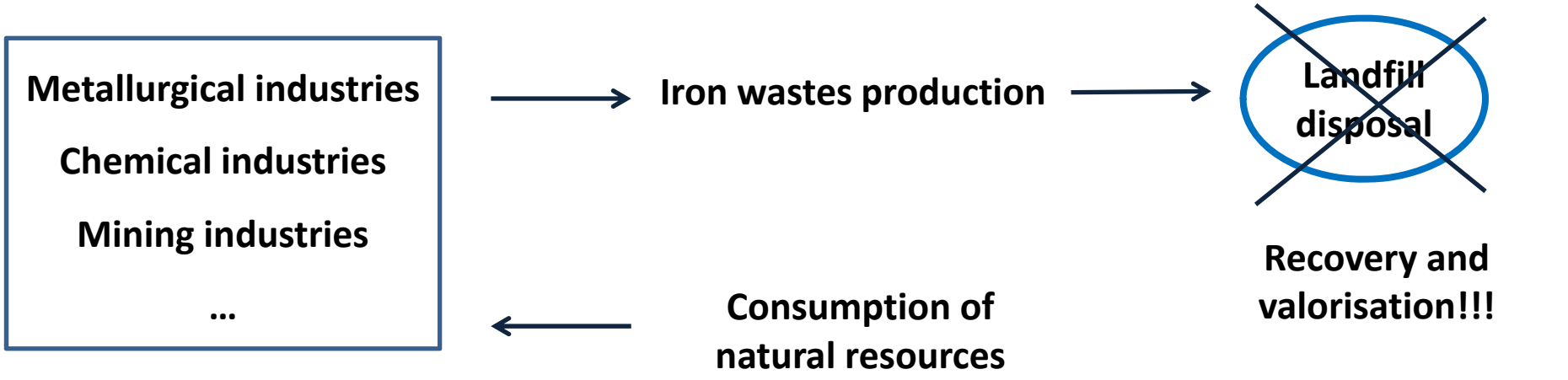
1. Introduction

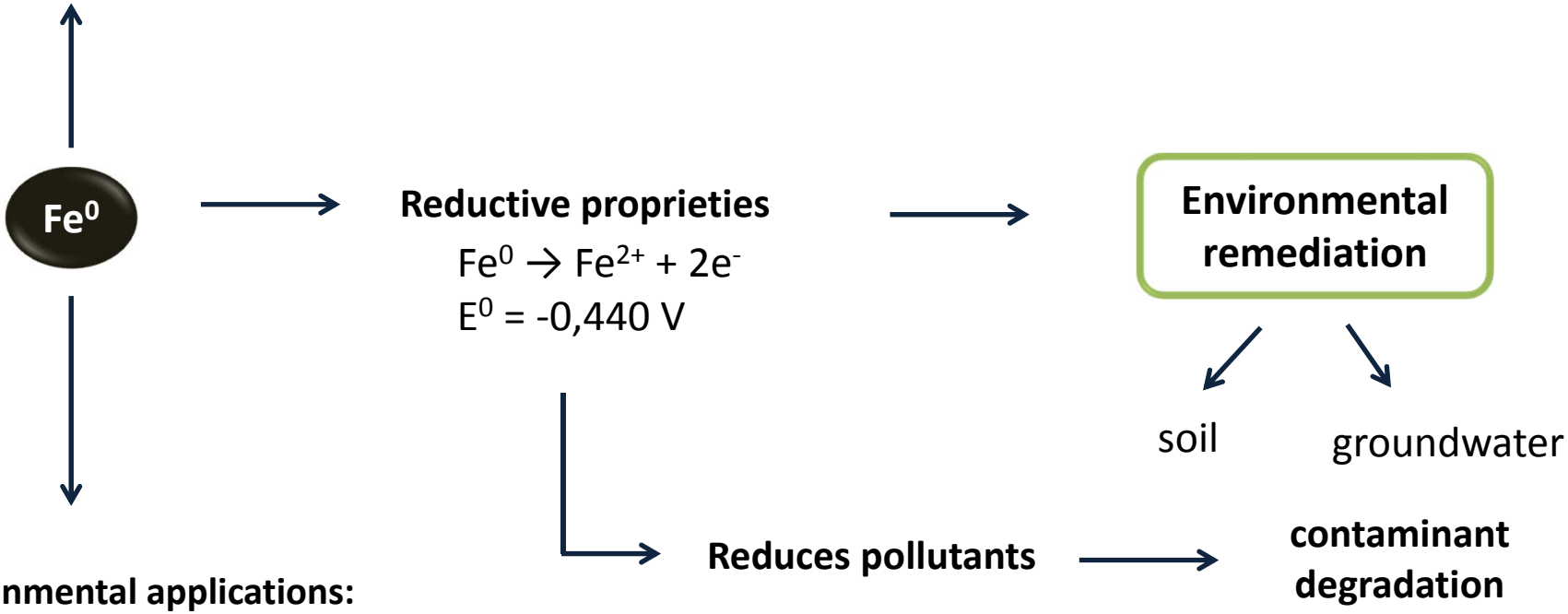


"end-of-waste status"

Directive 2008/98/EC, 19th November of 2008

1. Introduction

Zero-valent Iron (ZVI)



Environmental applications:

- chlorinated organic compounds;
- organochlorine pesticides (PCBs);
- organic dyes;
- metal ions (As(III), Pb(II), Cu (II), Ni(II) and Cr(VI));
- …

1. Introduction

Objective of the study

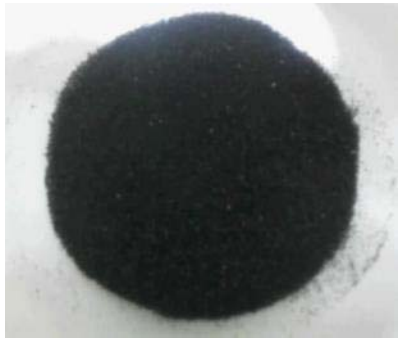
Main goal:
Use of iron wastes for the degradation of methyl orange

2. Experimental methodology

1) Screening of wastes:

Iron Fenton Sludge (IFS)

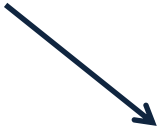
Cast Iron Shot (CIS)



Grind Precipitate Dust (GPD)

Iron Shavings (ISH)

Fenton's Process



Metallurgical industry

Carpentry workshops

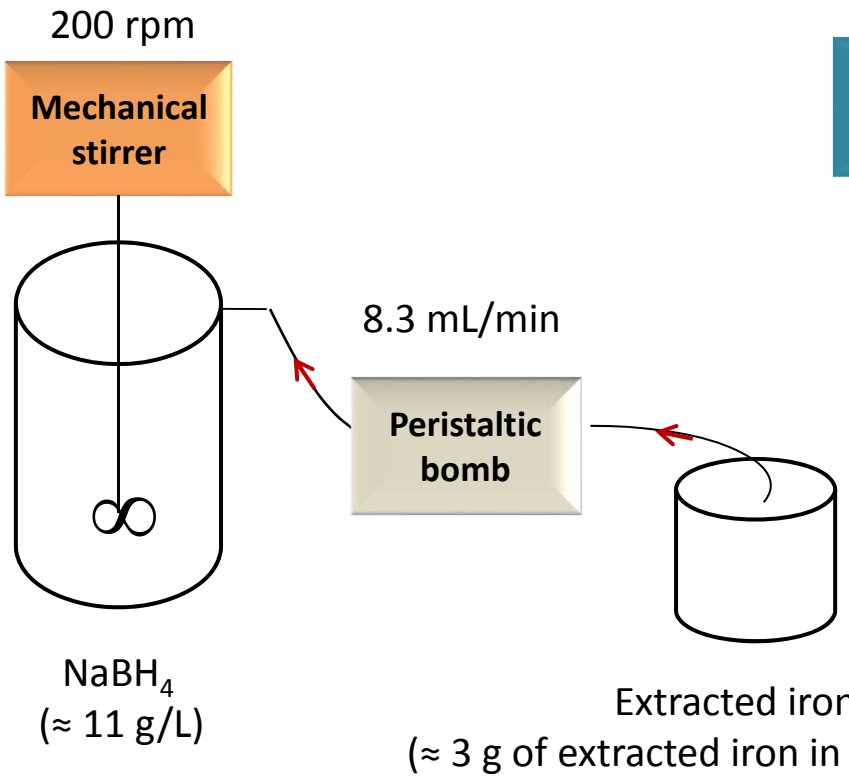
2. Experimental methodology

2) Chemical characterization of solid wastes:

- ✓ Solid wastes digestion – *Aqua regia (FAAS with Perkin Elmer 3300)*
- ✓ Elemental analysis *(Fisons EA1108)*
- ✓ Surface area with BET *(Micromeritics ASAP 2000)*
- ✓ Mineralogic characterization (XRD)

2. Experimental methodology

3) Chemical reduction of iron from Iron Fenton Sludges (IFS):

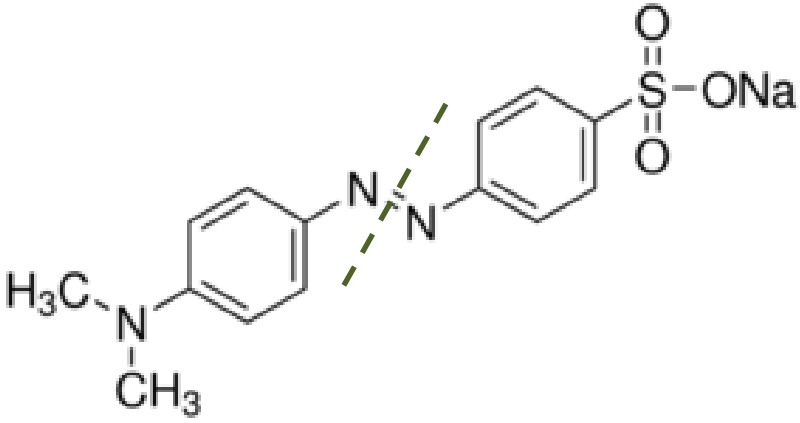


Chemical reduction of Fe^{3+} to Fe^{0}

It was not successful…

2. Experimental methodology

4) Treatment procedure for color removal of Methyl Orange (MO)



+ Fe^0

- ✓ 50 – 300 mg/L of MO
- ✓ pH tested: 5 – 10
- ✓ GPD waste was used in a range of 0.2 to 1 g/L
- ✓ 20 – 40 °C
- ✓ Water bath shaker, ≈ 100 rpm
- ✓ Color was measured at 465 nm with UV/vis spectroscopy after 90 min of reaction

2. Experimental methodology

5) Color removal with DOE

Design of Experiments (DOE): *STATISTICA V9* → **Box-Behnken** (response surface methodology at 3 levels)

30 experiments

$$Y = f(x) = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \times \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2$$

Factors analyzed:

x_1 – MO (mg/L)
x_2 – pH
x_3 – ZVI (g/L)
x_4 – T (°C)

Response variable:

y – Removal of color (%)
$(Abs_i - Abs_f)/Abs_i$

Factor	Units	-1	0	1
MO	mg/L	50	180	300
pH	-	5	7	10
ZVI	g/L	0.2	0.6	1.0
T	°C	20	30	40

3. Results and discussion

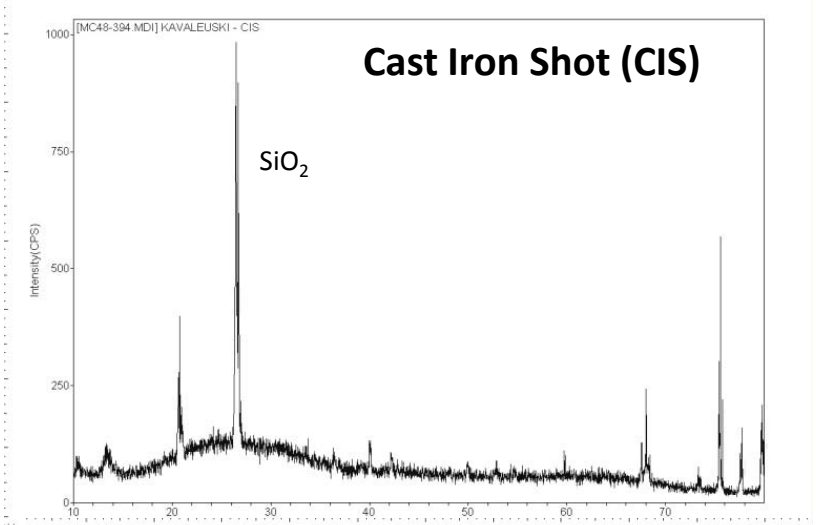
Solid wastes characterization

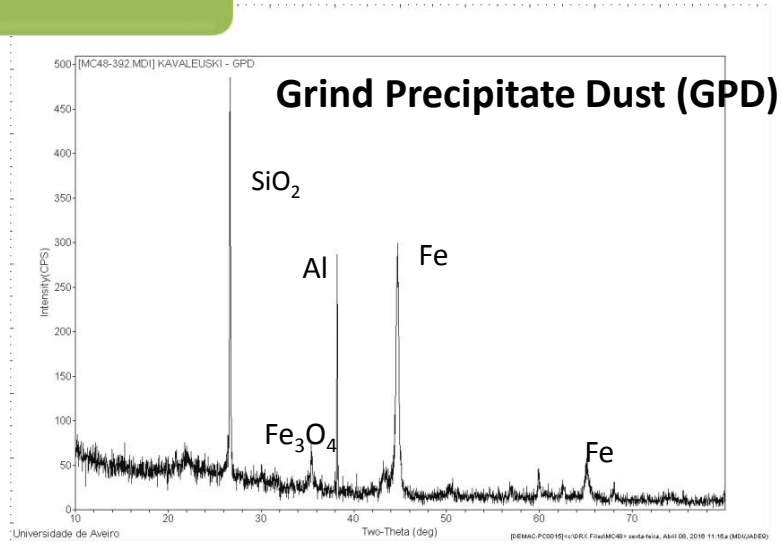
Wastes rejected!

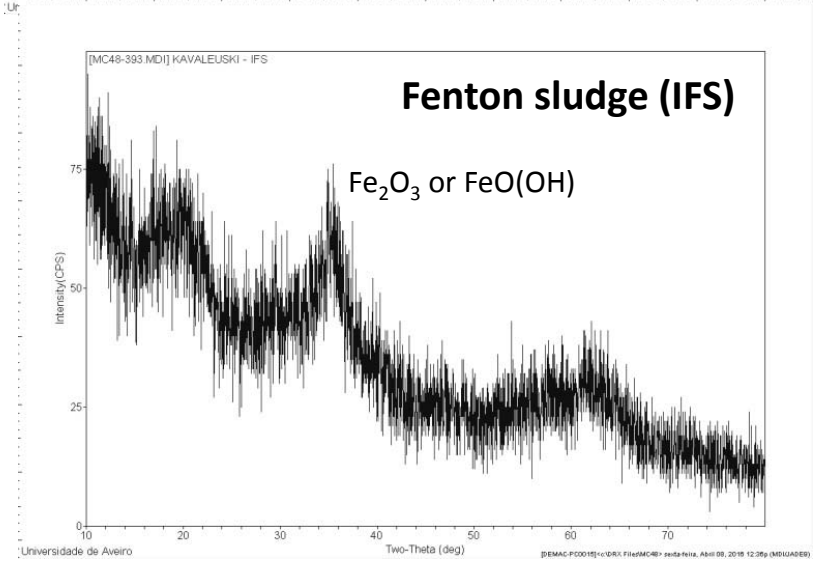
	IFS	CIS	GPD	ISH
Moisture (%)	52.3±0.7	0.1±0.01	0.6±0.01	≈ 0
VS (%)	52.8±0.1	1.3±0.4	≈ 0	≈ 0
Fe (g/kg)	302.0±17.5	0	447.7±24.3	981.8
A_{BET} (m^2/g)	0.58±0.03	-	5.30±0.05	1.14±0.04
Density (kg/m^3)	1717±19	-	5547±34	-
D_p	26 µm	< 0,1 mm	< 0,1 mm	< 0,5 mm
N (%)	1.56	0.33	0.25	-
C (%)	30.60	5.29	0.82	-
H (%)	5.51	0.19	0.09	-
S (%)	2.64	1.88	1.86	-

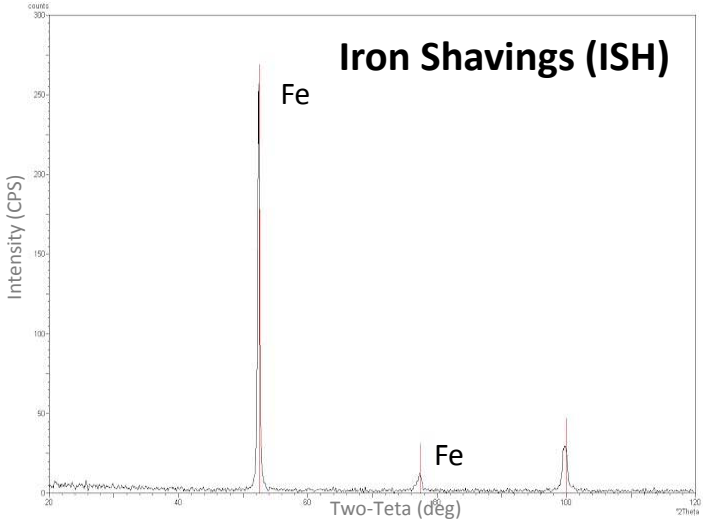
3. Results and discussion

Solid wastes characterization -XRD







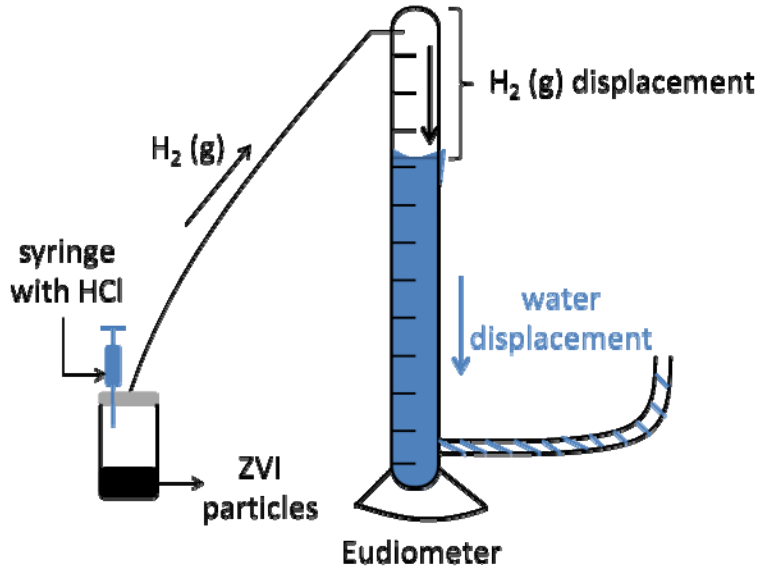


3. Results and discussion

Fe^0 quantification present in the wastes for MO degradation

$$Fe^0\ (s) + HCl\ (aq) \longrightarrow FeCl_2\ (aq) + H_2\ (g)$$

$$n_{H2} = \frac{PV_{H2}}{RT}$$



- ✓ 50 mL eudiometer;
- ✓ 50 mg of ZVI wastes (GPD ans ISH) were tested;
- ✓ 2 mL of HCl;

Fe^0 present in the wastes

- **GPD:** 90.3% of Fe^0 and 9.8% of oxides/SiO_2
- **ISH:** ≈ 60% of Fe^0 and ≈ 40% of oxides

3. Results and discussion

Design of Experiments

$$f(x_1, x_2, x_3, x_4) = 46,1498 + 0,0959x_1 - 27,0192x_2 + 65,4346x_3 + 4,8442x_4 - 0,0001x_1^2 + 1,5146x_2^2 - 7,2884x_3^2 - 0,0748x_4^2 + 0,0057x_1x_2 - 0,0697x_1x_3 - 0,0019x_1x_4 - 3,3687x_2x_3 + 0,0771x_2x_4 - 0,2550x_3x_4$$

$R^2 = 0,73017$

Factors analyzed:

x_1 – MO (mg/L)
x_2 – pH
x_3 – ZVI (g/L)
x_4 – T (°C)

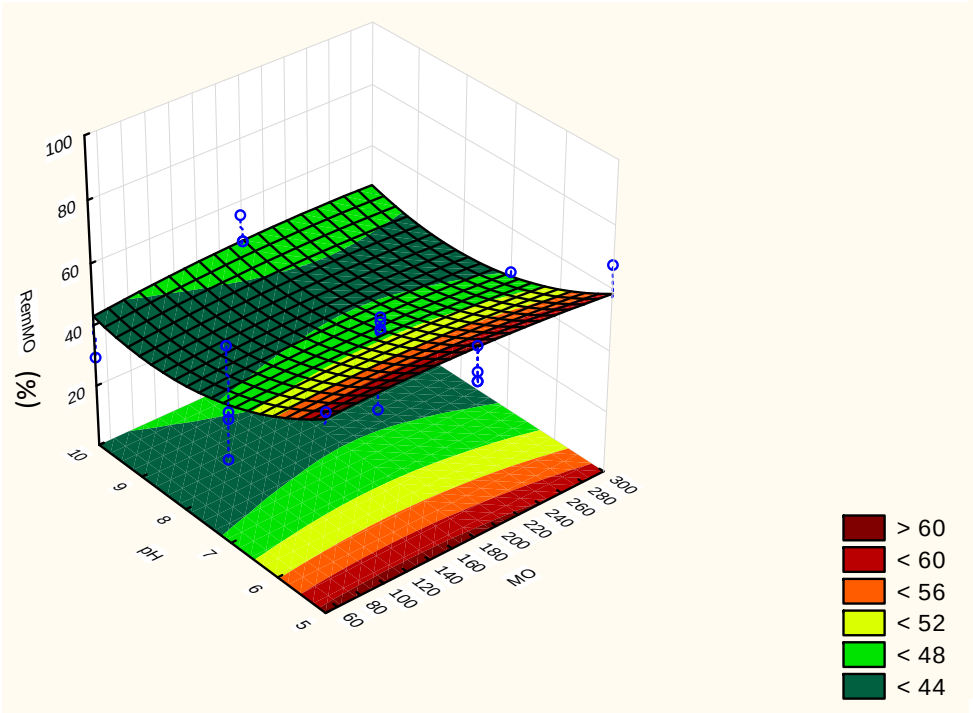
Response variable:

Removal of color (%

Factor	SS	df	MS	F	p
b_0	153,734	2	76,867	1,115	0,357
x_1	21,926	2	10,963	0,159	0,855
x_2	1070,176	2	535,088	**7,764**	**0,006**
x_3	253,662	2	126,831	1,840	0,198
x_4	620,329	2	310,165	**4,500**	**0,033**
x_1x_2	13,262	1	13,262	0,192	0,668
x_1x_3	48,580	1	48,580	0,705	0,416
x_1x_4	21,878	1	21,878	0,317	0,582
x_2x_3	46,603	1	46,603	0,676	0,426
x_2x_4	15,250	1	15,249	0,221	0,646
x_3x_4	4,162	1	4,162	0,060	0,810
Error	895,978	13	68,9214		

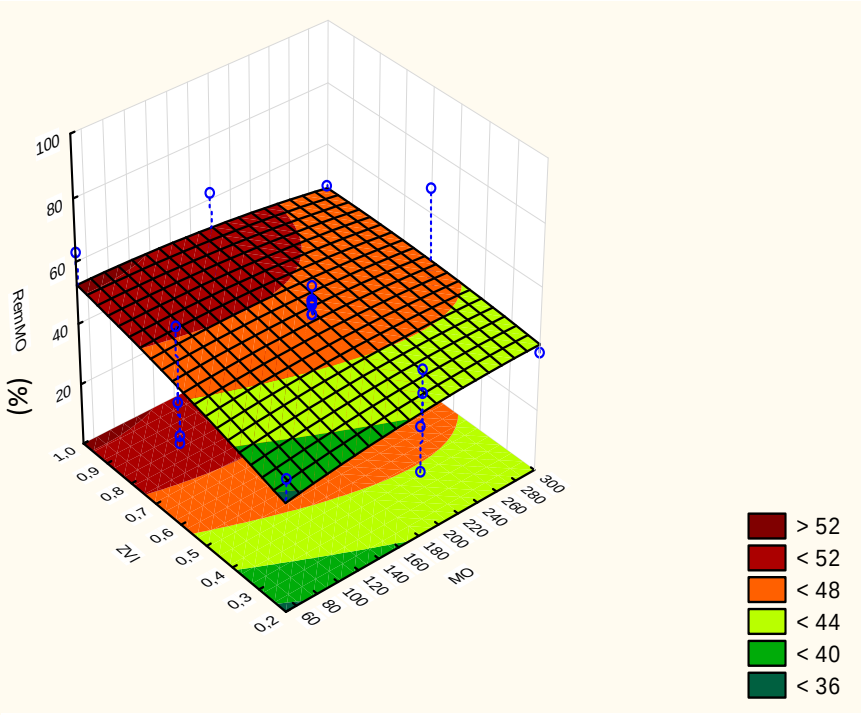
3. Results and discussion

Design of Experiments – Color removal (%)



pH vs MO_i (mg/L)

Acidic pH are better for color removal



ZVI (g/L) vs MO_i (mg/L)

Higher loads of ZVI lead to higer efficiencies of color removal to relatively lower MO (mg/L)

sults and discussion

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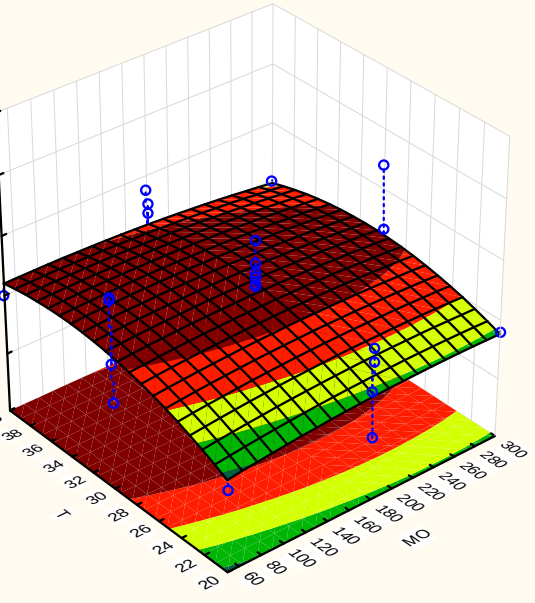
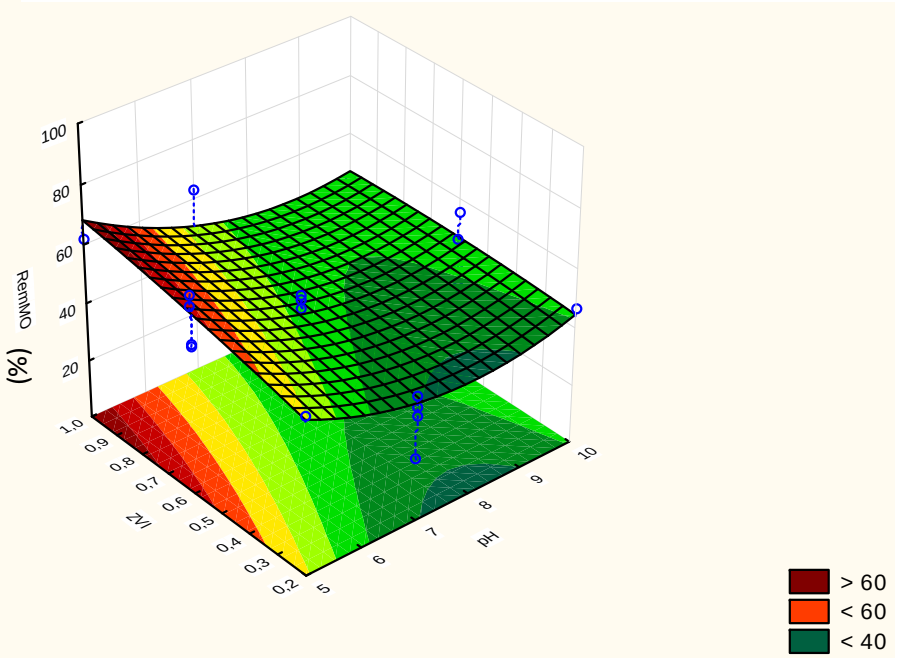
sign of Experiments – Color removal (%)



T vs MO_i (mg/L)



ZVI (g/L) vs pH

sults and discussion

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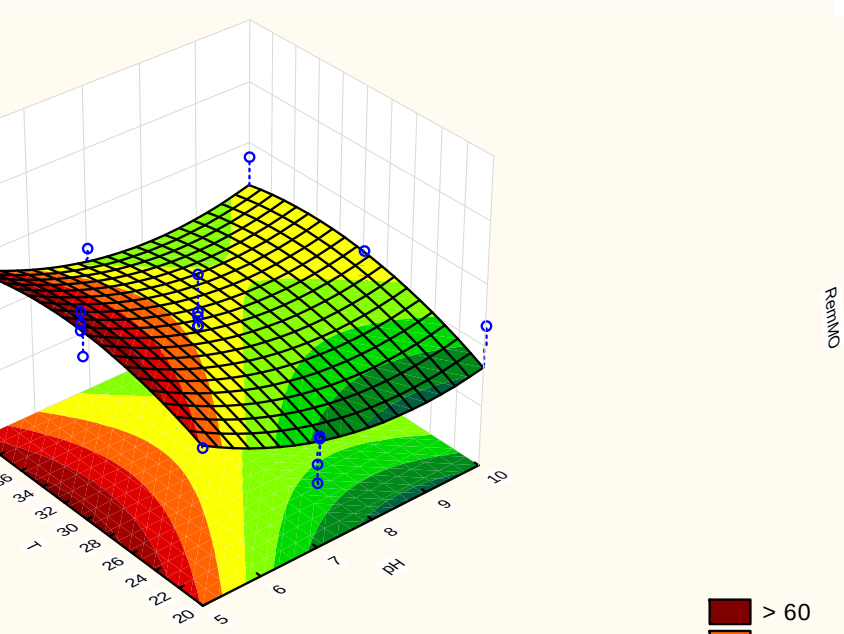
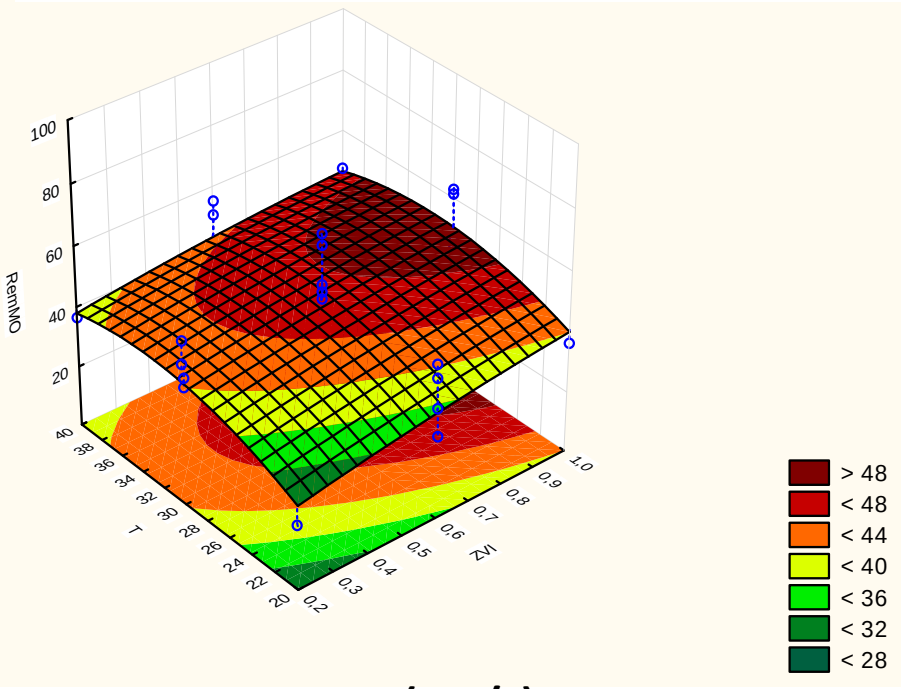
sign of Experiments – Color removal (%)



T vs pH



T vs ZVI (mg/L)

sults and discussion

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sign of Experiments – Color removal (%)

timal solution in the model with GPD:

MO (mg/L)	50
pH	5
ZVI (g/L)	1
T (°C)	32.6
r Removal (%)	**72.3**

Validation of the optimal solution in the model with GPD:

64.2±1.2% **(Error: 8.1%)**

e of iron shavings for the optimal solution: **59.4±0.4%**

nclusions and forthcoming work

Conclusions

emical reduction of Fe^{3+} from wastes seems to be challenging by sodim borohydride proach;

nd Precipitate Dust (GPD) and Iron Shavings (ISH) wastes can be used as ZVI in vironmental reactions;

E approach revealed to be relevant in order to compare the interactions of variables he model and to optimize the model (acidic pH is the most relevant factor in order to nove MO);

ound 60% of efficiency on the color removal of MO was attained with both wastes.

orthcoming work

Thank you for your attention

Daniela Lopes
dvlopes@eq.uc.pt

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