



PULSED ELECTROCHEMICAL CONSIGNED NANOIRON FOR WATER TREATMENT

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ABSTRACT

The application and utilization of nanotechnology in drinking water treatment, demeanor and pollution cleanup is promising, as demonstrated by a number of field based (pilot and full scale) and bench scale studies. In recent years, the use of zero valent iron (ZVI) for the treatment and demeanor of toxic contaminants in groundwater and wastewater has received wide attention and encouraging treatment and demeanor efficiencies have been documented. In this review, nano scale iron was prepared by pulse electrode position and circumstances of nano iron by chemical reduction of iron chloride and iron sulfate. Our research focuses on iron nanoparticles preparation and its use for aqueous Cr (VI) reduction.

The Cr (VI) reduction by the nFe^0 prepared by electrochemical and blasting method and procedure at neutral pH were carried. The results show that blasting nFe^0 show lower reaction than the electrochemical nFe^0 . It is because the blasting nFe^0 surface contains more Fe_2O_3 than the other one.

Keywords: *Blasting, Chromium (VI) Reduction, Electro deposition (Consigned), Nano Iron*

1. INTRODUCTION

Chromium is widely used in metallurgical, electroplating, production of paints and pigments, tanning, wood preservation [1] [2] [3], etc., thereby commonly identified in waters. Two primary oxidation states, Cr (VI) and Cr (III) species, are present in aqueous media. The former is highly toxic and carcinogenic to human and animals, while the latter is generally nontoxic [4] [5] [6]. Consequently, the reduction of the Cr (VI) to the Cr (III) is of environmental interest.

Nano iron powders have been used in permeable reactive barriers for aqueous Cr (VI) reduction in contaminated groundwater. Consequently, the reduction of the Cr (VI) to the Cr (III) is of environmental interest. Much work has been focused on the cleanup of Cr (VI) contaminated waters by various and disparate reducing reagents including hydrogen sulfide [7], divalent iron [8] [9], Fe (II) bearing minerals [5] [10], thios and thiols [11] [12], etc. Recently,



zero valent iron (Fe^0) has been tested for the remediation of polluted waters, and it is established that halogenated hydrocarbons such as nitro [13] [14], and chloro compounds [15], toxic metals nitrate and arsenate [16][17] [18] [19] [20] are effectively transformed by the Fe^0 to relatively more benign products. Nanoscale iron (NSI) can also be a promising material for Cr (VI) removal from wastewater because of its large active surface area and high arsenic adsorption capacity. All described properties and virtues of Fe (iron) nanoparticles can be even used for decomposition of pollutants contained in the wastewater, mainly for treatment of industrial sewage and hatch water. The usage of nanoiron can represent a significant qualitative step in the classical technologies of water treatment including drinking water. NSI can be also used for a reduction of the content of heavy metals, nitrates and phosphates in the drinking water. Nanotechnology has widespread application potential and offers also the possibility of an efficient removal of pollutants and germs in the area of wastewater treatment. The objectives of this study were to prepare NSI by pulse electrodeposition, consigned and to test its performance for efficient removal of pollutants from the wastewater. Electrochemical deposition and consigned is a cost effective, competitive procedures, which allows control over composition and microstructure of the powder.

The reduction of Cr (VI) by the thiol containing compounds cysteine and glutathione and by reduced sulfur in humic substances was monitored with sulfur and chromium X – ray absorption near – edge structure (XANES) spectroscopy in chromium – contaminated soils. Reaction of humic acids with Cr(VI) resulted in a reduction of the peak area of thiols and an increase in the peak area of disulfides in the sulfur XANES spectra. Analysis of the sulfur XANES spectra in various systems indicates that the reduction of Cr(VI) by humic substances involves a thiol/disulfide redox couple analogous to that of the Cr(VI) reduction by the simple thiol containing compounds cysteine and glutathione. A fraction of the hexavalent chromium present in industrially contaminated soils was not reducible by thiols. Reduction of Cr(VI) to Cr(III) in soils by thiols has little effect on the pH of the system in contrast to the pH decrease resulting from reduction by Fe(II) [12].

The reduction of Cr(VI) to Cr(III) decreases the toxicity and mobility of chromium contaminants in soils and water. In addition, the formation of a highly insoluble Cr(III) product would decrease the likelihood of future Cr (III) re oxidation. Amorphous iron sulfide minerals like mackinawite (FeS_{1-x}) have the potential to reduce large quantities of Cr(VI) and in the process form very stable $[\text{Cr, Fe}] (\text{OH})_2$ solids. In this study, we examine the effectiveness of amorphous FeS as a reductant of Cr(VI) by identifying the solution and solid phase products of the reaction between FeS suspensions and chromate[9].

Chromium, in the trivalent form (Cr(III)), is an important component of a balanced human and animal diet and its deficiency causes disturbance to the glucose and lipids metabolism in humans and animals. In contrast, hexavalent Cr (Cr(VI)) is highly toxic carcinogen and may cause death to animals and humans if ingested in large doses. Recently, concern about Cr as an environmental pollutant has been escalating due to its build up to toxic levels in



the environment as a result of various industrial and agricultural activities. In this review, we present the state of knowledge about chromium mobility and distribution in the environment and the physiological responses of plants to Cr with the desire to understand how these processes influence our ability to use low cost, environmentally friendly biological remediation technologies to clean up Cr-contaminated soils, sediments, and waters [7].

Permeable reactive barriers containing zerovalent iron are being increasingly employed for in situ remediation of groundwater contaminated with redox active metals and chlorinated organic compounds. This research investigated the effect of chromate concentration on its removal from solution by zerovalent iron. Removal rates of aqueous Cr(VI) by iron wires were measured in batch experiments for initial chromium concentrations ranging from 100 to 10⁴ µg/L. Chromate removal was also measured in columns packed with zerovalent iron filings over this same concentration range. Electrochemical measurements were made to determine the free corrosion potential and corrosion rate of the iron reactants. In both the batch and column reactors, absolute rates of chromium removal declined with increasing chromate concentration [4].

The supported zero valent iron nanoparticles (“Ferragels”) rapidly separate and immobilize Cr(VI) and Pb(II) from aqueous solution, reducing the chromium to Cr(III) and the Pb to Pb(0) while oxidizing the Fe to goethite (α -FeOOH). The kinetics of the reduction reactions are complex and include an adsorption phase. About 10% of the iron in the material appears to be located at active surface sites. Once these sites have been saturated, the reduction process continues but at a much lower rate, which is likely limited by mass transfer.

2. MATERIALS AND PROCEDURES

2.1 Synthesis of Nano Iron Powder

Iron nanoparticles were produced by pulse electro deposition (consigned). In pulse electro deposition (consigned), a DC current is applied for a short period time, ton, that is followed by a period of time when no current is applied, toff. Typical values for ton, and toff are between 5 and 200 ms and between 1 and 10 ms respectively. Through the use of a high current density as well as some grain growth inhibitors, such as saccharine, it is possible to increase the nucleation rate and reduce grain growth. The structure of the materials prepared was investigated using X – ray powder diffraction using Co K α radiation and with a high resolution SEM from JEOLJSM 5600LV.

Sacharin 0.3 gdm³ and magnesium sulfate (MgSO₄) between 0 and 0.5 M were added as grain refining agents, see Table 1. The temperature of the solution was 25°C and the pH varied from 3.5 to 6.0. Pulse current was between 10 and 20 mA. All cases deposition were made on titanium cathode in order to facilitate their removal from the substrate which allows to perform experiments on self supported samples. One should also mention that the more



additives are added to the solutions the larger is the contamination problem of the samples. For this reason, most of the experiments were done with the lowest amount of additive as possible.

3. RESULTS AND DISCUSSION

Pulse current electrodeposition and consigned of nanoFe was carried out to investigate the effect of $MgSO_4$ on the microstructure and the reactivity of the electrodeposited films. Electrodeposition and consigned without $MgSO_4$ electrolyte gave smaller grain size than with it.

XRD results in Figure 1, Figure 2. Demonstrated that no other component were presented within the Fe23 and Fe24 samples. We used $MgSO_4$ as a grain refining agent. The X – ray diffractogram calculated the grain size of the NSI using Debye – Scherrer equation:

$$\tau = \frac{K}{\beta \times \cos \theta} \times \lambda_{Co}(1)$$

Where, τ is the grain size; K is a dimensionless shape factor, with a value 0.9, λ_{Co} is the X – ray wavelength (1.788897Å); β is the line broadening at half and θ is the Bragg angle.

From the calculation, it turns out that the Fe23 grain size is about 19.47 nm and in the case of Fe24, it was 17.89 nm. The surface morphology of the nano Fe was characterized with SEM (scanning electron microscope). The surface morphology changed as rough surface, where the concentration of $MgSO_4$ increased. The reactivity of active surface of nano Fe increasing as a function of decreasing of grain size in presence of $MgSO_4$.

Table 1: Nano Fe electro deposition (Consigned) parameters and bath composition

Composition of bath	Fe23	Fe24	Fe25	Fe26	Fe27	Fe28
$FeCl_3$	+	+	-	-	+	+
$FeSO_4$	+	+	-	-	+	+
$(NH_4)_2Fe(SO_4)_2$	-	+	-	-	+	+
$MgSO_4$	-	+	-	-	+	+
$(NH_4)_2SO_4$	+	+	-	-	+	+
Saccharin	+	+	-	-	+	+
t_{on}	5	5	5	5	1	1
t_{off}	200	200	200	200	100	50
D (nm)	19.47	17.89	25.97	42.75	23.34	16.88
η (%)	61.7	41.7	16.7	21.5	29.2	10.5



3.1 Iron Oxide and Iron Ratio Measurements

Iron oxide and iron ratio measurements are destined for the measurement of zero valent iron nanoparticles content in a slurry. The procedure is based on the measurement of hydrogen volume, which is evolving during chemical reaction of zero valent iron and an acid. This test is very simple and particularly fair minded: the volume of hydrogen is directly proportional to the amount of zero valent iron; the amount of iron oxides does not influence the volume of generated hydrogen, and it only slows down the reaction speed.

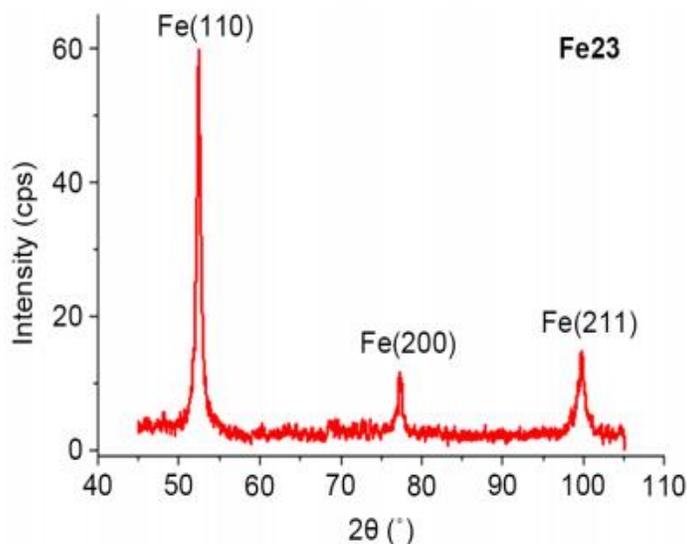
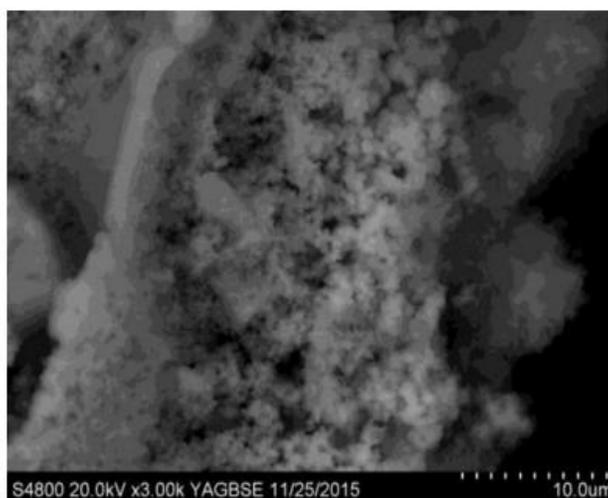


Figure 1. SEM and X – Ray diffractogram of the Fe23 samples prepared without added $MgSO_4$.

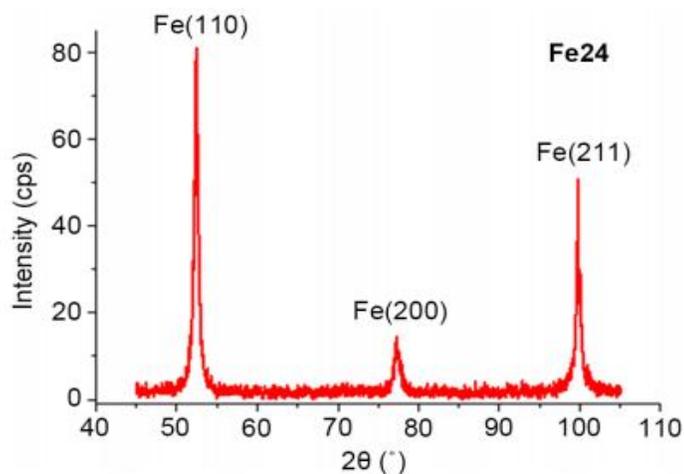
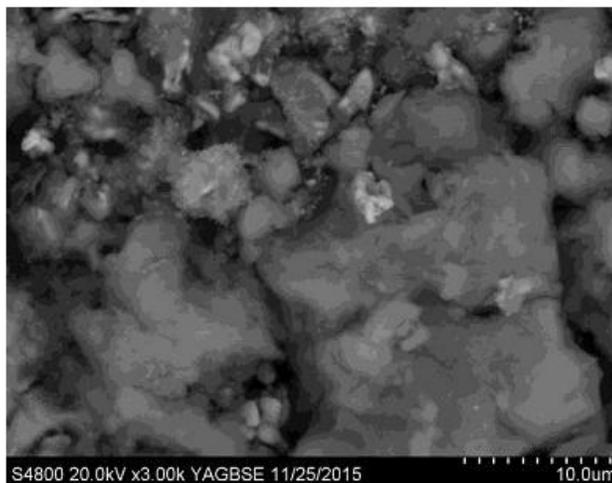
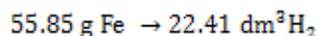
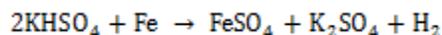


Figure 2: X – Ray diffractogram of the Fe24 samples prepared with added MgSO₄.

Reaction of nZVI and the acid (KHSO₄) proceeds according to the following formula:



From previous formula it comes through, that 22.41 dm³ of hydrogen is generated by reaction of 55.85 g of iron and sufficient amount of acid (2KHSO₄). The weight and the concentration of nZVI is consequently calculated from the volume of evolved hydrogen. For determination of the quality of nano iron, we should measure the amount of iron



oxide in the deposited (consigned) and in the further materials. First we used commercial zero valent nanoiron powder for water treatment or water demeanor as reference material. Using the above methods and procedures we could measure the quantity of H_2 gas from the chemical reaction where only the iron react with the potassium bisulfate. On the curves of Figure 3. You can see some examples for the speed of H_2 production. In average the total reaction time was about 12 – 14 minutes at the reference and at our samples; except for the sample nFe26 and the sample from nFeblasting. nFeblasting samples was prepared by iron wires blasting method and procedure under water. For the samples preparation we used a low value capacitor ($C \sim 10 - 100 \mu F$) and discharged a 100 – 500 microns this iron wire. The discharge will be successful if the circuit behaves as a damped resonant circuit, with the condition:

$$\frac{R^2}{4L^2} < \frac{1}{LC}$$

nFe23, nFe24 and nFe26 samples were prepared by electrochemical methods and procedures.

From Figure 3, it turns out that nFe23, nFe24 and nFe26 samples show the same results for the iron content as the commercial reference nZVI which has been used for water purification. Significant difference was not observed amount samples which were stored in different solution (see Table 2). In this case of sample stored under distilled water for the same time than the alcohol; the ratio of the iron was decreased but it is still acceptable. The reference iron oxide samples didn't occur any reaction. Blasting nFe sample was not too reactive because the iron contains was about 7 wt%, see Table 2.

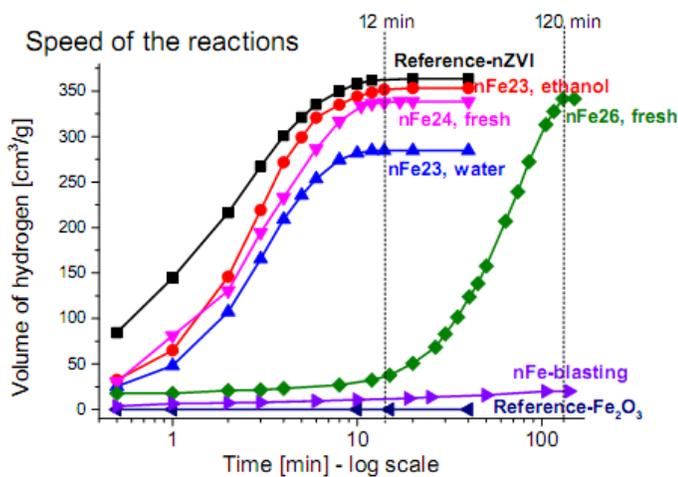


Figure 3: Iron oxide and iron ratio.

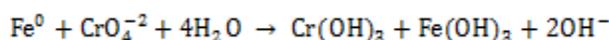
**Table 2: Summary of iron oxide and iron ratio measurements results.**

Sample	Average nanoiron content (wt %)	Average iron oxide content (wt %)
Reference commercial material	87.7	12.3
nFe23 stored under ethanol for 3 weeks	88.8	11.2
nFe23 stored under water for 3 weeks	68	32
nFe 24 freshly prepared	87	13
nFe26 freshly prepared	85	15
Reference Iron oxide powder	0	100
nFe prepared by blasting methods	5.5	94.5

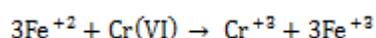
3.2 Cr(VI) Reduction by the nFe at Neutral pH

The Cr (VI) concentration was quantified by the diphenyl carbazide method and procedure [21] on a UV – vis spectrophotometer (Jasco V – 550 spectrophotometer). Figure 4 show the Cr (VI) reduction by the nFe⁰ samples prepared with different methods and procedures.

The other underlined an indirect electron transfer that had the following reactions:



Neutral PH → Basic PH



The Cr(VI) reduction by the nFe⁰ at neutral pH were carried out in batch mode in a home made setup that used a borosilicate glass vessel with 100 mL effective volume as the reactor. To prevent the oxidation of Fe⁰ surface by air, N₂ was supplied continuously into the setup during the experimental process. In each experiment, unless stated specially, 100 mL 10.0 mg/L potassium chromate was treated by 2.0 ± 0.2 mg Fe⁰ prepared by different methods. To investigate the effect of the co-existing organic matters on the Cr(VI) reduction, citric acid were added into the Cr(VI) solution.

Following the addition of the initial solution, pH was adjusted to 7.0 by adding H₂SO₄ and NH₃·H₂O, then 0.1 M ammonium acetate solution was added to buffer the reaction PH. Samples of 2.0 mL were taken at preset time intervals for an immediate analysis of Cr (VI) or Fe (II). Without the presence of co-existing organic matters in the



reaction solution, precipitate emerged in the solution, and the samples were filtered to remove it before the measurement.

3.3 Analytic Methods (Procedures)

The Cr (VI) concentration was quantified by the diphenyl carbazide method [21] on an UV – spectrophotometer (Jasco V – 550spectrophotometer).

It should be noted that reactions underlined that Fe (II) was a main electron donor for the Cr (VI) reduction to occur in the solution homogeneously. This tuned mechanism for the Cr (VI) reduction by the $n\text{Fe}^0$ with the co-existing organic matters was supported by the following results. From the Figure 4, it turns out that the water reduction released Fe(II) in the solution, then the Fe (II) reduced Cr(VI) to Cr(III) homogeneously. In this study, the above mechanism of both the direct and indirect electron transfers appeared to work but tuned. It could be seen that during the reaction the PH increased from 7.0 to 7.7, which was in the neutral range. No precipitate was observed in the solution with a neutral PH. Thus, we concluded that the iron species was present as the formation of Fe(II) prevented the precipitation of ferrous iron which otherwise occurred in the solution without any organic matter. The Fe(II) could also reduce the Cr(VI) homogeneously as a main electron donor.

The best results show the samples of nFe23, nFe24 and nFe26, but in the case of blasting-nFe, the reaction was not complete.

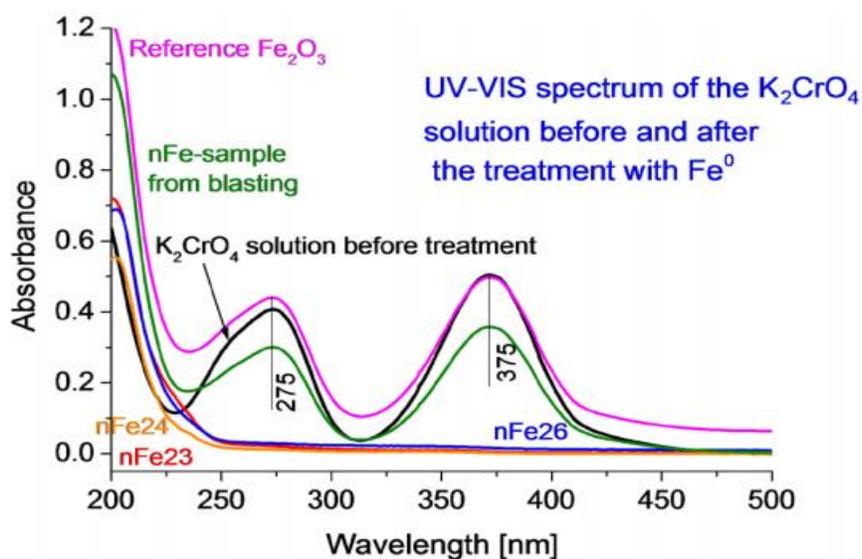


Figure 4: Spectrophotometer results of nFe prepared by different methods.



4. CONCLUSIONS

There is an increasing interest in the use of NSI for the removal of contaminants from groundwater and wastewater. NSI has been successfully applied for the remediation/treatment of groundwater and wastewater contaminated with chlorinated organic compounds, nitro aromatic compounds, arsenic, heavy metals, nitrate, dyes, and phenol.

Nano iron powder was successfully prepared by electrochemical and blasting methods and procedures. The Cr(VI) reduction by the $n\text{Fe}^0$ prepared by electrochemical and blasting method and procedure at neutral pH were carried, the results show that blasting $n\text{Fe}^0$ show lower reaction than the electrochemical $n\text{Fe}^0$. It is because the blasting $n\text{Fe}^0$ surface contains more Fe_2O_3 than the other one.

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