# Reduction of Hexavalent Chromium by Metallic Iron Nanoparticle

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*Metallic iron nanoparticles were synthesized by the hydrazine reduction method in three experimental versions. The average size and particle size distribution obtained by the three versions was determined with a particle size measurement system making use of dynamic light scattering. The presence of the aromatic solvent and anti-caking additive influences the average size and size distribution of the particles. The metallic iron nanoparticles obtained in the three experiments were used in the treatment of waters containing a 6.8 mg/l concentration of hexavalent chromium. Reduction of hexavalent chromium concentrations as well as total chromium, COD and TSS depend on pH and reaction times. Thus, the optimal conditions requires for* $Cr^{6+}$*reduction, for obtaining values lower than 0.1 mg/l, are: the pH value of 11, a duration of the process 10 hours.*

*Keywords: nanoparticles, chromium, wastewater, chemical oxygen demand, biochemical oxygen demand*

Chromium has a great economic importance for the industry being widely used in a variety of industrial processes. It is one of the most important pollutants in soil and groundwater and surface water in the world. Water-soluble Cr(VI) and insoluble Cr(VI) compounds are considered “confirmed humans carcinogens” [1]. Once in the aqueous phase, Cr (VI) exerts toxic effects on organisms due to its strong oxidizing nature of it [2]. Over time were improved strategies to reduce chromium (VI) using iron ion to lower valences, preferably zero-valent iron. Previous studies have demonstrated that zero-valent iron is an effective and inexpensive reductant for Cr (VI) [3-10]. Removal of Cr (VI) contaminant by zero-valent Fe can be achieved either by reactions of direct reduction mediated by zero-valent Fe (direct reduction) or by reducing the contaminant by oxidation products resulting from zero-valent Fe (indirect reduction). However, under normal conditions of operation, the reduction of Cr (VI) by the metallic iron can be inefficient, either due to inappropriate dimensions of the particles of zero valent iron or due to its reactivity in the presence of water and / or oxygen, which by processes of oxidation of metallic iron to iron ions favors the formation of inactive species with the tendency to agglomeration thereof. As a result of such reactions the efficiency of reduction process of Cr (VI) to Cr (III) decreases dramatically.

In a recent paper it was studied the possibility to use of nanoparticles in various fields [11,12]. The enhance of the colloidal stability of nanoparticles was carried out by adding “green” guar gum polymer. It has evaluated the properties of guar gum and its influence on the surface properties, particle size, aggregation and sedimentation of iron nanoparticles [13]. S. Machado s.a. where evaluate the viability of the utilization of several tree leaves to produce extracts which are capable of reducing iron(III) in aqueous solution to synthesis zero-valent iron nanoparticles [14-18]. Yuan-Pang Sun proposed a method for the synthesis of fully dispersed and reactive nanoscale particles of zero-valent iron. In the synthesis of the nanoscale zero-valent iron (nZVI) it was used polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (PV3A), a nontoxic and biodegradable surfactant. The addition of PV3A results in significant enhancements in surface chemistry, particle stability and subsurface mobility potential [19-22]. The presence of kaolinite resulted in decreased aggregation of iron nanoparticles, yielding composites with iso-electric points (IEPs) around 6.7–7.0. The reduction in $Fe^{2+}$ precursor concentration appeared to decrease further the extent of aggregation and the size of individual nZVI particles [23, 24]. Siskova K. M. report NZVI formation by wet chemical synthesis in the presence of selected L-amino acids, thus low-molecular weight and biocompatible species [25].

Wastewater treatment process must be constantly changing. Thus, it is takes account of the latest technologies, to reduce environmental impact and to minimize the amount of waste [26-28].

In this paper, we study the process of synthesis of zero-valent iron nanoparticles through the development of effective methods of reduction. Moreover the present paper outlines the possibility of using nanoparticles for wastewater treatment for the reduction process of Cr (VI).

## Experimental part

### *Materials*

The raw materials used in the experimental tests were: ferrous sulfate heptahydrate (Sigma-Aldrich), hydrazine sulphate 97% (Sigma-Aldrich), xylene mixture of isomers 98.5% (Sigma-Aldrich), sodium hydroxide reagent grade 98% (Sigma-Aldrich), ethylene glycol butyl ether 99.0% (Sigma-Aldrich), potassium dichromate 99% and nitrogen 99.998% (Linde).

The preparation of metallic iron nanoparticles by bivalent iron reduction was performed using a cylindrical glass reactor of 250 mL, outfitted with bubbler and mechanical stirring. The supply of nitrogen in order to remove the oxygen dissolved in water was conducted through a pipe that favoured the advanced dispersion of nitrogen bubbles inside the entire reaction volume.

Post reaction, the iron powder was recovered by decanting and centrifuging, and was followed by successive washing in ethanol and acetone.

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**Table 1**
SPECIFIC ANALYSIS METHODS

| Parameter | Methods | Equipment used |
|---|---|---|
| pH | SR ISO 10523 -2009 | pH-meter TOLEDO |
| $Cr^{6+}$, mg/L | STAS 7884-91<br>SR ISO 11083-98 | PG Instruments 990FGF |
| Total Cr , mg/L | SR EN 1233:2003 | PG Instruments 990FGF |
| COD, mg/L | SR ISO 6060/96 | DR 5000 |
| TSS, mg/L | SR EN 872:2005 | DR 5000 |

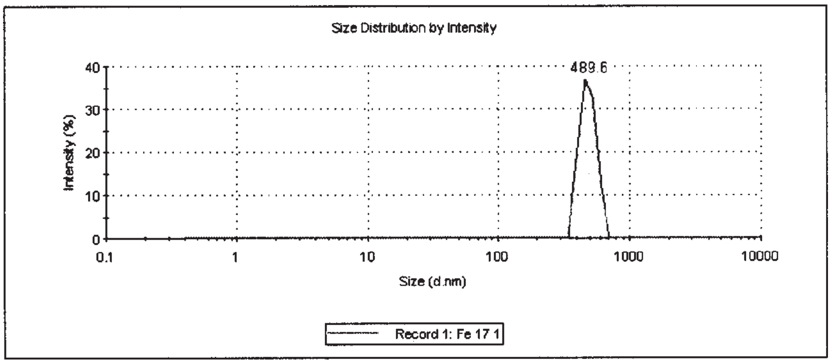

Fig. 1. The particle size of the metallic iron obtained in an aqueous medium

Measurements for the determination of particle size distribution were carried out using the method of dynamic light scattering (DLS) with a Malvern-Zetasizer NanoZS (Red badge) apparatus.

Iron nanoparticle synthesis was carried out in a stream of nitrogen (at a flow rate of 50 mL/h) and at a temperature of 80°C; the hydrazine sulphate aqueous solution of 3.7% concentration was dosed over a period of 3 h; the duration of the postreaction stage was approximately one hour. The experimental synthesis programme was conducted in three versions, which differed in liquid phase composition:

- NANO_A, where the mass ratio between reactants: ferrous sulphate / hydrazine sulphate / water was 1 / 2.06 / 82.73, and the *p*H was adjusted before the postreaction stage at a value of 10 with NaOH solution;
- NANO_B, where the mass ratio between reactants: ferrous sulphate / hydrazine sulphate / xylene / water was 1 / 2.06 / 12.4 / 82.73, and the *p*H of the aqueous phase was adjusted before the postreaction stage at a value of 10 with NaOH solution;
- NANO_C, where the mass ratio between reactants: ferrous sulphate / hydrazine sulphate / xylene / ethylene glycol butyl ether / water was 1 / 2.06 / 12.4 / 1.62 / 82.73, and the *p*H of the aqueous phase was adjusted before the postreaction stage at a value of 10 with NaOH solution.

*Experiments on reducing hexavalent chromium ion content*

The system that was used featured multiple components, i.e., a cylindrical reduction reactor outfitted with a frit at the bottom to ensure efficient dispersion of the gas in the reaction zone and ascending cooler and a thermostatic water bath. The ratio of the size of the reactor (length/diameter) was optimally chosen so that the dimension of the gas bubbles remains small along the length of the entire reaction zone. Nitrogen was supplied with a pipe which is located in the centre of the reactor so that the gas will have the same temperature as the reaction liquid before coming into contact with it. The volume of the reaction zone is 100 mL. The arrangement of the frit on the entire section in the bottom of the reactor favours the advanced dispersion of nitrogen bubbles inside the entire reaction volume.

Maintaining constant temperature in the reaction zone was achieved by immersing the reactor in a thermostatically controlled water bath. Temperature control was achieved using a thermometer immersed in the thermostatic bath.

Into the reactor were introduced 100 mL of 0.005M potassium dichromate (520 mg Cr/L) solution and 168 mg metallic iron. By bubbling an inert gas (nitrogen) at room temperature for 10 h the entire process was kept in stirring. The suspended particles were separated by centrifuging at 5000 rpm for 30 min.

In order to verify the capacity to reduce hexavalent chromium using prepared nanoparticles, tests were carried out on wastewaters whose contents of hexavalent chromium were analysed before and after the process. Knowing that nanoparticles influence other physico-chemical indicators of the wastewater treatment process the following sensitive parameters were identified, namely: $Cr^{6+}$ (hexavalent chromium ion), Cr total (chrom total), COD (chemical oxygen demand), TSS (total suspended solids). Specific analysis methods are given in table 1. The parameters that varied throughout the experiments were: mixing time – between 8 and 10 hours – and *p*H values – 7.5, 8, 9, 10 and respectively 11 units [29-31].

## Results and discussions

The DLS analysis shows that for synthesis NANO_A particles of an average diameter of 489.6 nm were obtained, having a minimum diameter of more than 350 nm and a relatively broad distribution (fig. 1).

The DLS analysis shows that for synthesis NANO_B particles of an average diameter of 336.3 nm were obtained, having a minimum diameter of more than 300 nm and a relatively broad distribution (fig. 2).

The DLS analysis shows that for synthesis NANO_C particles of an average diameter of 901 nm, were obtained, having a minimum diameter of more than 700 nm and a relatively narrow distribution (fig. 3).

All three laboratory-generated nanoparticles were tested in regard to their ability to reduce hexavalent chromium ion concentrations. The results gathered from the three types of nanoparticles as regards mixing time and pH variation are shown below.

The characteristics of the wastewater that was subjected to testing are presented in table 2.

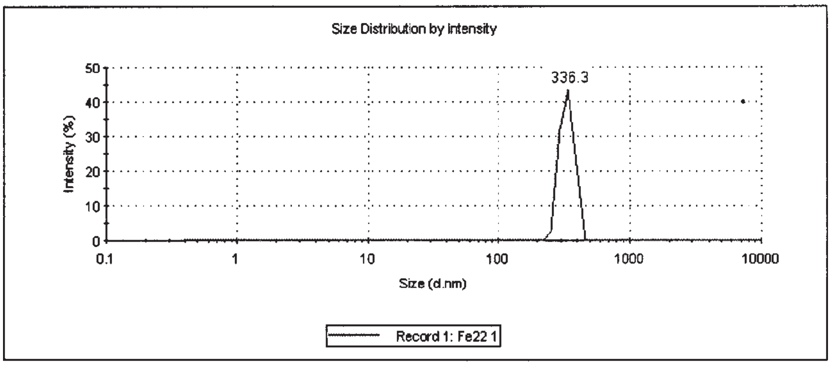

Fig. 2. The particle size of the metallic iron obtained in the presence of xylene and butoxy-diethylene glycol

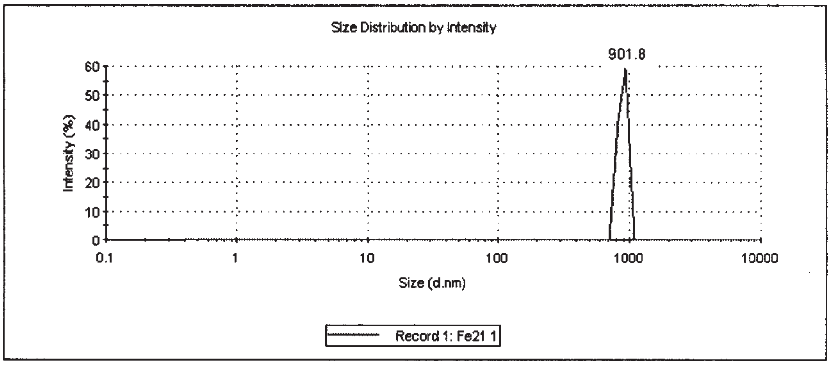

Fig. 3. The particle size of the metallic iron obtained in the presence of xylene

**Table 2**
THE WASTEWATER CHARACTERISTICS

| Parameter | Value |
|---|---|
| pH | 7.1 |
| Crom total, mg/L | 520 |
| Crom hexavalent, mg/L | 6,8 |
| COD, mg/L | 4240 |
| TSS, mg/L | 1424 |

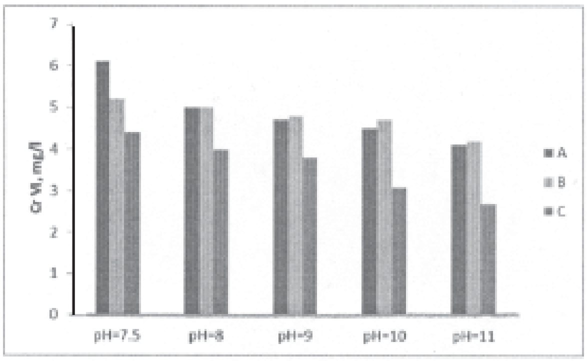

Fig. 5. Hexavalent chromium concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h(NANO_A)

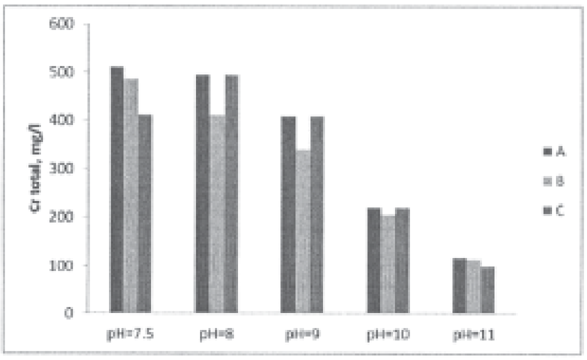

Fig. 4. Cr total concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h(NANO_A)

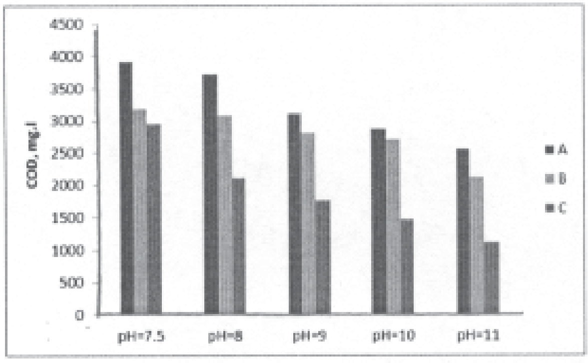

Fig. 6. COD concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h(NANO_A)

Nanoparticle NANO_A (mixing time of 8, 9 and 10 h and a *p*H between 7.5 and 11) recorded the following values shown in figures 4 - 7.

An increase in reaction time led to the decrease of total chromium concentration from a baseline value of 520 mg/L to 117 mg/L for *p*H = 11 and a reaction time of 10 h. An increase in reaction time led to a total chromium concentration within the range of 412-99 mg/L. The value of 99 mg/L was obtained when *p*H =11. Consequently, it is clear that *p*H has a positive influence on the treatment process in the sense that high values of pH lead to low concentrations of total chromium in treated water. The same variation is also valid for the hexavalent chromium ion whose concentration value decreased from its baseline value of 6.8 mg/L to 2.7 mg/L (*p*H = 11 and reaction time is 10 h). In conclusion, the optimal parameters for testing nanoparticle water treatment with particles having an average particle diameter of 489.6 nm are the following: a *p*H value of 11 and 10 h reaction time.

Nanoparticle NANO_B testing recorded a better separation of both total chromium and hexavalent chromium ion. Figures 8 -11 outline the variation of physico-chemical parameters analysed in the present paper depending on *p*H and reaction time.

The reduction of hexavalent chromium ion concentration is significantly improved compared to the previous version, the final concentration reaching a value of 1.1 mg/L. COD decreased to 2495 mg/L for a *p*H of 11

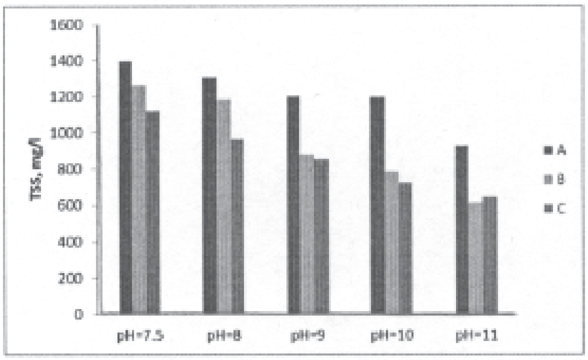

Fig. 7. TSS concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h(NANO_A)

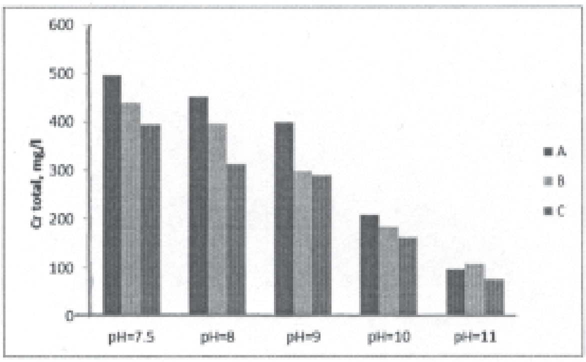

Fig. 8. Cr total concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h(NANO_B)

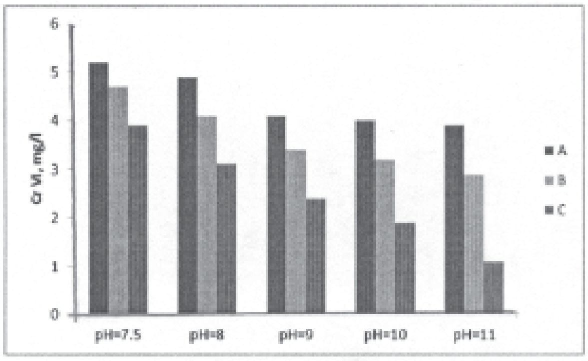

Fig. 9. Hexavalente chromium concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h(NANO_B)

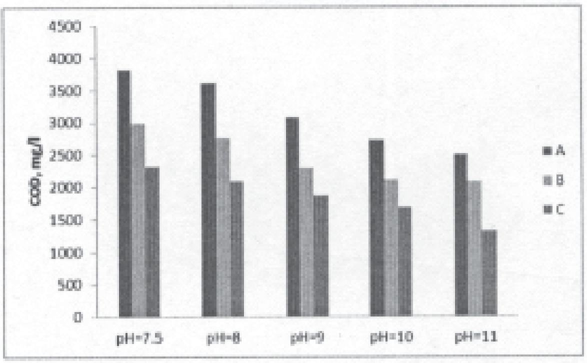

Fig. 10. COD concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h (NANO_B)

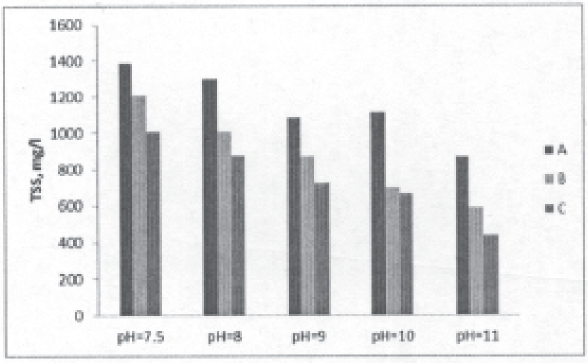

Fig. 11. TSS concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h(NANO_B)

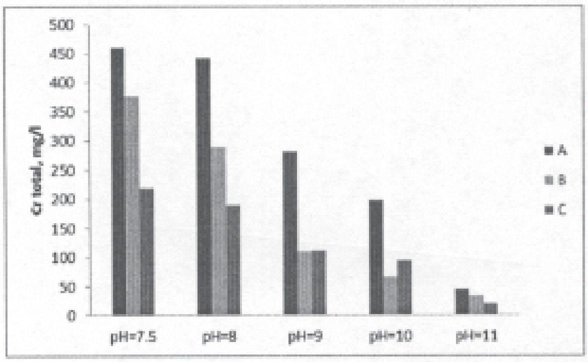

Fig. 12. Cr total concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h (NANO_C) (NANO_C)

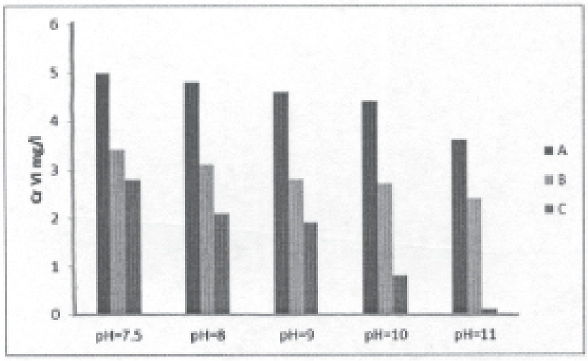

Fig.13. Hexavalente chromium concentration variation at different pH values according to mixing time: A = 8 hours, B = 9 h, C = 10 h

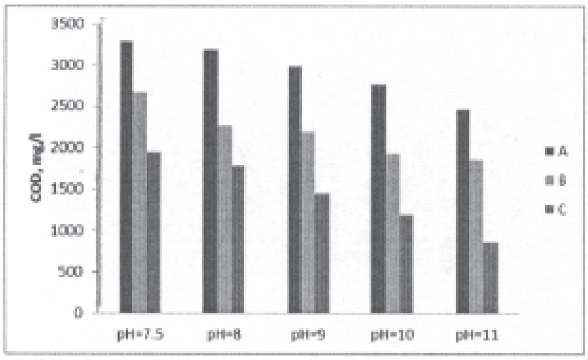

Fig.14. COD concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h(NANO_C)

and a mixing time of 8 hours and to 1315mg/L in the same reaction conditions and a time frame of 10 h. TSS had significant drops in the range of 1385 mg/L for *p*H = 7.5 and 867 mg/l for *p*H = 11. The necessity to increase reaction time and *p*H values for advanced treatment also applies to hexavalent chromium ion concentrations which decrease to a value of 1.1 mg/L. The theory that a larger size minimum pore diameter is beneficial for the process is proven to be true in this case. In the case of nanoparticle experiments carried out with the addition of particles whose minimum diameter is 901 nm (NANO_C), a significant improvement of reducing hexavalent chromium ion concentrations as well as COD, TSS and total Cr can be observed. Hence, for a reaction time of eight hours, total Cr values decreased to 196 mg/L, hexavalent chromium concentration dropped to 76 mg/L, while TSS and COD

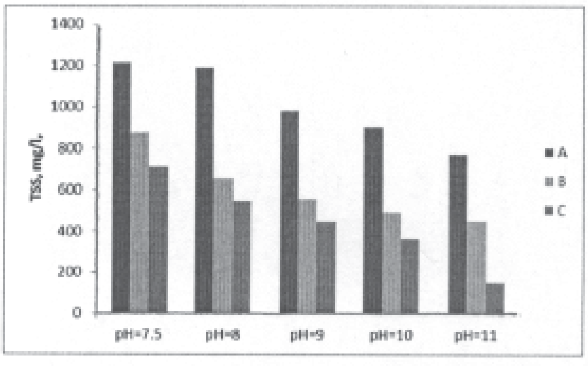

Fig. 15. TSS concentration variation at different *p*H values according to mixing time: A = 8 h, B = 9 h, C = 10 h(NANO_C)

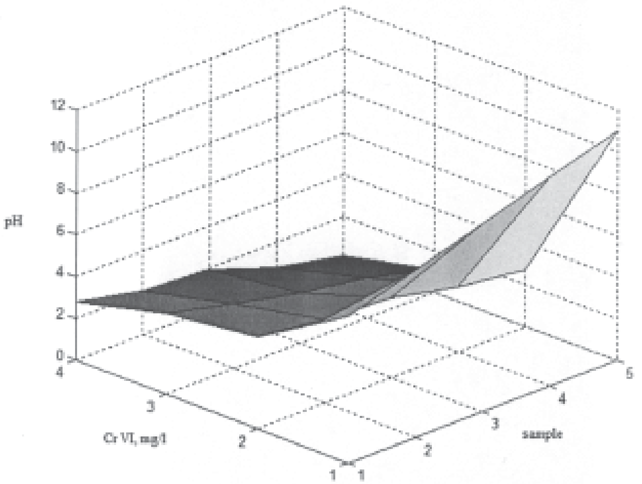

Fig. 16. Hexavalent chromium ion concentration according to *p*H

**Table 3**

PHYSICO-CHEMICAL RECOVERY LEVELS DEPENDING ON *p*H VALUES FOR A REACTION TIME OF 10 HOURS

| | NANO_A | | | | NANO_B | | | | NANO_C | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PARAMETER | pH=7.5 | pH=8 | pH=9 | **pH=10** | pH=7.5 | pH=8 | pH=9 | pH=10 | pH=7.5 | pH=8 | pH=9 | pH=10 |
| Total Cr, mg/L | 20.77 | 4.81 | 21.15 | **80.96** | 24.23 | 40.00 | 68.85 | 85.38 | 58.08 | 24.23 | 78.46 | 95.96 |
| Cr (VI), mg/L | 35.29 | 41.18 | 44.12 | **60.29** | 42.65 | 54.41 | 72.06 | 83.82 | 58.82 | 42.65 | 72.06 | 98.53 |
| COD, mg/L | 30.50 | 50.31 | 58.47 | **73.82** | 45.52 | 50.83 | 60.40 | 68.99 | 53.99 | 45.52 | 65.75 | 79.48 |
| TSS, mg/L | 21.56 | 32.37 | 40.45 | **54.85** | 29.21 | 38.48 | 53.30 | 69.03 | 50.00 | 29.21 | 68.54 | 89.04 |

dropped to values of 870 mg/L and 156 mg/L respectively for *p*H = 11 and 10 h reaction time. As in previous cases, the reduction of hexavalent chromium ion concentration decreases from 3.6 mg/L to a maximum of 0.1 mg/L for the same reaction conditions (*p*H = 11).

The mathematical model of the reduction process of hexavalent chromium in the presence of nanoparticles at different *p*H values was performed with a program MathLab (2013b). The equation describing the variation of the concentration of hexavalent chromium depending on solution *p*H is given in figure 16 and described by equation 1.

$$f(x) = -0.0917x^6 + 0.6169x^5 + 0.1124 \qquad (1)$$

The effectiveness of the nanoparticle treatment process is quantified by the achieved levels of pollutant recovery. The higher the recovery percentage is, the more effective the process is considered to be. Adopting a 10-h working time is a conclusion of previous experiments which showed that this is the value that provides minimal pollutant concentrations. This interpretation of the results also facilitates finding practical implementations for the nanaoparticle treatment process, i.e., as secondary or tertiary stage.

Analysing the data resulting from the experiment (table 3) it can be seen that the best results are obtained for nanoparticles whose minimum diameter is 901 nm and *p*H = Recovery of the hexavalent chromium ion in proportion of 98.53, 95.96% total chromium, COD and TSS of 79.48 and 89.04% is an indicator of the increased performance of this type of nanoparticle treatment process.

## Conclusions

Metallic iron nanoparticles were synthesized by the hydrazine reduction method in three experimental versions: *i)* in aqueous solution; *ii)* in aqueous solution in the presence of an aromatic solvent, i.e., xylene; *iii)* in aqueous solution in the presence of an aromatic solvent and anti-caking additive (butoxy-diethylene glycol).

The average size and particle size distribution obtained by the three versions was determined with a particle size measurement system making use of dynamic light scattering (DLS); a Malvern-Zetasizer NanoZS apparatus was used.

The presence of the aromatic solvent and anti-caking additive influences the average size and size distribution of the particles; hence, particle size distribution narrows in the presence of organic additives, while the average particle size decreases in the presence of anti-caking additives and increases in the presence of xylene.

The metallic iron nanoparticles obtained in the three experiments were used in the treatment of waters containing a 6.8 mg/L concentration of hexavalent chromium. Reduction of hexavalent chromium concentrations as well as total chromium, COD and TSS depend on *p*H and reaction times. $Cr^{6+}$ ion concentration variation depending on reaction time and *p*H. The optimal conditions requires for hexavalent chromium reduction, for obtaining values lower than 0.1 mg/L, are: the *p*H value of 11, a duration of the process 10 h.

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