Università degli Studi di Napoli

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Department of Hydraulic, Geotechnical end Environmental Engineering

Stevens Institute of Technology

Center for Environmental System

Master Thesis in Environmental Engineering

Chromium removal from aqueous solutions using zero valent iron and zero valent iron/copper

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Background and Problem

Continuous contamination of the environment with heavy metals has become a significant and well recognized problem of the modern world. Metal are particularly problematic contaminants because unlike most organic compounds, they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain, causing various diseases and disorders in living organisms.

Chromium (Cr) is one of the highest priority pollutants in surface water and groundwater released mainly from anthropogenic source, and in this work the focus is on chromium and its removal from aqueous solutions.

For this compound it is possible to distinguish two different forms, Cr(VI) and Cr(III). Hexavalent chromium is highly toxic to humans, animals, plants and microorganisms: it is a well-established human carcinogen. Trivalent chromium is rather harmless, hence Cr(VI) reduction to Cr(III) can be beneficial because a more mobile and more toxic chromium species is converted to a less mobile and less toxic form. There are different technologies developed over the years for its removal, that have shown their effectiveness. During the last two decades, there has been important interest in using zero valent iron (ZVI) as a Cr(VI) reducing agent. A considerable volume of research has been carried out in order to investigate the mechanism and kinetics of Cr(VI) reduction with ZVI.

The aim of this work is to provide information about the behavior of ZVI and ZVI/Cu particles for the treatment of Cr(VI) polluted solution, with different concentrations. The difference respect to previous works is the use of a new type of particle; in fact it has been used a granular ZVI and ZVI/Cu produced by a manufacturer of its own laboratory (patent pending).

The kinetics study has been performed through several tests using a discontinuous reactor (batch). Tests have been carried out using different reducing agents, i.e. ZVI and ZVI/Cu at different pH. The obtained results were good and these permitted to continue the analysis through a continuous reactor (column). The column test allows determination of the kinetics of the system closer to the real one and provides further details about life and performance of the system. In particular, at the beginning it has been noted a difference between the behavior of ZVI and ZVI/Cu, and then just ZVI/Cu was used in the other two applications, which described the use of the reagent in a drinking water and wastewater application.

The treatment of a synthetic solutions using ZVI and ZVI/Cu has led to a significant increase of total iron in the effluent. Some tests were carried out in order to reduce its amount using a sodium hypochlorite solution.

Results

Batch tests results

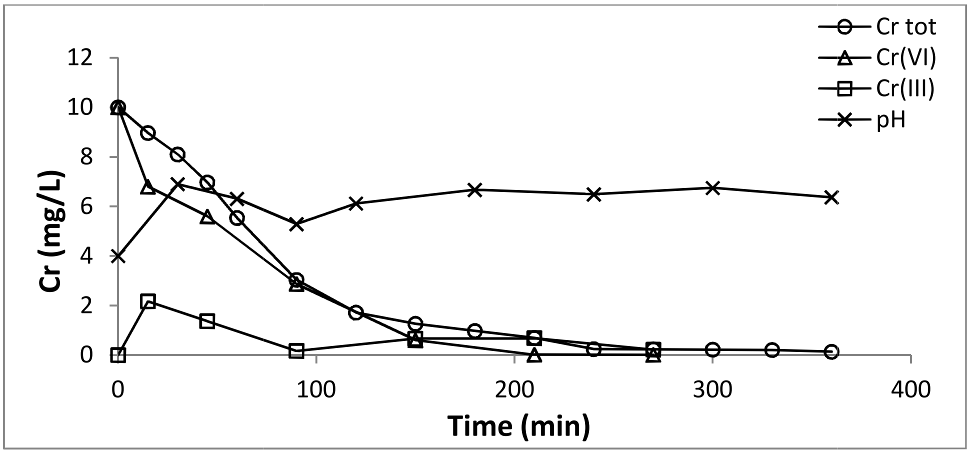

Fig. 1 *Chromium species concentrations vs. time for batch test using ZVI, at feed solution pH 4.*

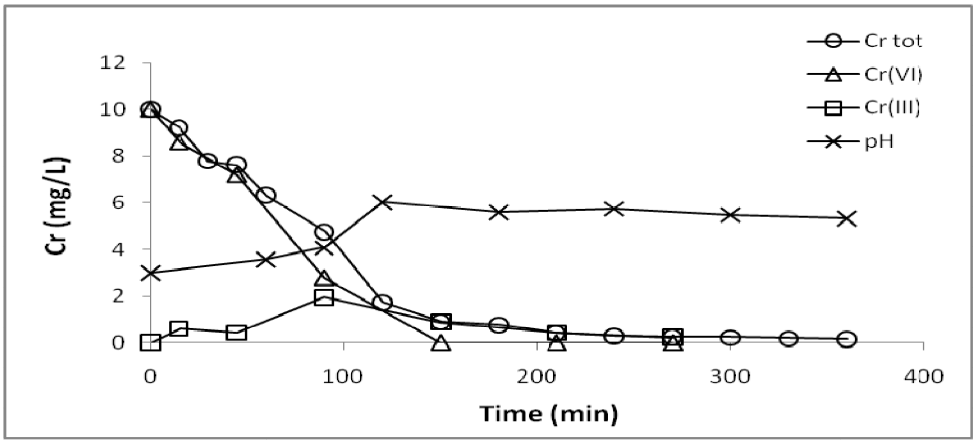

Fig. 2 *Chromium species concentrations vs. time for batch test using ZVI, at feed solution pH 3.*

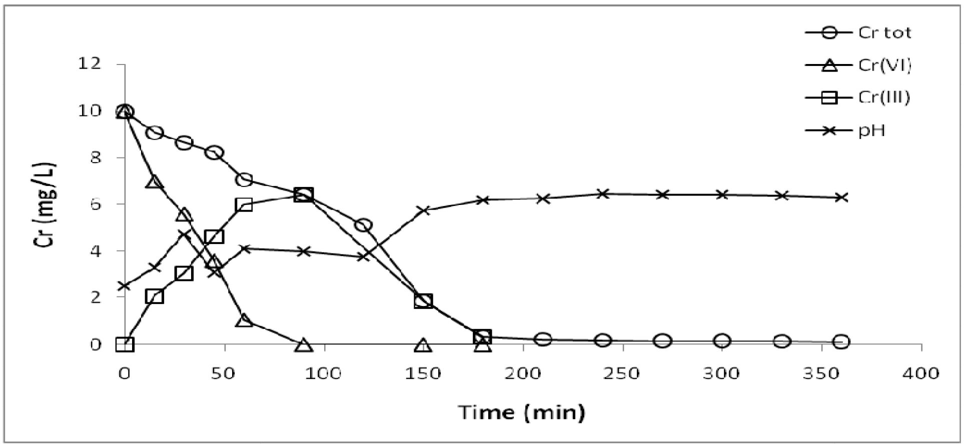

Fig. 3 *Chromium species concentrations vs. time for batch test using ZVI, at feed solution pH 2,5.*

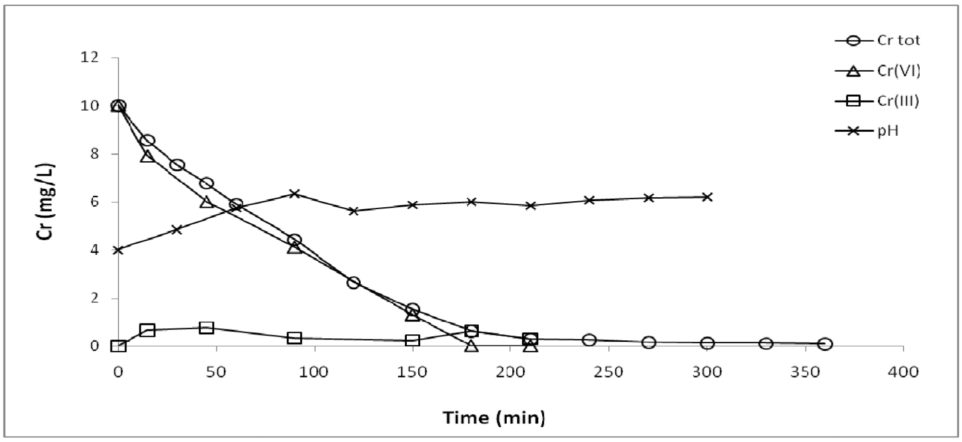

Fig. 4 *Chromium species concentrations vs. time for batch test using ZVI/Cu, at feed solution pH 4.*

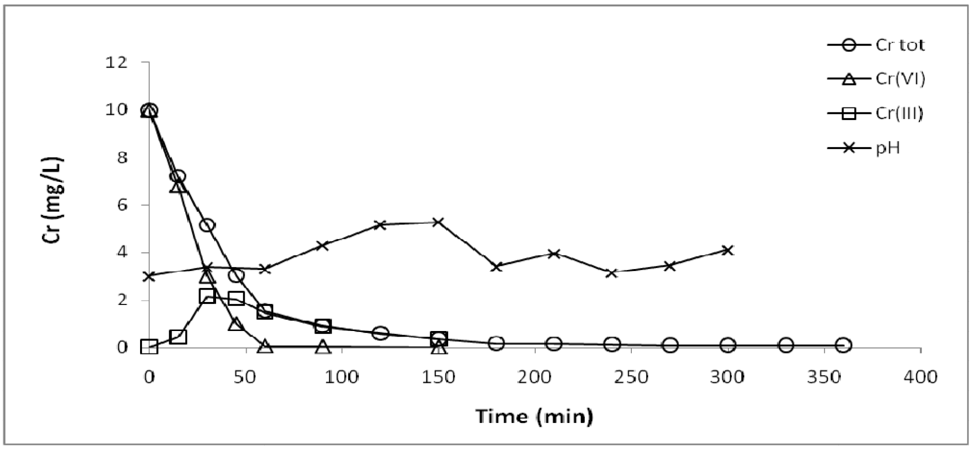

Fig. 5 *Chromium species concentrations vs. time for batch test using ZVI/Cu, at feed solution pH 3.*

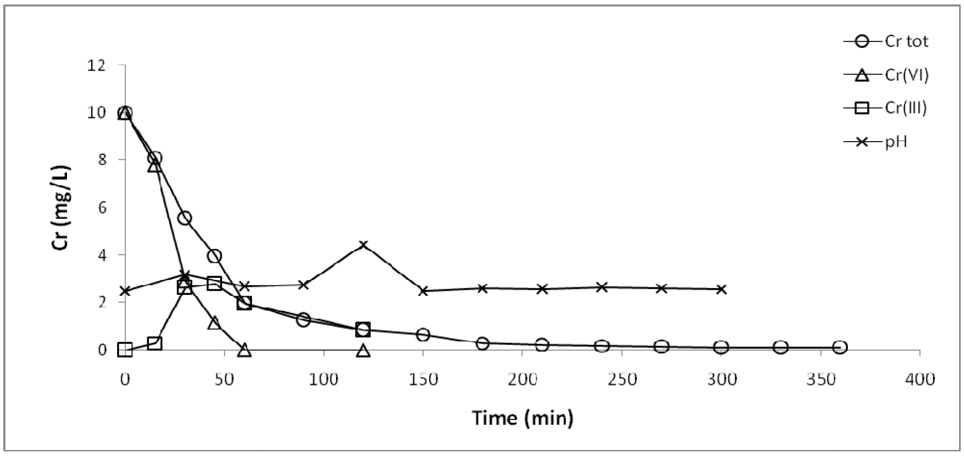

Fig. 6 *Chromium species concentrations vs. time for batch test using ZVI/Cu, at feed solution pH 2,5.*

Column tests results

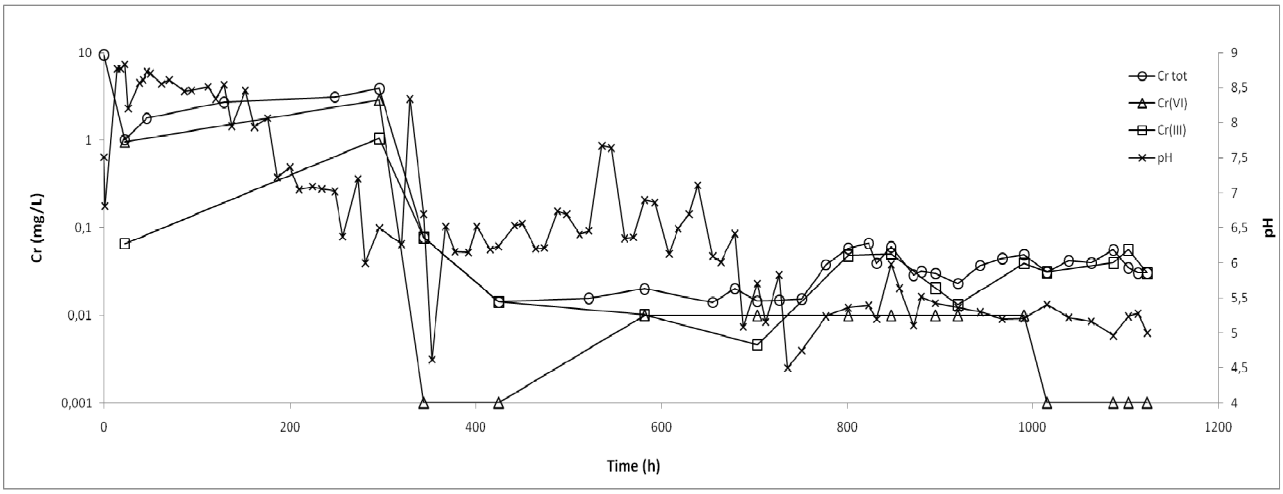

Fig. 7 *Column 1, Chromium species and pH vs. time.*

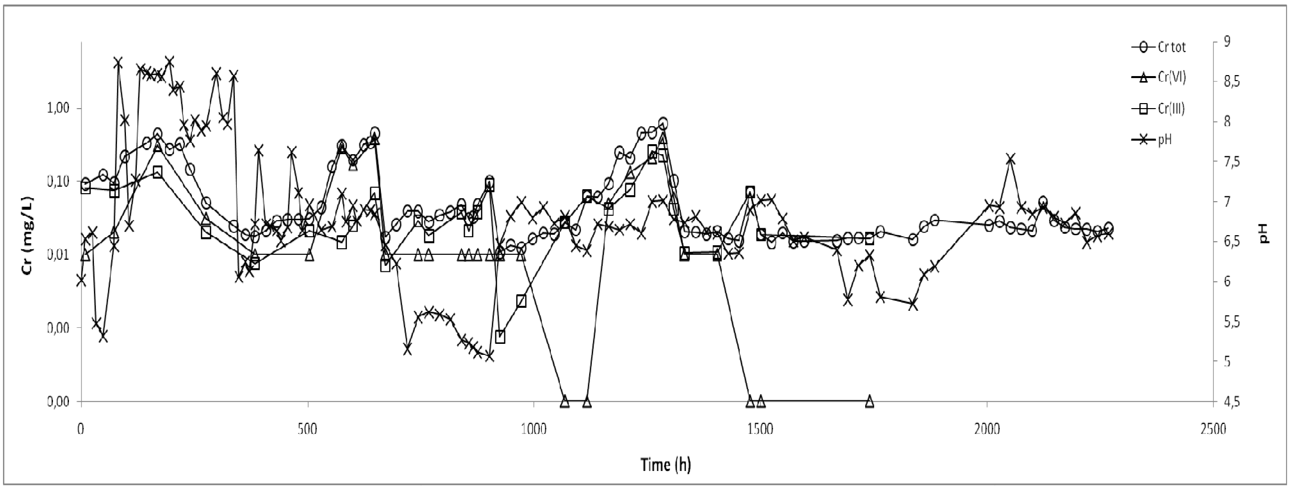

Fig. 8 *Column 2, ZVI/Cu column, Chromium species and pH vs. time.*

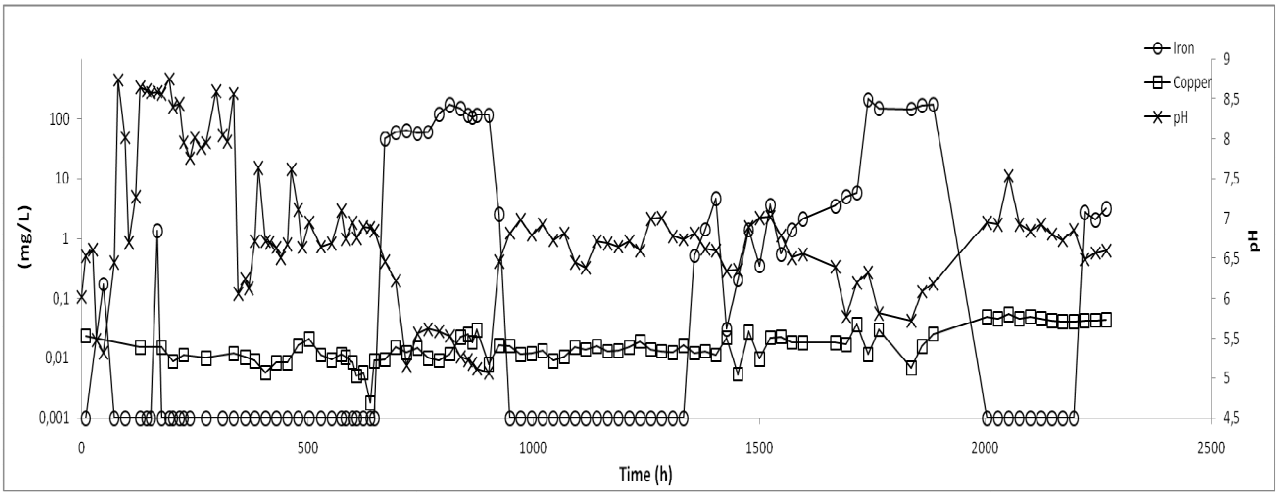

Fig. 9 *Column 2, ZVI/Cu column, total iron and copper vs. time.*

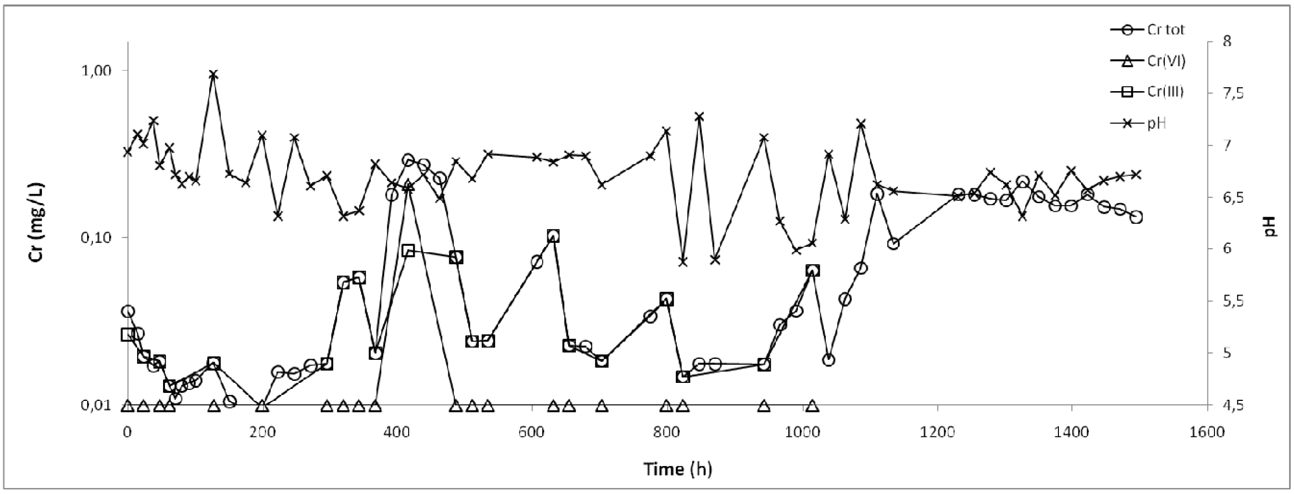

Fig. 10 *Column 3, ZVI/Cu column, Chromium species and pH vs. time.*

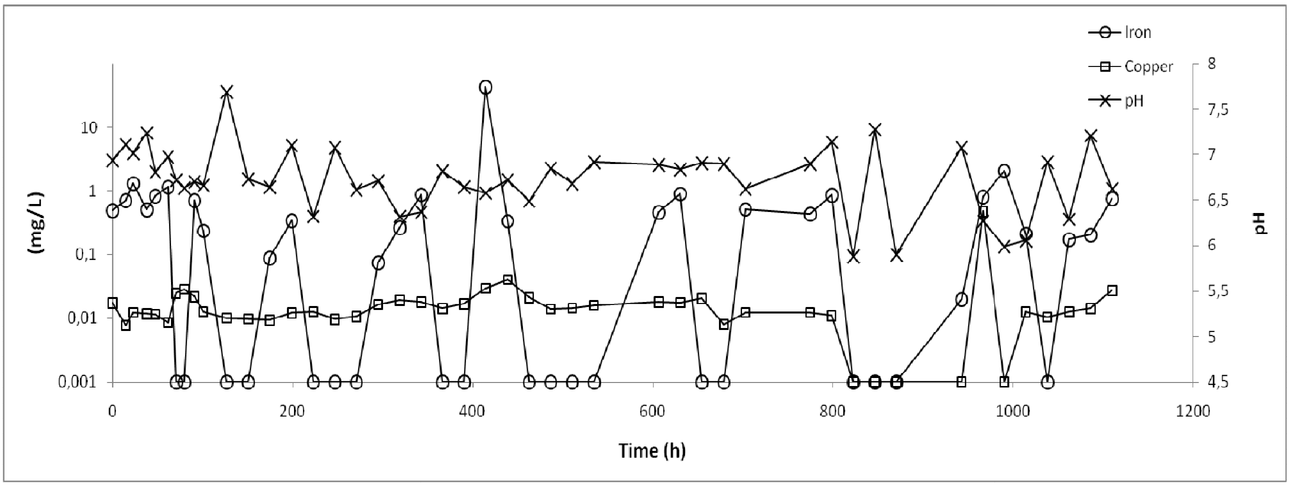

Fig. 11 *Column 3, ZVI/Cu column, total iron and copper vs. time.*

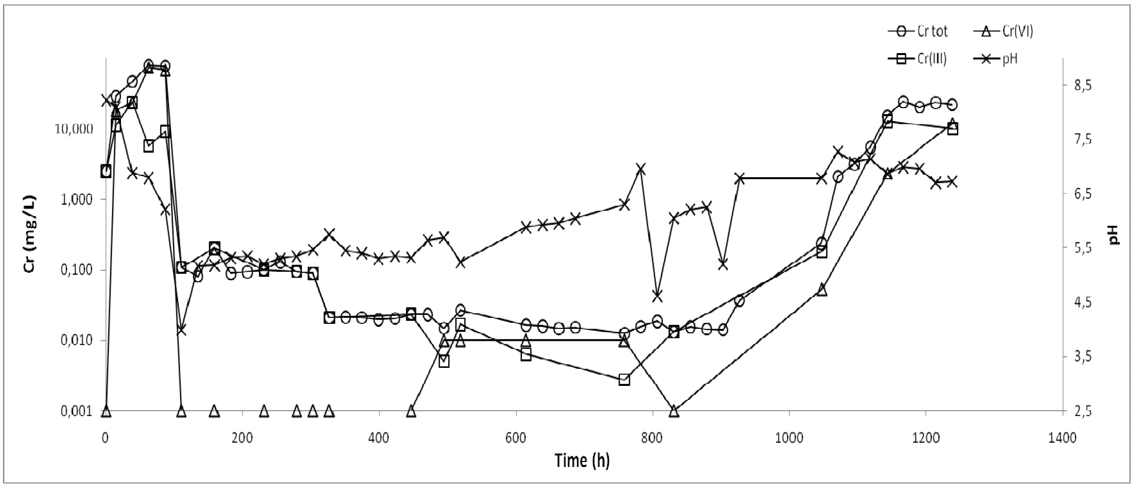

Fig. 12 *Column 4, ZVI/Cu column, Chromium species and pH vs. time.*

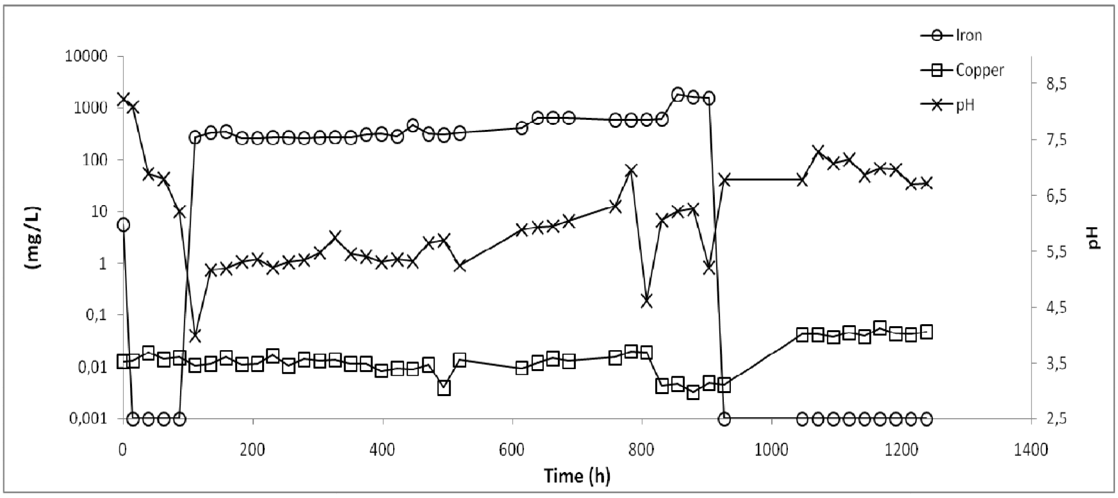

Fig. 13 *Column 4, ZVI/Cu column, total iron and copper vs. time.*

Iron removal tests

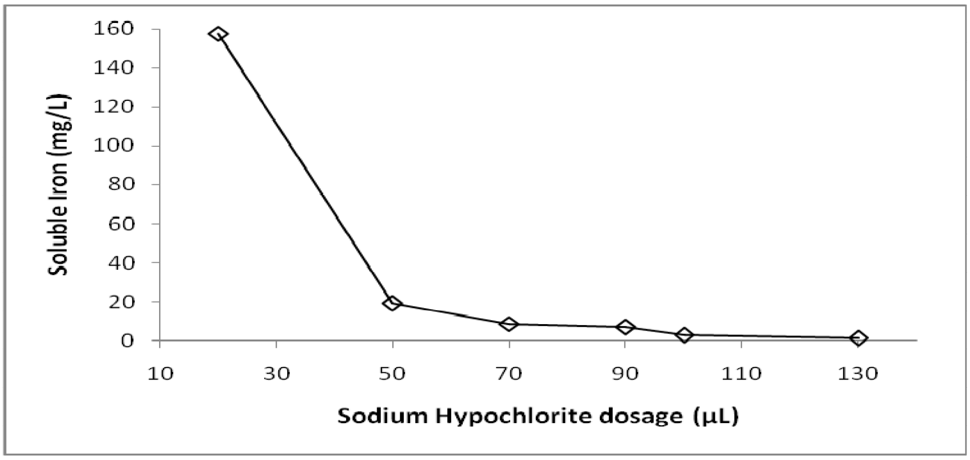

Fig. 14 *Soluble Iron concentration vs. Sodium Hypochlorite dosage, first test.*

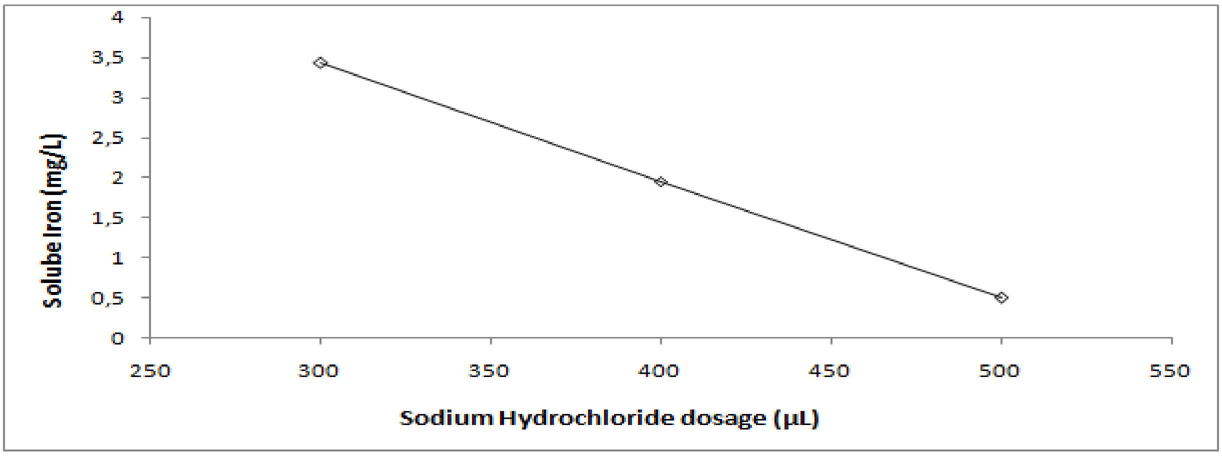

***Fig. 15** Soluble Iron concentration vs. Sodium Hypochlorite dosage, second test.*

Conclusion

Reduction of Cr(VI) by Fe^0 granulate particles as a reductant was studied using potassium dichromate solution as a contaminant.

The tests that have been carried out through batch and column tests, have shown that zero valent iron is an efficient and fast solution. The main advantage of this system is that it doesn't require high costs for energy and chemicals: the direct mechanism of Cr(VI) reduction is based on the capacity of ZVI to operate as electron donor. Additionally, ferrous iron released during Cr(VI) reduction by ZVI may also contribute to the reduction process.

Furthermore, the use of the mix ZVI/Cu has revealed its superior properties respect to the ZVI in the tests performed.

In fact, batch tests have shown a better performance of ZVI/Cu, which is capable of giving the same results of ZVI with worse pH working conditions. Although working with pH 2,5, the ZVI system didn't reach the efficiency of 99% for the removal of total chromium, contrarily to the system that used ZVI/Cu, that achieved the goal after 240 min and isn’t needed at pH 3. The latter system at the same working condition, after 60 min has allowed to reached the complete removal of Cr(VI), with a ratio S/L of 1%.

The results achieved through the batch tests were confirmed by column tests.

Column 1 didn't work at pH 4, but only at the more acidic pH such as 3 and 2,5. Contrarily, the Column 2 that has been packed with ZVI/Cu gave a good performance at pH 3 and 3,5 as well. When ZVI column has been disposed of, it reached an efficiency of 86,6%, and the performance of the ZVI/Cu column was higher (96,67%) for the treatment of the same volume of solution; at the end, the performance of the second column was 99,05%.

The tests performed with Column 3 and 4 have allowed identification of the keys parameters, i.e. the contact time and the pH, that with the concentrations are the parameters that determine the success of the test; inter alia, long contact times and low pH are suitable for a good removal. The drawback of using acid conditions, is the large dissolution of iron (total iron), which is released into the solution. The dissolved iron in the column effluent is an contaminant that must be removed, together with Cr(III), in a final treatment step. Very acidic conditions also lead to a mass reduction of the granular medium.

The solution used for Column 2 and 3 had the adoption of the sand column; in the last column test, it reached high values of total iron (1800 ppm), and the chemical reaction with sodium hydrochloride was provided. With a ratio of 10% of NaClO solution/water the performance of iron removal was of 99,97%, and was checked the chlorine's limit also.

Both the solutions (Sand column or NaClO solution) have been determined to have an excellent performance. In the case of drinking water, it must be given another treatment, since the law's limit are more stringent for iron; in the case of wastewater, it must be evaluated if it is more convenient to use a chemical as sodium hydrochloride solution, or try to use another ZVI/Cu column, since in the real case there are a large amounts of solution to treat.