intersol'2009

Analyse, Méthodologies de Traitement et Réhabilitation des Sols et Eaux Souterraines Pollués

Analysis, Treatment Methodologies and Remediation for Polluted Soils and Groundwater

Treatment of hexavalent chromium polluted groundwater by use of scrap iron

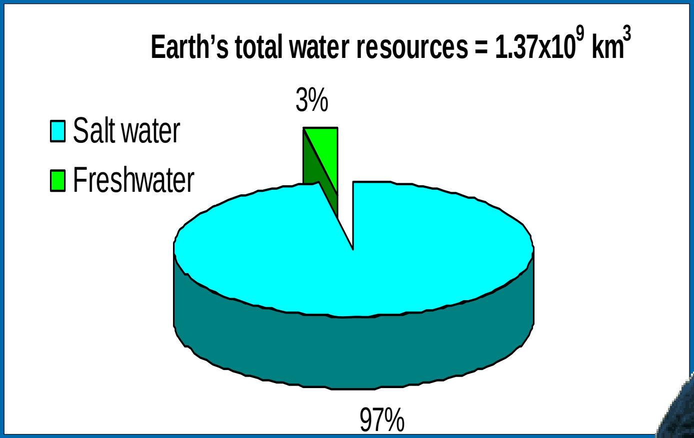
Marius Gheju

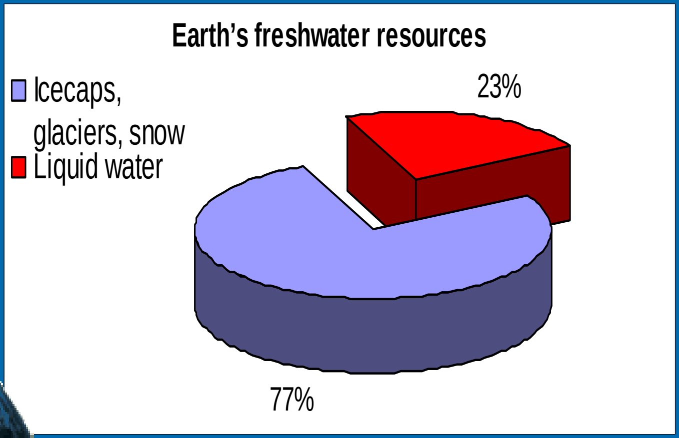
"Politehnica" University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering,
Bd. V. Parvan Nr. 6, Et. 4, Timisoara, 300223, Romania
e-mail: marius.gheju@chim.upt.ro

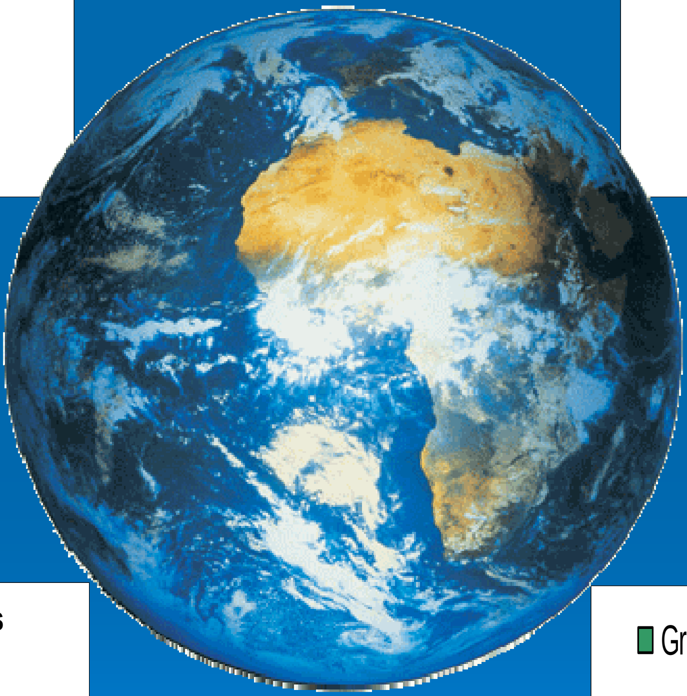
Ionel Balcu

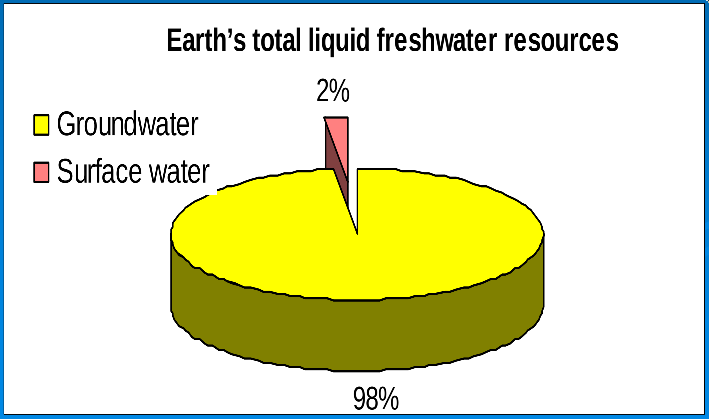
National Institute for Development in Electrochemistry and Condensed Matter,
Str. Dr. Aurel Păunescu Podeanu Nr. 144, Timisoara, 300587, Romania
e-mail: ionel_balcu@yahoo.com

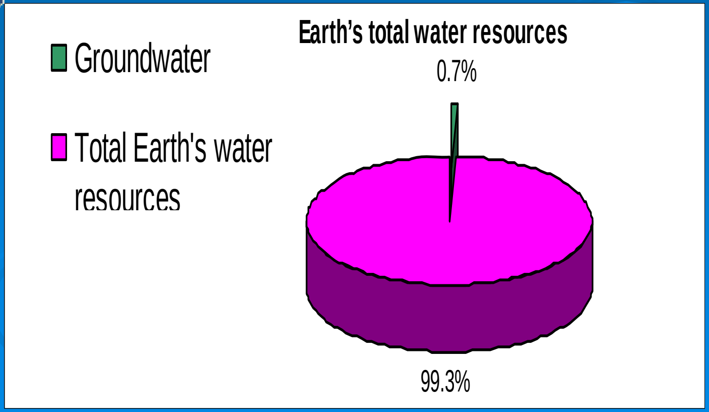
Earth’s water resources











Groundwater

- In most cases, groundwater is cleaner than surface water, because it's usually protected against contamination from the surface by soils and covering rock layers;
- This is why most drinking water in many areas of the world is groundwater. Groundwater is used by about two billion people worldwide, making it the single most used natural resource;
- Rising world population, changes in land use and rapid industrialization increasingly place groundwater in jeopardy;
- Groundwater supplies are polluted in 90% of China cities (P.R.C. State Environmental Protection Administration);
- Over 50% of the EU's groundwater sources are polluted (European Environmental Bureau);
- 50% of groundwater samples tested in the U.S.A. contains pesticides (US Geological Survey);
- Therefore, in last decades, attention has been focused on contaminated groundwater remediation.

Groundwater pollution by metals

- Metals environmental contaminants are particularly problematic because, unlike most organic contaminants, they do not undergo degradation. Therefore, they have a long-term persistance in the environment;
- Redox reactive metals often do different degrees of toxicity, depending on the specific metal oxidation state;
- Chromium is usually encountered in natural environments in two main oxidation states: Cr(+III) and Cr(+VI), characterized by different chemical behaviour and toxicity.

Chemical and toxicological behaviour of chromium

- Cr(VI) is known to be highly toxic and carcinogenic. Because of its significant mobility in the subsurface environment, the potential risk of groundwater contamination is high;
- Cr(III) is less toxic and readily precipitates under alkaline or even slightly acidic conditions.

Methods available for the decontamination of polluted groundwaters

- ***Natural attenuation*** - the concentration of groundwater pollutants is reduced to an acceptable level by natural processes;

- ***Pump-and-treat*** - polluted groundwater is pumped to the surface where conventional water treatment methods are applied to clean the groundwater;

- ***In situ treatment*** - bioremediation, adsorption, redox processes, precipitation.

Mechanism of in situ Cr(VI) removal by Fe(0)

1. $Cr_2O_7^{2-}{}_{(aq)} + 2Fe(0)_{(s)} + 14H^+{}_{(aq)}$ ------> $2Cr^{3+}{}_{(aq)} + 2Fe^{3+}{}_{(aq)} + 7H_2O$

2. $Cr^{3+}{}_{(aq)} + 3H_2O$ ------> $Cr(OH)_{3(s)} + 3H^+{}_{(aq)}$

   $Fe^{3+}{}_{(aq)} + 3H_2O$ ------> $Fe(OH)_{3(s)} + 3H^+{}_{(aq)}$

   $(1-x)Fe^{3+}{}_{(aq)} + (x)Cr^{3+}{}_{(aq)} + 3H_2O$ ------> $Cr_xFe_{1-x}(OH)_{3(s)} + 3H^+{}_{(aq)}$

   $(1-x)Fe^{3+}{}_{(aq)} + (x)Cr^{3+}{}_{(aq)} + 2H_2O$ ------> $Cr_xFe_{1-x}(OOH)_{(s)} + 3H^+{}_{(aq)}$

Objective of the study

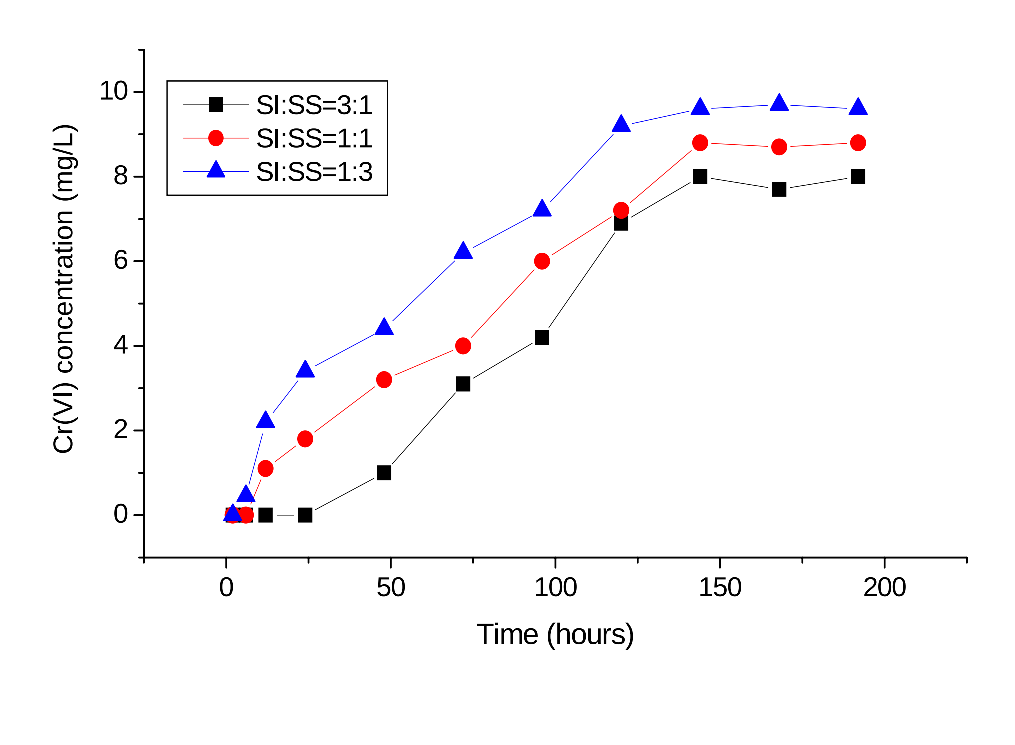
To investigate the use of an unconventional reducing agent, scrap iron, a cheap and locally available industrial waste, for the continuous reduction of hexavalent chromium.

Materials and methods

- Cr(VI) reduction column experiments were conducted by using scrap iron shavings and silica sand that pass trough 2.5 mm screen and remain on 1.25 mm screen;
- The column was packed with 40 g scrap iron-silica sand mixture at folowing mass ratios: SI:SS = 3:1, 1:1 and 1:3;
- 10 mg Cr(VI)/l aqueous solution with pH = 7.2 was passed through the column, from the bottom to the top, by using a Unipan peristaltic pump;
- The effluent column was sampled periodically for the analysis of Cr(VI), Cr(total), Fe(II) and Fe(total) concentration;
- The analysis of hexavalent chromium in solution was carried out by the 1,5-diphenylcarbazide colorimetric method. The total chromium concentration was determined by oxidizing any trivalent chromium with potassium permanganate, followed by analysis as hexavalent chromium. Trivalent chromium was then determined from the difference between total and hexavalent chromium;
- Fe(II) was determined by the 1,10-phenanthroline method. Total Fe was determined by the 1,10-phenanthroline method, by reduction of any Fe(III) to Fe(II) with hydroxylamine hydrochloride and subsequent analysis as Fe(II). Fe(III) was then determined from the difference between total and bivalent iron.

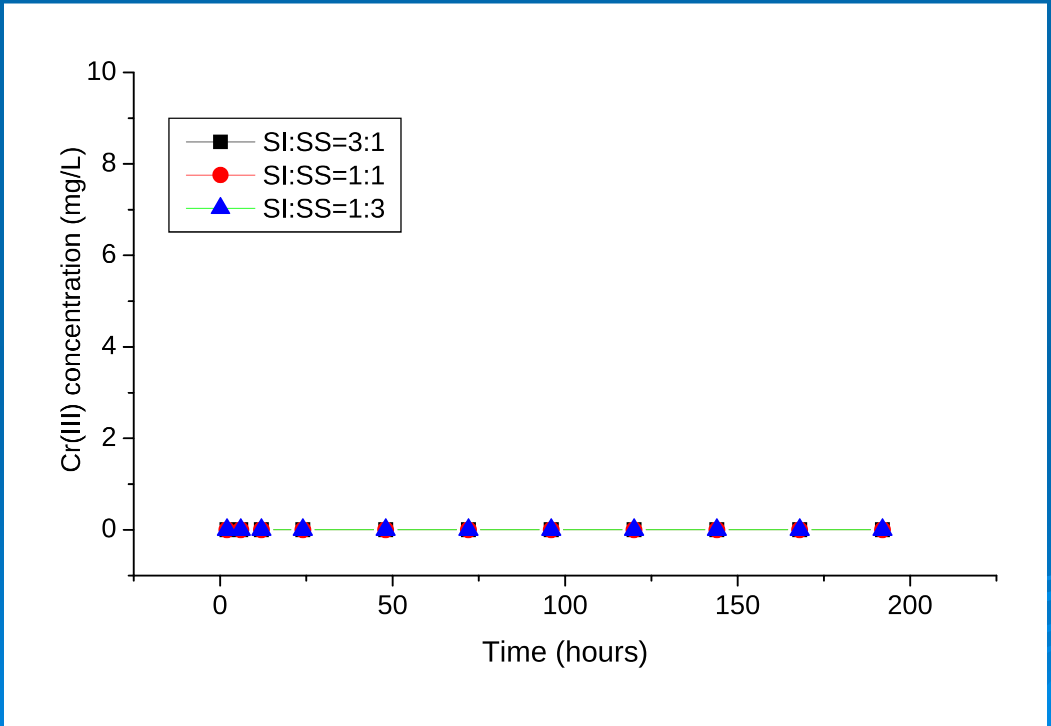
Results

Figure 1. Cr(VI) concentration in column effluent, as a function of elapsed time and SI:SS mass ratio



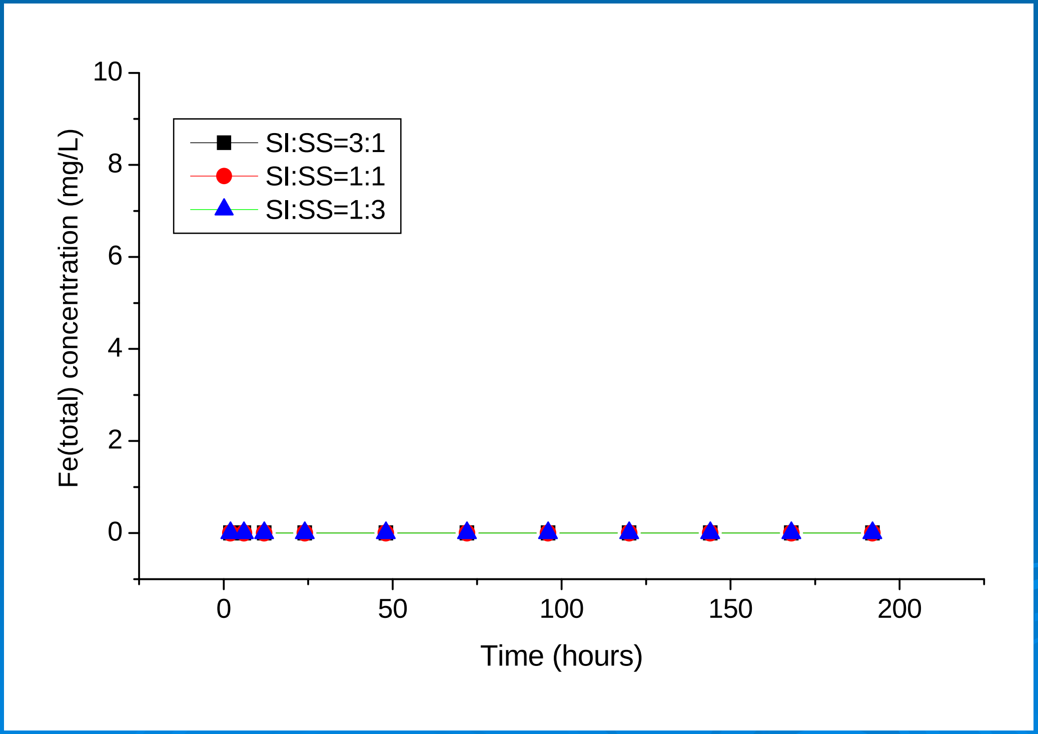
Results

Figure 2. Cr(III) concentration in column effluent, as a function of elapsed time and SI:SS mass ratio



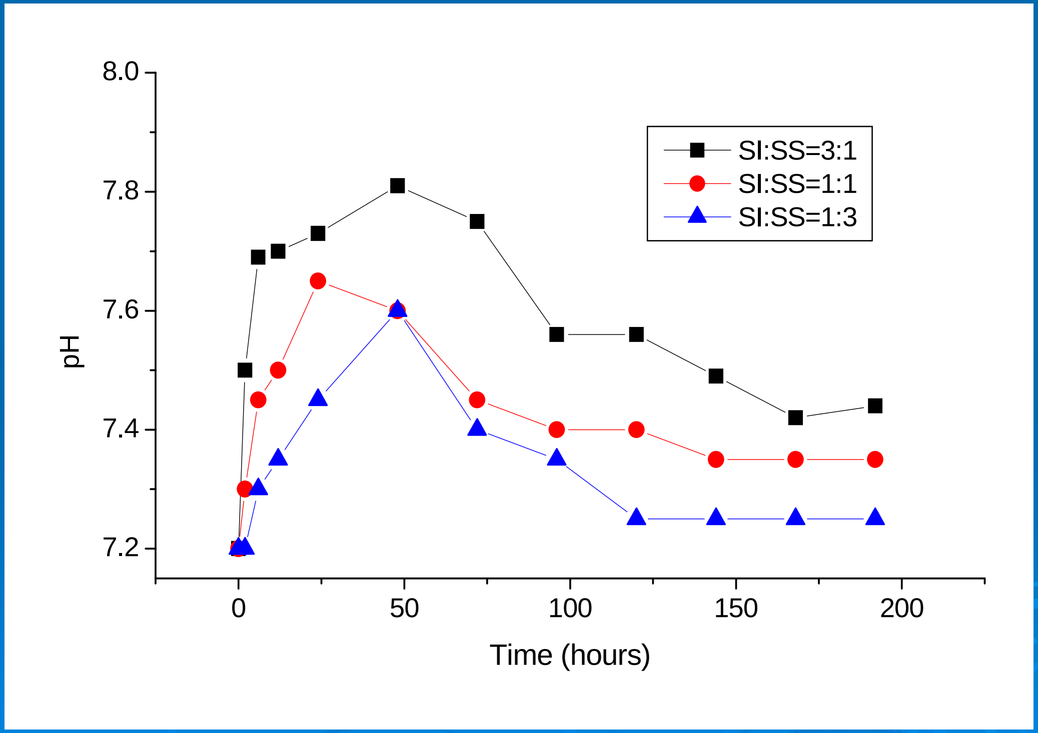
Results

Figure 3. Fe(total) concentration in column effluent, as a function of elapsed time and SI:SS mass ratio



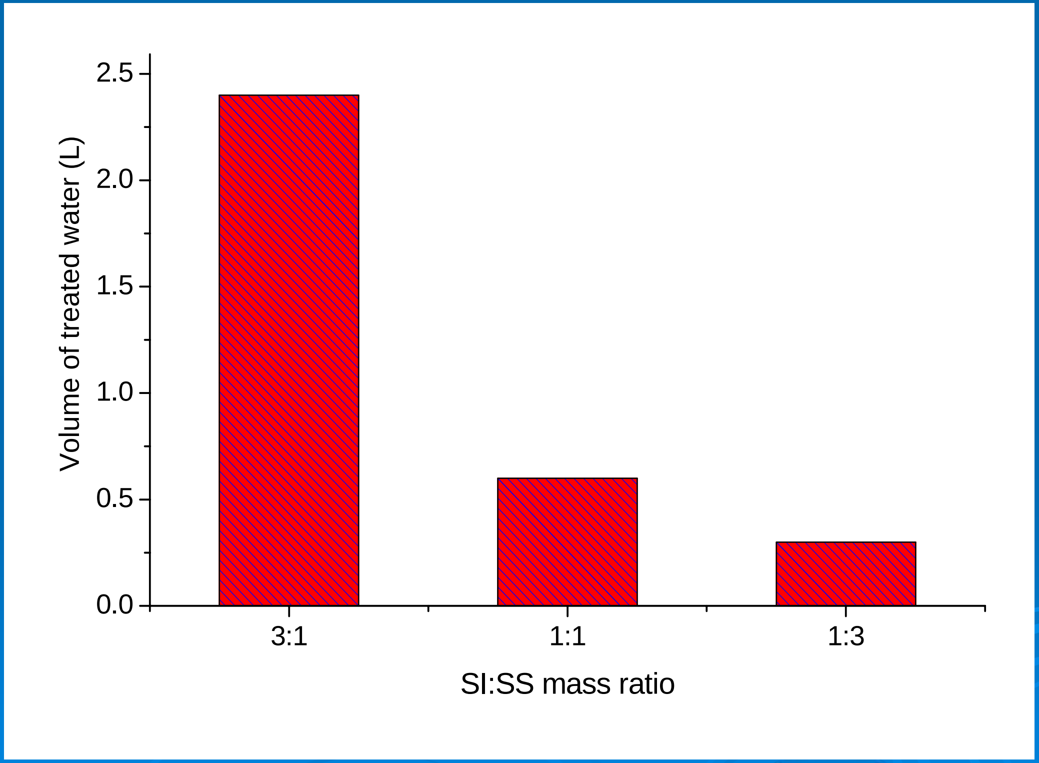
Results

Figure 4. Column effluent pH, as a function of elapsed time and SI:SS mass ratio



Results

Figure 5. Volume of treated water, as a function of SI:SS mass ratio



Conclusions

- Hexavalent chromium is a toxic metal and needs to be removed from polluted groundwater;
- The use of waste materials for water treatment can become a crucial component for poor communities from developing countries in their efforts to treat the pollution associated with industrial applications;
- Complete reduction of Cr(VI) in water solutions was possible by using a waste material, scrap iron, as reducing agent;
- The mobile and toxic Cr(VI) was converted, via corrosion of the elemental Fe, to the less toxic and insoluble Cr(III), which presumably forms a simple or/and mixed Cr-Fe (oxy)hydroxide insoluble phase;
- The amount of treated water, calculated up to the moment of Cr(VI) breakthrough, increased with increasing the amount of scrape iron in the SI-SS mixture. The highest reduction efficiency of the scrap iron from the SI-SS mixture was observed at SI:SS = 3:1, when 2.4 L Cr(VI) contaminated water were treated, and decreased with increasing the SS proportion in SI-SS mixture, up to 0.3 L treated water at SI:SS = 1:3;
- Over the entire studied SI:SS range, Cr(III), Fe(II) and Fe(III) were not detected in column effluent, for the entire duration of the experiment. This is an advantage because the treated water was free of iron and chromium species;
- The experimental results from this study indicate that scrap iron seem to be a suitable material for the treatment of Cr(VI) polluted groundwater, that could replace granular zerovalent iron.

References

1. D.E. Kimbrough, Y. Cohen, A.M. Winer, A critical assessment of chromium in the environment, Crit. Rev. Environ. Sci. Technol. 29 (1999) 1-46.
2. M. Perez-Candela, J.M. Martin-Martinez, R.Torregrosa-Macia, Chromium(VI) removal with activated carbons, Wat.Res. 29 (1995) 2174-2180.
3. F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced inorganic chemistry, John Wiley & Sons, Inc., 1999.
4. S.E. Fendorf, Surface reactions of chromium in soil and waters, Geoderma 67 (1995) 55-71.
5. M. Cieslak-Golonka, Toxic and mutagenic effects of chromium(VI). A review, Polyhedron, 15 (1995) 3667-3689.
6. L.B. Khalil, W.E. Mourad, M.W. Rophael, Photocatalytic reduction of environmental pollutant Cr(VI) over some semiconductors under UV/visible illumination, Appl. Cat. B: Environ. 17 (1998) 267-273.
7. D.Rai, B.M. Sass, D.A. Moore, Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide, Inorg. Chem. 26 (1987) 345-349.
8. R.W. Puls, D.W. Blowes, R.W. Gillham, Long-term performance monitoring for a permeable reactive barrier at the U.S. Coast Guard Support Center, Elizabeth City, North Carolina, J. Hazard. Mater. 68 (1999) 109-124.
9. D.W. Blowes, C.J. Ptacek, S.G. Benner, C.W.T. McRae, T.A. Bennett, R.W. Puls, Treatment of inorganic contaminants using permeable reactive barriers, J. Contam. Hydrol. 45 (2000) 123-137.
10. Anderson, R.A., Essentiality of chromium in humans, Sci. Total Environ. 86 (1989) 75–81.
11. P. Cheryl, M.B. Susan, Reflections on Hexavalent Chromium: Health hazards of an industrial heavyweight, Env. Health Persp. 108 (2000) 48-58.
12. M.Z. Hauschild, Putrescine (1,4-diaminobutane) as an indicator of pollution-induced stress in higher plants: barley and rape stressed with Cr(III) or Cr(VI), Ecotoxicol. Environ. Saf. 26 (1993) 228-247.