

## METHODS OF MONITORING AND DECONTAMINATION OF SOILS CONTAINING HEXAVALENT CHROMIUM

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*Abstract: Heavy metals pollution has become a topical issue caused by excessive industrialization at present human activities with a large number of sources of pollution with these compounds.*

*The high toxicity of chromium and its compounds caused important measures to prevent pollution with them, fixing rules governing maximum permissible concentrations or recommended for chromium in drinking water, food, sewage to be discharged into sewers or emissaries from natural air, soil.*

*CMA (maximum permissible concentration) for total chromium varies from 1.5 mg/dm<sup>3</sup> to water according to SR ISO 9174: 1998, and hexavalent chromium concentration is 0.2 mg/dm<sup>3</sup> according to SR EN 1998: 11083. CMA for chromium in soil is 100 mg/kg.*

*In biological terms, hexavalent chromium is classified in risk group 1 carcinogen and is known as a powerful lung carcinogen. This has sparked the interest of researchers on the heavy metal, with numerous studies of characterization and its recovery of affected environments.*

*Several issues related to the adverse effects of chromium, hexavalent and human health in particular, and some preliminary results for its adsorption on the surface of magnetite, are presented in this paper.*

*Keywords: heavy metals, chrome, magnetite, industry analysis.*

### 1. INTRODUCTION

The presence of heavy metals in the soil, the air, the water has become a global problem, because they are a growing threat for humanity.

Heavy metals are metals that have a density greater than 5 and are known as having a toxic action on concentration exceed certain limits of tolerance: Cd, Cr, Cu, Hg, Ni, Pb, Zn. They have a wide application in industry. [1]

Heavy metals are chemical species that do not degrade, they are distributed to air, water and soil, sometimes changing and oxidation state, or reaching living organisms. Adsorption processes and training complexes in the natural environment are responsible for the fact that the vast majority of heavy metals accumulate in the soil where they quickly recorded the highest concentrations of these contaminants.

Heavy metal toxicity is very high. Their action on human beings is to block biological functions through enzymatic inability to form compounds and sulfhydryl groups of proteins, causing irreversible adverse effects in the body. [2]

Some of these metals, micronutrients and trace elements are absolutely necessary in small amounts in living organisms, but concentrations in excess are toxic. It is important to know the concentrations required in order to avoid negative effects on living organisms (plants and animals) but also on humans.

Soil pollution involves direct or indirect modification of the composition or the state, as a result of human activity.

Each component has its own dynamic environment, different in space and time, contrasting self-cleaning capabilities. Of these, the soil is the environmental component storage. The ground has a stockpile of

appropriation, for long periods of time, in the tens or even hundreds of years ago, elements and inorganic chemicals and has an degrading effect much faster on organic chemicals. For this reason, the results of research of soil can develop the history later, or more distant phenomena occurring in the environment. [3]

In the Netherlands, at a first inventory of 6.000 ancient deposits has found that about 70% of the land is distinguished by a high concentration of heavy metals. These processors are responsible for damage to the metal, tempering salts, waste exhaust air cells and powder constitute secondary contaminants such industries.

### 2. THE TOXICITY OF HEAVY METALS

Harmful action of heavy metals on water and the effects of this action on the fauna, flora and the human origin depend to a great extent the origin of metals, their breakdown and change processes to which they are subject in the ecosystem. Some metals can appear in different chemicals forms in the environment and be absorbed by organisms, causing significant changes to their level

Uptake of living organisms can be described by the following factors:

*a. Availability* includes the quantity of an item or a compound, quantity accessible to a body. This depends on:

- mechanisms of spread on different paths from the source to the issuing body;

- a one-size (very small particles containing heavy metals are carried through the air over a great distance and penetrate the airways or submitted directly to food);

- the diluted concentration of a metal;

**b. Bioabsorption** depends mainly on:

- the concentration of certain types of metals that can be absorbed by the body;
- physiological and ecological properties of the body in question (for example, depends on the relative speed of absorption, which vary from one metal to another, in the lungs, intestines, skin and the speed of transport in the body from the place where the metal was absorbed by the State in which the harmful act occurs).[4]

### 3. MATERIAL AND METHOD

Determinations concerning the concentration of heavy metals in soils are carried out in accordance with the standards in force. The method used is that by flame atomic absorption spectrometry with atomic absorption spectrometer.

**Atomic absorption spectrometry (AAS)** is based on measuring the radiant power adsorbed by a population of free atoms.

Figure 1 shows the overall structure of an atomic absorption spectrometer, which uses a sprayer as a source of flame.

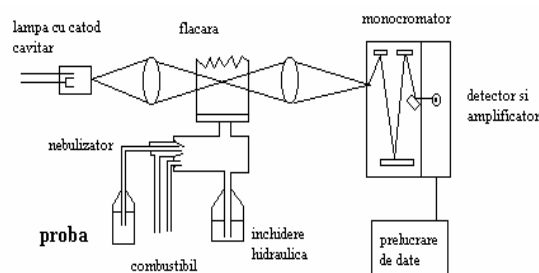


Figure 1. Atomic Absorption Spectrometer

Whereas the average temperature only metallic mercury can provide vapor atoms free samples must be atomized by heating. Means of evaporation and atomisation-conditions which have been imposed in AAS are the flame and electrotermic evaporation.

Due to the temperature of the flame, the solvent evaporates and is decomposed by phase atoms. Also, depending on the temperature of the flame, the atoms can remain on a fundamental level energy or undergoing a process of arousal, in which pass through one or more levels of the excited. Unlike broadcasting, operating with excited atoms, atomic absorption operates with ground state atoms.

The use of a flame as a source of atomisation is characterized by a much lower temperature than a plasma, most atoms remain in the ground state, giving particularly sensitive atomic absorption.

In other words, the lead role in absorbing is the sample atomization. Radiation source, usually a hollow cathode lamp (HCL), emits a narrow spectral line, characteristic for the feature element to be analyzed. Emitted light beam modulated mechanical or electronic, passes through the flame containing atoms of analyte vapors.

Atoms situated on the fundamental energy level, absorb part of the radiation source, which causes a decrease in radiant power transmitted through the flame. By analogy with Spectrophotometric molecular absorption, flame can be considered a "vat of atoms" dynamic, where free atoms are formed continuously. Light signal transmitted through the flame is turned by a photodetector, in an electrical signal which is then amplified. After demodulation, the signal is recorded and converted to a size that is displayed digitally.

Monocromator is the spectral pattern of isolation and positioning on the maximum bit-analytical, emitted by the hollow cathode lamp.

Hollow cathode lamp is selected depending on the item to be measured. This gives the atomic absorption to increased sensitivity and selectivity. Usually, the emission spectrum of the lamp resonance line is selected. It also fixes monocromator spectral interferences that may arise between resonance and background spectral line emitted by the flame.

Atomic absorption sensitivity depends on two factors: the degree of atomization of the sample and absorbing radiation from the hollow cathode lamp, by the atoms in the ground state. Sensitivity is directly proportional to the degree of the sample sprayer, especially in the case of hard tissue using special methods of sample sprayer, one of them being the technique hydrides.

Furthermore, the sensitivity is higher if the absorption line is wider than the emission line. This condition is fulfilled by a hollow cathode lamp, which emits very narrow atomic lines. [5]

### Atomic emission spectrometry with inductively coupled plasma (ICP-AES)

ICP-AES is a modern analytical technique using inductively coupled plasma as excitation source in atomic emission spectrometry.

Atomic emission spectrometry with inductively coupled plasma (ICP-AES) is a method used in many scientific fields.

A plasma source is used to separate the sample into atoms or ions constituents exciting them on a higher energy level. They will return to its original state by the emission of a photon of energy characteristic. This emission is recorded by an optical spectrometer. Radiation intensity is proportional to the concentration of each element in the sample and internal recalculated a set of calibration curves to obtain directly measured concentrations.

Solid sample is first dissolved and mixed with water. The technique allows analysis of liquid samples. Sample solution is converted to aerosol by nebulizer. Larger droplets are separated from those smaller in spray-room. Small droplets (1-10 mm) are transferred through the flow of argon in the "heart" of ICP-AES, argon plasma. Larger droplets (> 90%) are discharged.

**Advantages:** Analyzes multielement sequential/ at the same time, rapid; Small sample size needed; High sensitivity for many items; Low detection limits – 5-6 orders of size; Interelement interference relative weak;

High-precision 0.5 - 5%; Possibilities for the analysis of liquid, solid and gaseous samples.

Monoelement detection limits in water are generally low, ranging between 1-100 ppb for most elements. It is known, however, that these limits of detection may increase several times or even 1-2 orders of magnitude, depending on the array are determined.

**Disadvantages:** Spectral interference; Effects of matrix; The inefficiency of the introduction of the sample; Difficulties in analysing solids without winding up; Detection limits that are too large for some applications; Drift precision and insufficiency for some applications

#### Spectrometric method using 1,5 diphenylcarbazide

Spectrometric method for determination of chromium (VI) in water, apply to the determination of chromium (VI) dissolved in water in the field of concentration between 0.05 mg/L and 3 mg/L. The scope can be expanded by diluting the sample to be analyzed.

#### Principle of the method

After the sample pretreatment in order to stabilize the totality of the values of chromium (VI) and chromium (III), if present, chromium (VI) reacts with 1,5-difenilcarbazida forming a complex of Red-purple chrome-1,5-difenilcarbazona. Absorbance of this complex is measured after 5 min. to 15 min. at a wavelength between 540 nm and 550 nm using water in the reference cell.

Calculate the mass concentration of Cr (VI), expressed in mg/L, using the equation:

$$\rho_{(CrVI)} = \frac{f(A_s - A_b)}{b}$$

or

$$\rho_{(CrVI)} = \frac{f(A_s - A_t - A_b)}{b}$$

(if the patch was made for coloured or murky solutions)

Where:  $A_s$ - sample absorbance

$A_b$ - witness absorbance

$A_t$ - absorbance of the witness

f - dilution factor ( $f = 100\sqrt{V}$ )

b – sensitivity (slope calibration graph)

#### 4. CHROMIUM EFFECTS ON HUMAN HEALTH

Chromium is present in two oxidation states Cr (III) and Cr (VI). Hexavalent chromium is found in various anionic forms:  $\text{HCrO}_4^-$  when  $\text{pH} < 6.5$ ;  $\text{CrO}_4^{2-}$ , when the pH is 6.5;  $\text{Cr}_2\text{O}_7^{2-}$ , at pH values between 2 and 6 at very high concentrations of chromium in soil. Bichromate ion presents a hazard to health, much larger than the chromate ion. Both the ionic species in which the chromium is in oxidation state (VI) are more toxic than chromium species in which has the oxidation state (III).

*Factors affecting retention of hexavalent chromium in soil are:*

- chrome ion is adsorbed by oxides of iron and aluminum in acid and neutral;

- the presence of chloride ion and nitrate ion chromate ion adsorption does not change the soil, while the presence of phosphate and sulfate in the medium leads to inhibition of hexavalent chromium sorption process;

- in the pH range 2-9, not revealed the existence of precipitates of hexavalent chromium

- hexavalent chromium has been shown to be very mobile in soil.

For proper understanding of the evolution of this potentially toxic element is necessary to know the reactions it is involved in soil and aqueous medium. [6]

In biological terms, hexavalent chromium is classified in group one of carcinogenic risks. It crosses the cell membrane by a carrier mechanism that is based on anion exchange phosphate-sulphate. At intracellular level, hexavalent chromium is reduced to the trivalent chromium and produce potentially mutagenic lesions at the level of DNA. [7]

As a result of research carried out in 2007, Dana Mateş and collaborators have come to the conclusion that concentration levels of chromium in the lungs of people exposed are higher compared to concentrations measured in unexposed persons. Occupational respiratory exposure chromium is found in many occupations and different jobs.

In 1980, a team of Japanese researchers report a high concentrations of chromium in lung tissue, at 6 workers at a chromates factory. Patients were diagnosed with lung cancer and environmental content of chromium was 36.7  $\mu\text{g/g}$  wet tissue in the outermost regions of lung and 0,51  $\mu\text{g/g}$  wet tissue in the large bronchi. Unexposed patients had the values of concentration of 0.11 respectively 0,22  $\mu\text{g/g}$  humide. [8]

#### 5. ADSORPTION CHROMIUM USING HEXA-MAGNETITEI-VALENT O WERVIEW

In general, when speaking of affected soil remediation of heavy metal pollution, use one of these methods, [9]:

a. chemical stabilization is a method that actually reduces the solubility of heavy metals by the addition of nontoxic materials in the soil;

b. the replacement portion of soil contaminated with clean soil;

c. making a "wash" in situ, with certain agents; dilution, which consists of a mixture of soil polluted with the unaffected by machinery so as to reduce the concentration of heavy metals;

d. dilution, which is unaffected by mixing soil polluted with using such equipment to reduce the concentration of heavy metals;

e. phytoremediation.

All these methods have certain disadvantages, and we will list a few, namely: ad methods are avoided due to the economic side, the operations involving high costs and heavy metal concentration in soil remains. Also, phytoremediation can be effective but requires a longer period of time in order to be implemented, and the

downside is the problems that arise when it is a question of storage plants resulting from remedial process.

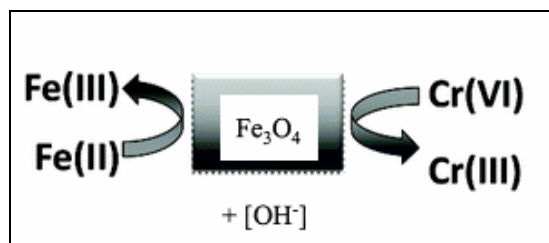
Because the use of magnetite was found to be very effective in recovering one of the most toxic heavy metals, namely, hexavalent chromium in a short time and costs are minimal in the following, we develop this topic. Magnetite is one of the most important iron oxides can be found anywhere in nature. The presence of magnetite in nature is often the result of certain biological processes, but can also have lithogenic origin. Magnetite can be obtained in laboratory from solutions containing ferric and ferrous ions, showing the good characteristics of adsorption on a variety of compounds such as dissolved metals, particulate matter, organic matter and biological, can be used successfully the decontamination of the environment, it also having economic advantage.

Primary interest is the surface adsorption properties of magnetite are present as a prominent iron oxide, therefore, organize the process of adsorption and adsorption safely remove the decontaminated solutions. [10]

Magnetite contains the mono-coordinate groups between 3 and 5 groups OH/nm<sup>2</sup>.

Oxidation of surface groups > Fe — OH is responsible for enhancing the positive surface charge of magnetite to pH values < 7. There is a relationship of proportionality between the amount of magnetite added to the solution and pH. By increasing the amount of magnetite matter, its pH buffering increases dramatically.

Cr<sup>6+</sup> adsorption on the surface of magnetite is based on electrostatic interaction of Cr<sup>6+</sup> and OH<sup>-</sup> but especially at pH above 7, so that it favored the formation of OH<sup>-</sup> groups.



## 6. CONCLUSIONS

In recent years, pollution of the environment with heavy metals has become a major problem, this being due to the chaotic development of large urban agglomerations and industrial sector. To gain a better understanding of the components of the degree of anthropogenic environmental change, complex research is needed, which gathers specialists from different fields but all connected to the same problem, namely environmental protection.

Because, in biological terms, hexavalent chromium is one of the most toxic heavy metals with negative impact

on human health, it is classified in group one of carcinogenic risks by the Environmental Protection Agency in the U.S.A, this aroused the interest of researchers on the metal hard and there are numerous characterization studies but also the recovery of affected environments.

As a result of this study, we can assert that magnetite is one of the materials that can be successfully used in recovery of hexavalent chromium from aqueous solutions with various advantages, of which the most important is the economic but also the fact that the process of adsorption is one fast.

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