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ASPECTS REGARDING THE POLLUTION OF NATURAL RESOURCES WITH HEAVY METALS

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Abstract. The natural resources of water (surface and groundwater) are frequently polluted because of the spreading in aqueous media of the different organic and inorganic pollutants. Among inorganic pollutants often present in water at concentrations over the imposed limits are heavy metals ions (Fe, Mn, Zn, Cu, Cr, Pb and As) with toxic characteristics on aquatic ecosystems and human health. In the paper are presented data regarding to: variation domain for heavy metals ions and other pollutants in some sources of groundwater situated in different counties of Romania (Arad, Bihor, Bacau, Dambovita, Giurgiu, etc.); identification of the pretreatment/treatment possibilities according with the specific pollution context. The main physicochemical processes included in the treatment flows are: chemical oxidation, precipitation, coagulation-flocculation, settling, filtration and adsorption on different materials. The performed studies were finalised with the selection of the proper treatment schemes for advanced removal of heavy metals from natural sources in accordance with: physico-chemical characteristics of the water sources, respectively the specific pollution context; type and concentration of metallic compounds; imposed limits for identified pollutants.

Keywords: underground water, heavy metals ions, coagulation-flocculation, adsorption.

AIMS AND BACKGROUND

The metallic ions, in a simple ionic form (metallic cations) or in a complex form (oxanions, humic matter and, in some cases, complex cyanides), which overtake the stipulated limits referring to water supplies quality of drinking treatment plants, are placed into high frequency appearance category of pollutants.

Referring to above, it could be mentioned the following ions: iron, manganese, copper, cadmium, aluminum, chromium, arsenic, etc. Their presence could be from natural reasons (solubilisation of rocks components because of groundwater contact) or because of negative impact of industrial activity to environmental factors (discharging of low treated waste water, inadequate disposals of wastes, etc.).

The highly increase of the pollution level of drinking waters resources, the diversity of pollutants and concentrations levels, demand to accelerate the pre-

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vention activities, the systematic control of water quality and local or/centralised treatment in order to assure the compliance with the enforced legislation.

The process/processes selection, in order to achieve an advanced level for metal ions removal, is done taking into account the following aspects:

- the type and characteristics of the source, the pollution context, respectively;
- the concentration and type of metallic compounds;
- the imposed limits for this pollutant category.

The treatment processes, which are frequently used for removal of metallic ions from natural resources, are based on: chemical oxidation[1,2], precipitation[3], coagulation-flocculation-settling-filtration[4], adsorption[5]/ion exchange and membrane processes[6].

EXPERIMENTAL

The experimental studies were focused, in the first stage, on emphasising the variation ranges for metallic ions concentrations, which were over the stipulated limits, for the following types of sources:

a. Surface water used/proposed water supply for drinking water treatment plant of some cities and small towns:

- Aries river – Turda,
- Arges river – Bucharest and Pitesti,
- Danube – the Black sea channel – Constanta,
- Ialomita river – Targoviste,
- Mures river – Ludus,
- Prut river – Raducaneni, Iasi county,
- Sacovat river (Tungujei barrier lake) – Tibanesti, Iasi county;

b. Groundwater (fountains, wells) from different localities of Arad, Bihor, Bacau, Dambovita, Giurgiu, Prahova, Botosani, Vaslui, Ilfov and Olt counties;

c. Mineral springs from Dorna Candrenilor and Sarul Dornei areas.

Based on systematic experiments, there were elaborated, for the identified pollution cases, optimal flow sequences and operating conditions, using adequate processes (oxidation with chemical reagents, precipitation, coagulation-flocculation, settling, filtration, adsorption on different carrier) for advanced removal of the heavy metals ions from polluted natural sources.

The analytical determinations of heavy metals were performed by specific analytical methods (atomic absorption, VIS spectrometry).

RESULTS AND DISCUSSION

There were analysed, in order to identify pollutants from heavy metals class, 7 surface water samples from different areas, 15 sources of groundwater and mineral groundwater, respectively.

According to pollution context, there are following cases:

a. Surface waters – polluted with heavy metals having concentration levels over the stipulated limits by NTPA 013/2002 (characteristics of surface waters for drinking water treatment plants):

- $Fe_{total} \leq 3.3$ mg/l (admitted 0.3 mg/l);
- $Mn \leq 1.7$ mg/l (admitted 0.1 mg/l);
- $Cu^{2+} \leq 0.36$ mg/l (admitted 0.05 mg/l);
- $Pb \leq 0.14$ mg/l (admitted 0.05 mg/l).

The frequency of appearance (%) is as follows:

$$Fe_{total} > Mn > Cu \equiv Cd \equiv Pb$$
$$100\% \quad 86\% \quad 14\% \quad 14\% \quad 14\%$$

Generally, the metals are presented into the disperse phase (turbidity) as inorganic precipitates or as humic complex.

In case of the Aries river, which presented the highest pollution level because of mining activity from the neighbourhood, the heavy metals (Cu, Zn and Mn) were in soluble phase as complex cyanides.

b. Groundwater (soft and mineral water) polluted with heavy metals ions over the stipulated limits:

- $Fe_{total} \leq 4.1$ mg/l (admitted 0.1 mg/l);
- $Mn \leq 1.4$ mg/l (admitted 0.05 mg/l);
- $As_{total} \leq 2$ mg/l (mineral waters admitted 0.05 mg/l);
- $Cr^{6+} = 0.12$ mg/l (admitted 0.05 mg/l);
- $Cd^{2+} = 0.008$ mg/l (admitted 0.005 mg/l);
- $Cu^{2+} \leq 0.2$ mg/l (admitted 0.05 mg/l);
- $Pb \leq 0.08$ mg/l (admitted 0.05 mg/l).

The frequency of appearance referring to the number of studied sources is as follows:

$$Fe \cong Mn\ (53\%);\ Cu \cong Cd \cong As\ (7\%)$$

Most of the analysed underground sources overtake the stipulated limits (NTPA 013/2002) for global organic load (CCOMn), turbidity, ammonia, and casually sulphides, nitrogen and phosphate. The increase of heavy metals concentrations, over the stipulated limits could affect the survival, growth, reproducibly, ability for competition of existent aquatic species and, respectively, the human health.

There are distinguished concentrations values of various heavy metals ions having sublethal effect, which affect the aquatic organisms and generally fauna and plants.

There is a large range of values, for aquatic species, according to pH, temperature, dissolved oxygen, etc. ($As_{organic} \leq 1.3$ mg/l; $Cr^{6+} \leq 2.5$ mg/l; $Cu^{2+} \leq 0.0325$ mg/l; $Cd^{2+} \leq 0.031$ mg/l).

The flow treatment sequences, which assure the advanced removal of heavy metals from natural resources, are based on different treatment processes according to oxidation state, metallic ions concentrations and specific pollution context.

The treatment/pretreatment flows, recommended for different pollution cases and concentrations levels above presented, are as follows:

• *groundwater with Fe^{2+}, Fe^{3+} and sulphides content* to lower concentrations levels (Fe^{2+}; $S^{2-} \leq 0.3$ mg/l):

– aeration – sand filtration (filtration rate = 10 m/h);

• *groundwater with Fe^{2+}, Fe^{3+}, Mn content*:

– adsorption on resins – Purolite MZ 10 type (filtration rate = 6 m/h),

– oxidation (O_3/ClO_2) – sand filtration ($O_3 \leq 1$ mg/l; filtration rate = 8-10 m/h);

• *groundwater with Pb^{2+}, Cd^{2+}, Cu^{2+}*:

– coagulation – flocculation – sand filtration (doses $FeCl_3 \leq 25$ mg/l; filtration rate = 8 m/h),

– adsorption on oxidised charcoal (contact time = ≤ 30 min.);

• *groundwater As content (III, V)*:

– oxidation (O_3/ClO_2) – coagulation-flocculation ($FeCl_3$) – sand filtration (doses $FeCl_3 \leq 25$ mg/l; filtration rate = 8 m/h);

• *mineral waters with As (III, V), $Fe^{2+/3+}$ content*:

– degasification (CO_2 removal): As III oxidation (O_3) – settling – adsorption on alumina carrier ($O_3 \leq 1$ mg/l);

• *surface water with $Fe^{2+/3+}$ content, humic acids* (turbidity):

– coagulation – flocculation ($FeCl_3$ or $Al_2(SO_4)_3$) – settling – sand filtration (coagulant doses ≤ 50 mg/l; settling time ≤ 2 h; filtration rate = 8-10 m/h);

• *surface waters with Cu, Zn, Cd, Mn content* as cyanide complex:

– oxidation (O_3)/CN^- decomplexing – coagulation – flocculation ($FeCl_3$ or $Al_2(SO_4)_3$) – settling – sand filtration ($O_3 \leq 2$ mg/l; coagulant doses ≤ 50 mg/l; settling time ≤ 2 h; filtration rate = 8 m/h).

The proposed treatment/pretreatment flow sheets, for metallic ions removal from groundwater and surface water, could be individual applications or flow sequences, taking into account the demand of total pollutant removal, which are concentrations levels over the stipulated limits by the Romanian legislation.

CONCLUSIONS

Many natural water sources, groundwater (including also some mineral springs) and surface water are improper for human consuming because of heavy metal ions presence (Fe, Mn, Cu, Cd, Pb, Cr and As) over the admitted limits by the Romanian legislation.

In order to assure the adequate quality of drinking water it is necessary to follow the next stages:

- analytical investigation of natural resources in order to establish the concentrations levels of the pollutants, which are over the admitted limits, and the distinct pollution matrix;
- implementation of some advanced removal processes of heavy metallic ions according to specific pollution context and their integration into general flow sheet, in order to assure the limits for all stipulated indicators.

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