

BIOSORPTION OF HEAVY METALS FROM POLLUTED WATERS BY USING THE WASTE AS A BIOMASS FROM EXTRACTION OF HERBA HYPERICUM

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Abstract

In the latest years, there is an increase of an interest for cleaning industrial polluted waters containing heavy metals, which threatens the human health and pollutes the environment as well. A high amount of toxic metals in industrial polluted waters are shed in the environment in several forms. The metallurgic processes are producing a high amount of solid and liquid waste that are dumped into the water and in this way creates significant harmful effects for the environment and human health. It is known that heavy metals such as manganese, iron, nickel, chrome, arsenic, cadmium, cobalt, uranium, copper, etc. are very toxic elements, therefore, by dumping them into waters they will pollute the environment as well as living beings directly through the food chain. The critical toxicity of heavy metals has caused several disasters in the environment in the human history, so there is a fear of a catastrophic pollution nowadays, therefore new methods for treatment are required which do not have side effects. Biosorption is a special method of extraction and elimination of heavy metals from polluted waters and the same is done with natural wastes which are relatively cheap and easily approachable (biomass), these are food waste and the phyto-pharmaceutical waste. Vegetative waste from extraction of Herba Hypericum can be used as a biomass in order to eliminate completely or to reduce extremely toxic metals from the polluted water, especially chrome, cobalt and nickel that are considered as highly toxic metals which are very difficult to extract compared with other methods. This kind of treatment of metallic polarities is of a great importance for developing countries, in economic aspects and the aspect of accomplishing strict criteria of green technology.

Keywords: Adsorption, biosorption, isotherm, biomass.

1. Introduction

The quality of water is determined by the physical, chemical, biological and radiologic factors. Water is a great solvent of a big number of chemical components, so the clean waters and the polluted ones as well, are rich of solvable components.

Classification of the quality of water is done according to physical features (colour, aroma, taste, suspended substances, dry residues), chemical features (dissolved oxygen, nitrogen, phosphorus, sulphur and other chemical components, and also toxic heavy metals) and biochemical, biological and microbiologic features (general number of bacteria, bacteria coliform).

Determining the quality of water is not possible to be done by being based only on the values of one or some parameters, it should be based on a general analysis of all the factors that affect the quality of water.

The source of pollution of water can have a geogene and anthropogenic origin. Processes of erosion come as first natural (geogenic) sources of water pollution. Erosion, which is a result of the wind or water, damages the pedosphere, this pollutes exclusively surface waters by leaving in them a big amount of minerals and organic substances that are formed with the rinsing of the pedosphere. Sometimes, these may be very toxic, and on the other side when we speak of waters of heavy rain, the water becomes feculent in a certain amount. As a result of human activity (anthropogenic pollution), polluted waters can be divided into: public, industrial, agricultural and other.

Sewage that come from industries are often polluted with different toxic substances. In some precipitation streams that come from different industries, the concentration of these substances is over the maximum allowed margins, therefore the sewages must be treated appropriately in order to reduce the concentration of toxic substances below the levels of allowed margins. The industry is one of the biggest contaminants of the water, as 50% of the sewage is derived from industrial segment, where often without cleaning, they are released on surface waters directly or indirectly. Depending on the industrial origin, these waters may be grouped in sewages from mines, chemical metallurgy, petrochemical, metallurgic, nutritive, textile, paper, rubber, leather and other [1-7].

2. Experimental part

Methods of cleaning polluted waters

The primary cleaning is the first level, and often sufficient, of the treatment of sewages, especially when we speak about elimination of bigger particles or small solid ones that have mineral or organic origin, which float along the water surface or they precipitate, depending on the density. With the primary cleaning (mechanic, physical, chemical) of polluted water, not all organic components can be eliminated, especially those that are in a solute form or dispersed in colloidal form.

Hence, the process continues with the secondary cleaning, which in essence is a biochemical process. It is developed under the stimulus of metabolic activity of microorganisms that result in a decomposition of the organic substance. In the presence of oxygen, bacteria oxidizes the organic substance into carbon dioxide and water, whereas the insoluble component binds in a form of braziers, in this way the only requirements to clean water contaminated with organic substance is the presence of an adequate number of microorganisms which are fed with the organic component as well as the sufficient amount of oxygen. The tertiary methods used to clean waters are: adsorption, electrolysis, Ion exchange, filtration, ultrafiltration and other methods.

Adsorption – Different substances that have high capacity of adsorption are used, such as the activated carbon. Organic substances that are not eliminated with the primary and secondary cleaning are being eliminated by passing the water through a layer of the granular activated carbon. When the active carbon is replete (full), it may be regenerated and reused.

Electrolysis – The essence of this method consists to the passing of electric power through contaminated water, where electrolyte ions are directed into anode or cathode, and the same are neutralized there. If iron electrodes are used, there are created hydrate oxides of the iron which act as coagulator.

Ion exchange – Is used to clean waters, that is used for special aims and require that water should have e special chemical structure. In the laboratory, the resulted water is used as a substitution for the distilled water, in industry this procedure is used in order to minimize water hardness, to eliminate some specific ions e.g. Heavy metals. Natural and synthetic materials are used as ion exchanger.

As ion exchanger, are used natural and synthetic substances, which have an ability to exchange their ions with the present ions in water. Natural ion exchangers such as aminosilicate, have a low capacity and are non-persistent in acid and basic environment. Synthetic substances, on the side, have a high capacity (polymeric organic) and are more persistent relating to the chemical reactions, therefore they are mainly used in practice.

Filtration – this process is performed in designed filters – for a faster filtration made of several layers of sand with different size of granules, usually with a diameter from 0.5-1.0 mm and also may be used coal (anthracite) as a special layer, or mixed with sand.

Absorption isotherms and equilibrium

The system solid-liquid substance, positive “adsorption” is based on elimination of adsorbate from the water dissolution and its concentration in a particular adsorbent. The process is developed until there will be created a dynamic equilibrium between the left amount of adsorbate in the solution and the adsorbed amount in adsorbent. Dynamic equilibrium means spreading the adsorbate in mass unit of the adsorbent as a function of the left sum at liquid phase, in equilibrium conditions. The mathematic term of this kind represents the adsorption equilibrium. There are several experimental isotherms of the equilibrium, these are used in order to define the capacity of adsorption, as well as choosing the most suitable adsorbent and preliminary definition of adsorbent amount. Adsorption capacity is the necessary information in modeling analysis and designing the absorbing systems. Adsorbing isotherms are also used to make dynamic researches for a given system.

Four types of adsorption isotherms that are most frequently used in literature are the following: Langmuir, Freundlich, combined Langmuir-Freundlich and isotherm Ridlich-Paterson

Biosorbents are natural materials that have a potential ability to eliminate heavy metals from underground and surface waters. Plants, algae, fungus are only a part of biosorbents that are in a condition to extract heavy metals from liquid solutions by adsorption. In order the efficiency of adsorption of the biosorbents to be raised, in some cases it is necessary to rinse or modificate the used biomass by using different types of chemical reactants such as tartaric acid or NaOH. Biosorbents have a tendency to form metallic compounds with ions of heavy metals, because of the presence of their functional groups as follow: carboxylic, hydroxyl, amino, phosphate, sulfate, phenol, amide, etc. After their use, biosorbents are regenerated by using basic answer, acid or other, therefore they can be used in several cycles and finally eliminated without any risk of contamination.

Precipitation from extraction of Herba hyperici peforatum

After the extraction process of the pharmaceutical herbal substance Herba hyperici, the solid precipitation which is left may be used as a biosorbent for extraction of heavy metals from polluted waters. The adsorbing affinity of this kind of material makes the biosorption process to be performed very easily for the several heavy metals.

The precipitation left after the extraction in its structure has one more ration of alcoholic solution which is used for extraction even if one part of the alcohol evaporates in a regular temperature, therefore it is necessary to do rinsing and cleaning with distilled water in order to extract the ethanol which is left. Drying is realized at temperature of 105 °C until a minimum of the moisture. The same undergoes grinding and homogenization in favor of enlarging the contact surface with adsorbent. The biosorbent derived after the biosorption process may be used again by regenerating the same, this means cleaning, washing, drying etc.

The amount of this type of precipitations is high and requires making a deposition or combustion, therefore this represents a good base which is put in the group of biosorbents for extraction of heavy metals from polluted water, as this biosorbent has a specific feature of a high absorbing capacity because of its quantitative structure.

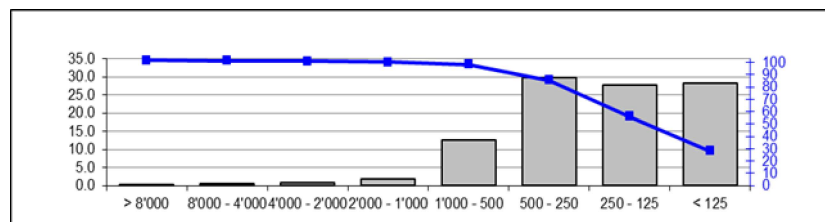
It is important that during preparation of this absorbent in the cleaning process, the washing with distilled water to be performed with a higher intensity in order to eliminate completely the waste of remained substance which is drawn during extraction and usually has dark red colour, as Hypericine, which inhibits during the process of absorption measurement because of its colour. But by rinsing it adequately, all the color is eliminated.



Figure 1. The waste as a Biomass from Extraction of Herba Hypericum

Table 1. Granulometric analysis of the precipitation from extraction of Herba Hypericum prepared as biosorbent

The size of the strainer	Net weight after analysis	Spreading by the size of granules
8	0.16	0.32
4	0.23	0.45
2	0.35	0.69
1	0.98	1.93
0.5	6.37	12.57
0.25	15.07	29.75
0.125	14.02	27.67
Ground	14.34	28.31



From the granulometric analysis we can state that the size of granules at biosorbent moves in the borders between 1.0 mm until a satisfying minuteness smaller than 0.125 mm. Seeing from the technical aspect, this is a size of granules which enables the process of adsorption to be performed without any obstacles with a very high active surface of granules with absorption, and this result with a faster process of absorption.

Table 2. Chemical structure of the precipitation from extraction

Chemical structure of the precipitation from extraction	
Cellulose	33.4
Semicelluloze	22.01
Lignin	21.12
Dust	14.26
Moist	9.21
Extractive substance	1.96

Table 3. Chemical structure of dust

Substances	
Minerals	12.493
Phosphor	0.0118
Calcium	0.3269
Magnesium	0.0236
Zinc	1.2364
Manganese	0.0686
Mat volatile	0.0365
Other	0.0631

Biosorption of heavy metals from water solutions

To define biosorption features as the affinity of adsorption and the capacity of materials which are used as biosorbent and intend extraction of heavy metals (Co (II), Ni (II) and Cr (VI) from polluted waters, as well as monitoring the dynamics of the studied process, there are performed many laboratory experiments. These experiments are made on glass reactors with a working volume of 2 dm³, supplied with a mixture of constant values of rotation speed of the mixer 450 rpm, by following the equilibrium and kinetics of the studying process. Analyses are made in an environment pH 5.5.



Figure 2. Practical experiment presentation

Solutions of pertinent metals are used to prepare standard solutions, $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ and $\text{K}_2\text{Cr}_2\text{O}_7$ which are used as standard during measurement by using a photometer.

Table 4. / Diagram 1. Alteration of ion concentration at Co, depending on the time of biosorption for different amount of concentration CKP (g/dm^3) $0.2 \text{ g}/\text{dm}^3$, $0.35 \text{ g}/\text{dm}^3$, and $0.45 \text{ g}/\text{dm}^3$

T (min)	$C_{\text{CKP}}(\text{gr}/\text{dm}^3)$	$C_{\text{Ni}}(\text{gr}/\text{dm}^3)$	$C_{\text{Cr}}(\text{gr}/\text{dm}^3)$
0	0.2	0.35	0.45
20	0.18	0.32	0.41
30	0.16	0.3	0.4
60	0.14	0.27	0.36
90	0.11	0.25	0.3
120	0.1	0.2	0.22
140	0.09	0.18	0.19
160	0.07	0.15	0.13
180	0.07	0.1	0.11

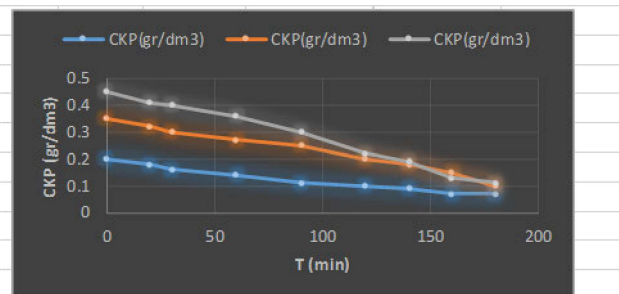


Table 5. / Diagram 2. Alteration of ion concentration at Ni, depending on the time of biosorption for different amount of concentration CKP (g/dm^3) $0.2 \text{ g}/\text{dm}^3$, $0.35 \text{ g}/\text{dm}^3$, and $0.45 \text{ g}/\text{dm}^3$

T (min)	$C_{\text{CKP}}(\text{gr}/\text{dm}^3)$	$C_{\text{Ni}}(\text{gr}/\text{dm}^3)$	$C_{\text{Cr}}(\text{gr}/\text{dm}^3)$
0	0.2	0.35	0.45
20	0.16	0.3	0.41
30	0.13	0.29	0.4
60	0.11	0.25	0.36
90	0.1	0.21	0.3
120	0.08	0.15	0.25
140	0.07	0.12	0.21
160	0.06	0.1	0.16
180	0.05	0.1	0.12

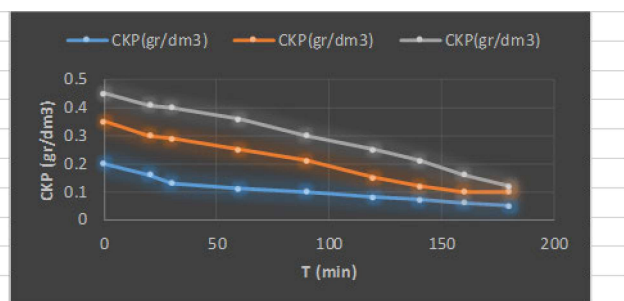
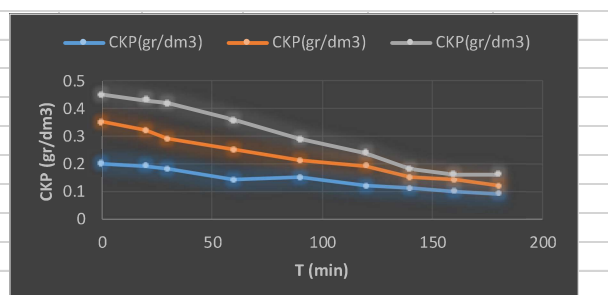


Table 6. / Diagram 3. Alteration of ion concentration at Cr, depending on the time of biosorption for different amount of concentration CKP (g/dm^3) $0.2 \text{ g}/\text{dm}^3$, $0.35 \text{ g}/\text{dm}^3$, and $0.45 \text{ g}/\text{dm}^3$

T (min)	$C_{\text{CKP}}(\text{gr}/\text{dm}^3)$	$C_{\text{Ni}}(\text{gr}/\text{dm}^3)$	$C_{\text{Cr}}(\text{gr}/\text{dm}^3)$
0	0.2	0.35	0.45
20	0.19	0.32	0.43
30	0.18	0.29	0.42
60	0.14	0.25	0.36
90	0.15	0.21	0.29
120	0.12	0.19	0.24
140	0.11	0.15	0.18
160	0.1	0.14	0.16
180	0.09	0.12	0.16



3. Conclusions

From the analysis we can see that for a short time in this case 180 min for a different amount of biosorbent concentration, different results of biosorption are reached, being more specific there was a decrease of the level of concentrations of metals in water solutions.

According to results from the above diagrams, the process of biosorption can be divided into three stages:

1 – First stage (5-15 min) refers to the extraction of generated aggregates of the cellular micellar mass and its spreading into the liquid stage.

2 – The second stage defines a sharp decrease of ion concentration Co, Ni and Cr in the liquid stage, resulting in an increase of biosorption level in the system.

3 –Third stage defines the equilibrium put in the research system.

Based on of results reached, we can conclude that: the ideal amount of biomass is 5 g/dm³ for all metals Co, Ni and Cr.

- Optimal parameters of biosorption are pH 4, mixing speed 160 rpm in temperature 20 °C and the maximum time of biosorption 180 min.
- Experimental optimal results for biosorption of Ni ion, are reached by the initial concentration of Ni ions, 0.20g/dm³ and adsorption time 120 min, as for Co ions, the initial concentration of Co ions 0.45 g/dm³ and an adsorption time 180 min.
- Experimental results show that for ions Cr⁶⁺ this type of biosorbent is very good but needs to be seen still, therefore the prepared biomass must undergo a modification process so the biosorption coefficient can be higher and also eliminating polluted waters with Cr⁶⁺ to be more effective. Better results are reached with the lower concentration of ions at Cr 0.2 g/dm³.
- In general, we can conclude that the biomass which results as a by-product from the pharmaceutical industry may be used as a biofilter for the extraction of heavy metals from polluted water.

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