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Original scientific paper

REMOVAL OF HEAVY METALS NI AND CD FROM POLLUTED WATERS USING ORANGE PEEL AS A BIOSORBENT

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Abstract

Water resources are decreasing day by day, not because of nature but because of the human factor. Every year, large amounts of toxic metals are discharged from the metallurgical and chemical industries into the environment in various forms. As a result of metallurgical and chemical processes, large amounts of solid waste are produced in various forms, whether solid or liquid, which are discharged into water, polluting the environment and also endangering human health. Mainly, heavy metals such as Mn, Cr, Fe, Ni, Cd, Co, U, and Cu are very toxic elements, and their discharge into water has a very high impact on environmental pollution and human health directly through the food chain. As a result of the toxicity of these toxic metals, today there is a fear of catastrophic pollution, therefore, today scientists are increasingly looking for new methods that do not have side effects. Biosorption is a very advanced method for removing heavy metals using various wastes that show a high affinity for metal ions that are present in polluted waters. Orange peel has a high absorption capacity, where very good results are achieved for removing heavy metals and cleaning polluted waters, and is an advanced biosorbent both from an economic and ecological point of view.

Keywords: biosorption, Orange peel, toxic metals

1. Introduction

The presence of heavy metals in contaminated waters can have biogenic and anthropogenic origins. Industrial production is the main polluter with heavy anthropogenic metals, since many of these metals are toxic even at very low concentrations because they have the potential to bioacummulate in the food chain. Heavy metals released in the aquatic ecosystem are mainly related to waste and eventually accumulate in sediment. (Mahi Latifi, Jeton Kuqi, Ejup Latifi, Kiril Lisichkov, Mirko Marinkovski, Stefan Assemblyziev 2018) Unlike natural resources, metals produced by human activity appear in unusual physical and chemical forms, against which the body has not yet created a mechanism for protection. The main criterion of damage (toxicity), is the functioning of body organ cells in the presence of a certain amount of metals (Neverre, N., Dumas, P. 2015). Water cleaning is done in many ways: By primary cleaning there are removed suspended solid granules of mineral or organic origin that float over the surface of the water, and the same sink due to greater density. Secondary cleaning, which represents a biochemical process performed by the metabolic activity of microorganisms, and ends with the destruction of organic substances. In the presence of oxygen, the bacteria oxidize organic substances into carbon dioxide, and insoluble components are divided into floccules. Tertiary cleaning is mainly done for industrial waters and is one of the most expensive cleaning, which includes adsorption, electrolysis, ionic exchange, and filtration. (Biswas, A. 2008). Conventional methods, used for removing heavy metals from the contaminated waters, are based on precipitation (oxidation/precipitation and concentration/precipitate) are not always sufficient for accomplishing requirements for water, as with perception can only be removed

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the amount of metals that is soluble in water, therefore other methods are used for further cleaning (Shiklomanov, I. 2000), Adsorption has many advantages comparing to other water cleaning methods because the process is cheaper, more simple, and it is done superior removal of heavy metal ions. Adsorption can be a physical and chemical. Sources of water pollution are classified as geogenous and anthropogenic. Geogenic pollution mainly occurs during erosive processes from water or winds, these are classified as pedosphere pollution, which brings with it large amounts of organic substances by polluting superficial waters, and the same may be highly toxic. Waters polluted by the human factor originate from municipal, industrial, and agricultural sources (Mahi Latifi 2015), The main water polluter is the industry, about 50% of the polluted waters is caused by various industries that, without cleaning them, they pour the same on the land surfaces, which, after rain they go into surface and underground waters. The largest polluters are those of metallurgy, mining, paper processing industry, tires, and leather (Brown, MJ, Lester, Jn 1982). Based on the level of pollution, the waters are classified into five types: Clean, which requires only a small treatment, as they contain only small amounts of impurities from food products that can only be treated by disinfection, and the same can then be used as drinking water. In the second group, there are the least polluted waters, which may be treated by coagulation, filtration, disinfection, or other methods, so that they can then be used in the food industry, but can also be used for drinking. The third group is the waters used for watering of land, which are also treated very easily and the same can be used in industry where high-water purity is not required, such as for cooling in various processes. The fourth group includes highly polluted waters that cannot be used for drinking as there is a high amount of the presence of oxygen, or on the contrary, there could be a total oxygen deficiency, which creates the chances to grow algae. These waters contain solutions of organic compounds, which contain toxic substances. In the fifth group, there are highly polluted waters where there is a total deficiency of oxygen with an extraordinary toxicity, these waters should be treated with special care with various methods. These waters cannot be used for drinks at all, nor in any technological process. (Shumate, E.S., Strandberg, W.G. 1985). Regardless the type and quantity of pollution, the last alarm has been raised in terms of water resources, where every day, more and more we have a flow of polluted waters into the lakes and seas, the same increase their risk for the humanity as well as living organisms in those environments, the same are transmitted in a chain in the human body (Mukhopadhyay, M., No-ronha, S.B., Suraishkumar, G.K. 2008). It is an unwritten method that brings us to a finding that the measures that should be taken for the quality of the surface water begin with the most rational use of them, and on the other hand, also the crime of running water infrastructure, as well as their recycling after using the same in the industry by cleaning them. Regardless of where the source of pollution is, it is very important the treat of polluted industrial and municipal waters so that those waters to be turned into clean waters that will be used for drinking, or in the worst case, to be used in the food industry or similar.(Veglio, F., Beolchini, F. 1997),

2. Body of Manuscript

Cleaning contaminated water is realized in three stages. In the initial phase, there is the removal of mechanical impurities, whether in the form of precipitation or mechanical removal of impurities, which automatically gives the opportunity to increase the active surface between the polluted water and the reagents used for cleaning. In the second phase it water cleaning is performed from fine particles that are present in the polluted water, and these are suspended in the water. This is reached by precipitation due to the various densities of contaminated water, and mechanical conductors in the form of fine particles. The third phase represents the application of adequate methods of cleaning. By the end of the last century, a priority has always been given to the methods of absorption of impurities and heavy metals by using different

adsorbents, starting from cox to the use of zeolite, but the process was developed with great difficulty, first because of the high costs of the process, and low efficiency of adsorption for various heavy metals. The greatest difficulties particularly have to do with the hexavalent chromium as well as uranium, which on one side are very toxic, and on the other side, the very small amount present in the polluted waters is deadly and has a high risk. Cadmium and nickel are also considered toxic metals, which in most cases are present in polluted waters that are poured into water by various industries such as metallurgical and mining industries, as well a paper and rubber industries. Nowadays, the classic methods used which are very expensive, but not quite efficient should be replaced with advanced methods, first by absorption by using different absorbent that are much cheaper and have high adsorbing ability, and on the other side, they are highly favoured from the ecological point of view, and the multiple use of the same biosorbents by cleaning it and putting it again in the cleaning process. Biosorption is the ability of materials used for cleaning to do absorption of toxic metal ions. This is a very complex chemical process that is realized in various forms. Many types of biosorbents are tried today, starting from different types of biomasses, different types of mosses, or even different microorganisms that are fed with various impurities having a very short lifetime. In this case, the orange peel has a high adsorption capacity specifically for Ni and Cd ions. Before the biosorption process, the orange peel is dried and then ground at a certain degree to create the highest active surface between the adsorbent and the polluted water. It is made granulometric analysis of orange peel, which is shown in Table 1 and Figure 1. In a 1000 ml laboratory container, there were prepared Ni (($Cd(NO_3)_2$)and Cd ($Cd(NO_3)_2$ salts with different concentrations of Ckp biosorbent (0.2 gr/dm3), Ckp (0.4 gr/dm3) and Ckp (0.5 gr/dm3) to see the adsorption ability for concentrations of ions of Ni and Cd. In the laboratory container is placed a mixture of about 180 rot/min, and in each laboratory, container is added by 2.5 grams of ground orange peel. For the solvents of the relevant metal salts, there was an attempt to regulate a pH between 6.5-7.0, and in the present case is measured pH 6.9, it was not necessary to regulate the same to be regulated, but normal water. PH value of the environment is of great importance, as for low or high values of pH the biosorption process is hindered, and for low values, protonization of the solution occurs, while for high values, there are created. Six analyses were conducted in total, which means three analyses of Ni ions and three analyses of Cd)ions, with different concentrations of related metal salts. The biosorption process lasts 160 min. For different times of biosorption, different samples are taken to find the number of ions at Ni and Cd that have remained in solution. The 10 samples taken are put in closed chemical containers, and the same are measured. Measures are done in a laboratory that is equipped with probes, which for a very short time of few seconds may detect the number of ions in the solution. For each metal it is used special probe for ions of certain metals. The re -territories are shown in Table 2,3 Figure 2,3.

Table and Figures

Table 1: Granulometric analysis of orange peel

Size of strainer	Measuring vessel gr	Vessel + raw material gr	Netto gr
8.00 mm	450.76	451.86	1.1
4.00 mm	430.20	431.40	1.2
2.00 mm	400.36	404.37	4.1
1.00 mm	361.87	368.67	6.8
0.50 mm	322.56	332.26	9.7
0.25 mm	289.54	302.34	12.8
0.125 mm	280.18	290.68	10.5
Sludge	400.68	405.08	4.4

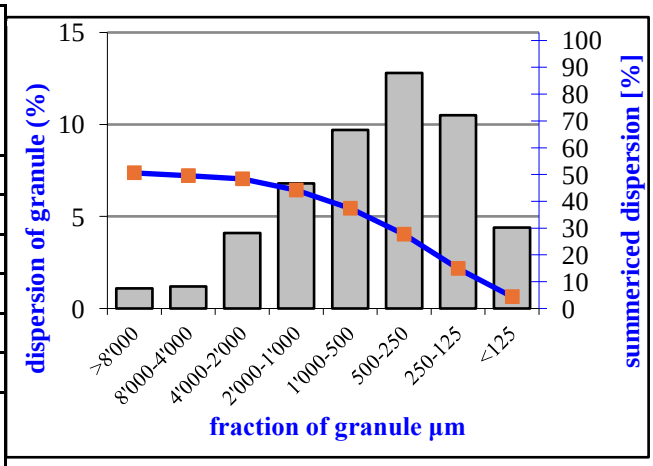

Figure 1: Fraction of granule orange peel

Table 2 Alteration of ion concentration at Ni depending on the time of biosorption for different amount of concentration
Ckp(0.2 gr/dm3) Ckp(0.4 gr/dm3) Ckp(0.5 gr/dm3)

T(min)	Ckp(0.2 gr/dm3)	Ckp(0.4 gr/dm3)	Ckp(0.5 gr/dm3)
0	0.2	0.4	0.5
20	0.16	0.34	0.44
40	0.12	0.31	0.39
60	0.09	0.29	0.33
90	0.08	0.25	0.26
120	0.06	0.19	0.21
160	0.03	0.08	0.06

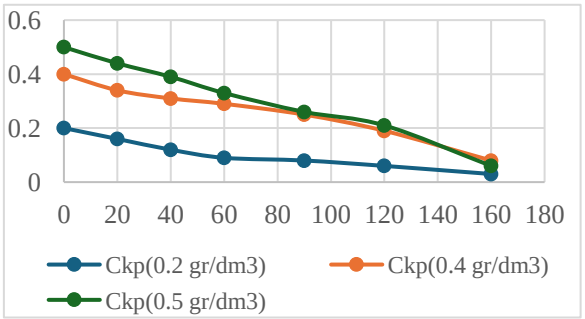

Figure 2 Outline of biosorption Ni

Table 3 Alteration of ion concentration at Cd depending on the time of biosorption for different amounts of concentration Ckp (0.2 gr/dm3) Ckp(0.4 gr/dm3) Ckp(0.5 gr/dm3)

T(min)	Ckp(0.2 gr/dm3)	Ckp(0.4 gr/dm3)	Ckp(0.5 gr/dm3)
0	0.2	0.4	0.5
20	0.16	0.34	0.43
40	0.12	0.28	0.38
60	0.08	0.22	0.32
90	0.05	0.14	0.19
120	0.03	0.06	0.12
160	0.01	0.02	0.03

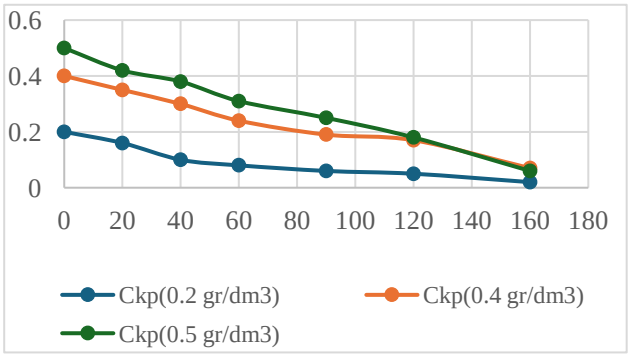

Figure 3: Outline of biosorbtion Cd ions

Conclusion

Based on the results, we can conclude that the use of the orange peel as a biosorbent shows a very high affinity of the biosorbent to the ions of Ni and Cd, which causes almost complete removal of ions of toxic metals. Very satisfactory results have been reached for both metals; this can be seen in Tables 2 and 3. We can conclude that the amount of used biosorbent, 2.5 grams, is sufficient for the conduction of the biosorption process, and it is noticed that the process is much more dynamic in the first 60 minutes, which was expected because the adsorbent at the beginning is cleaner, in the second phase there is a slower adsorption, but the biosorbing does not have equilibrium. It may be preferable to try the same biosorbent to eliminate other toxic metals. Cleaning the waters with the orange peel is very economical, ecological, and practical, because we clean the impurities with the waste, namely, removing toxic ions from the waters.

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