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BIOSORPTION OF HEAVY METALS FROM THE MULTI-COMPONENT SYSTEMS OF THE GALVANIC INDUSTRY USING BREWER'S GRAIN AS ADSORBENTS

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Abstract:-
Wastewaters from the galvanization process contain high concentrations of heavy metals representing a great danger to human health as well as to the environment. Heavy metals in the galvanization process are used in the coating process, whereby the coatings of certain metals are formed. The treatment of wastewaters generated by the galvanization process can be conducted by a number of methods, however, today more research is being done on processes which are efficient, economical and cost-effective, but environmentally acceptable. One of those techniques is adsorption. The adsorption process of Cd^{2+}, Ni^{2+} and Cr^{2+} ions from galvanization water using brewer's grain as the adsorbent, at different pH values and adsorbent granulation of 0.5 mm is analyzed in this paper. The percentage of moisture and ash was determined, and the FTIR analysis was performed confirming the presence of certain functional groups. Based on the obtained values, it has been shown that the brewer's grain can be successfully used as a natural adsorbent to remove Cd^{2+}, Ni^{2+} and Cr^{2+} ions from galvanization waters, and also that high level of efficiency is obtained at all analyzed pH values. The analysis has also shown that the affinity of adsorbents to Cd^{2+}, Ni^{2+} and Cr^{2+} ions is in correlation with physical and chemical properties, but that the best removal efficiency is achieved at the pH 4 value.

Key words:-*Heavy metals, galvanization wastewaters, brewer's grain, adsorption.*

1. INTRODUCTION

In the present time, the surface treatment of metals is of great importance in order to protect the material from corrosion by which the material is exposed on a daily basis. In the process of metal processing and application of coating, chemical compounds which have very harmful effect on the environment are used, and these are mainly heavy metals, their salts, organic solvents, acids and bases, which lead to a number of physical and chemical changes of water quality parameters, i.e. color, odor, taste, pH value, hardness.

Galvanic wastewaters represent a great danger to watercourses, either by indirectly flowing into via public drainage system, if not purified before discharging to the degree prescribed by the legislation or in a way of directly flowing into them. For this reason, the treatment of these galvanic wastewaters is of great importance for maintaining the balance and biodiversity [1]. Accordingly, a number of methods have been developed for their removal and treatment of galvanic wastewaters, and the most efficient one among them for its simplicity and costeffectiveness is *adsorption*. The most commonly used is adsorption with activated carbon, but its application is limited due to high production costs and regeneration of activated carbon as adsorbent. Due to the above fact, adsorbents derived from agricultural waste, industrial byproducts, natural materials and modified biopolymers can be used as adsorbents to remove heavy metals from wastewaters in the adsorption process. In this paper brewer's grain, occurring as a by-product in the beer production process, is used as an adsorbent in this paper. Aqueous solution of extracted malt ingredients is wort, and insoluble ingredients make the grain [2]. The grain is lignocellulosic material, rich in proteins and fibers making 20%, i.e. 70% of the brewer's grain composition. It occurs throughout the year and, due to the high content of proteins and carbohydrates, it can be used as a raw material in biotechnology: for lactic acid production, bioethanol, phenolic acid, xylitol, pullulan, and biogas and as a substrate in microbiology. The brewer's grain is also used as a livestock food, raw materials for the production of building materials, and it has the potential to be used as an adsorbent [3].

2. Material and methods

The brewer's grain obtained by the wort production for light beer is used in this paper. The grain was dried for 24 hours at a temperature of 25ºC. The dried brewer's grain was sieved through a sieve to a granulation of 0.5 mm, after which it was further used for analysis. For thus prepared grain, the physicochemical characterization of the material (FTIR analysis, moisture and ash content were determined by gravimetric method) was determined. The influence of pH values on the biosorption efficiency at different pH values was determined. The pH values were adjusted with 0.1/0.01 M HNO_3 and NaOH. The wastewater generated from the galvanization process, containing Cd^{2+}, Ni^{2+} and Cr^{2+} ions, with concentration of 10 mg/l at the pH value of 1.25 was used in the adsorption experiments. In addition to this pH value experiments were also performed at pH value of 4, 5 and 6. The pH values were adjusted with nitric acid solution (0.1/0.01 M HNO_3) and sodium hydroxide solution (0.1/0.01 M NaOH). The experiments were performed at room temperature by 250 ml of wastewater being contacted with biosorbent in an amount of 1 g. The time of adsorbent and adsorbate contact was 100 min, and the samples were taken at time intervals of 5, 10, 20, 30, 50 and 100 min which were filtered through the HPLC in diameter of 0.45 µm, after which the metal ion content was determined in the filtrate after the adsorption process, by inductively coupled plasma mass spectrometry (ICP-MS). Based on the obtained data, the amount of adsorbed Cd^{2+}, Ni^{2+} and Cr^{2+} ions was calculated per mass unit of biosorbent (q) and adsorption efficiency (E), by means of the following relations:

$$q\left(\frac{mg}{g}\right) = \frac{(C_0 - C)\cdot v}{m} \quad (1)$$

$$E\ (\%) = \frac{(C_0 - C)}{C_0} x100 \quad (2)$$

where : q–adsorbent mass per mass unit of adsorbent (mg/g), C_0 –initial concentration of ions in water (mg/L); C- ions concentration in water after adsorption (mg/L); v- solution volume (ml); m- added adsorbent mass per volume unit; E-efficiency in %.

3. Results

3.1 Analysis of the grain

3.1.1 Analysis of the moisture and ash

Based on the analysis performed by the gravimetric method, the ash content was 4.2 %, while the moisture content was 5.5%. Such moisture and ash show that adsorbent does not retain a large amount of water in its structure, which is why it can be stored in the air without agglutinating the particles and changing the granulation, which is of particular importance when applied in large water treatment systems.

3.1.2 FTIR analysis

Different functional groups present on the adsorbent surface can participate in binding cations due to dissociation in the aqueous environment [4], and to a certain extent, the binding of heavy metal ions takes place by donating electronic pair to form a complex with metal ions. The assumption that there is a change in metal ions was confirmed by the FTIR analysis. The FTIR analysis was performed before and after the adsorption process. A large number of adsorption peaks in the FTIR spectrum of adsorbent indicates the complexity and heterogeneity of the tested materials and possible presence of different functional groups. In the sample of brewer's grain prior to the adsorption process (Figure 1), the first peak was found at 3292cm^{-1} (which normally appears in the range of 3200- 3600 cm^{-1}) belonging to the elongations valence O-H group which occur in a wide spectrum of frequencies, indicating the presence of "free hydroxyl groups and O – H carboxylic acid bonds"[5]. The peaks at intervals of 2920-2851 cm^{-1} can be attributed to symmetric or asymmetric elongation vibrations of –C-H bond of hydrocarbon chains [6], while the peaks at interval of 1647 to 1517 cm $^{-1}$ indicate the presence of the valence band of the C=C aromatic ring bond, which in the literature are attributed to carbonyl elongation vibrations in carboxyl groups of hemicellulose [7]. The peak at 1035 cm^{-1} (occurring in the range of 1000 – 1200 cm $^{-1}$) indicates the presence of the valence band of the C-O bond.

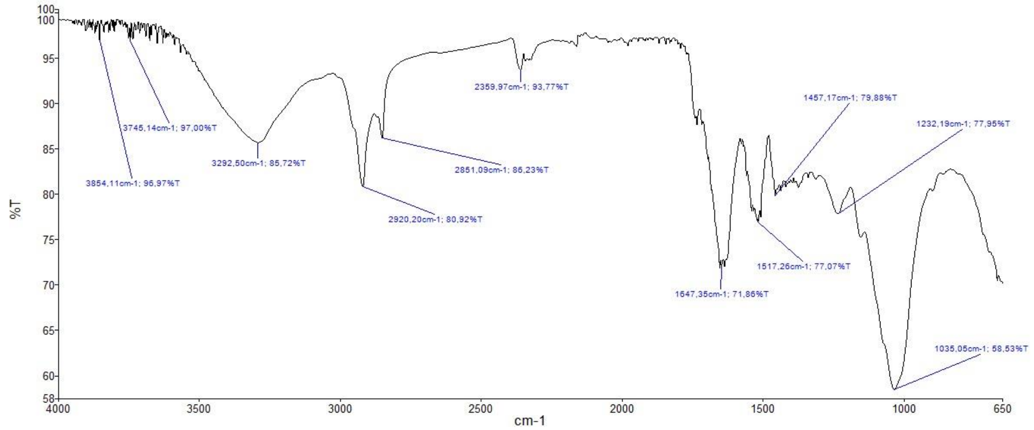

Fig.1. FTIR analysis of the brewer's grain before the adsorption process

A more detailed analysis of the spectra before and after the adsorption process revealed several differences. Comparing FTIR spectrum before and after adsorption with metal ions, it is noted that movement of functional groups occurs at higher values (3292 to 3293 cm^{-1}, 1647 to 1653 cm^{1}) which indicates possible interaction of metal ions with these functional groups (Figure 2). Otherwise, these functional groups are highly reactive and become deprotonated during the adsorption process. The first peak indicates strong O-H bonds, while the second peak indicates strong carboxyl C=O bonds, and C=C bonds that occur within the aromatic ring and confirm the lignin composition. The peak at 1035 cm^{-1} is of lower intensity and slightly shifted to 1031 cm $^{-1}$, probably due to the metal ions binding. Therefore, it can be said that the functional groups in the spectrum range of 3200-3600 cm^{-1}, and 1750-750 cm^{-1} i.e. OH, C-H and C=C have a significant role in metal ion binding during the adsorption process.

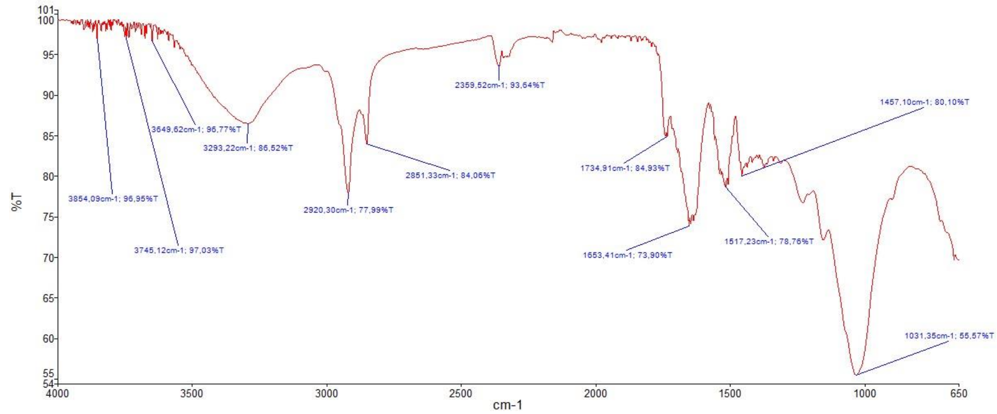

Fig. 2. FTIR analysis of the brewer's grain after the adsorption process

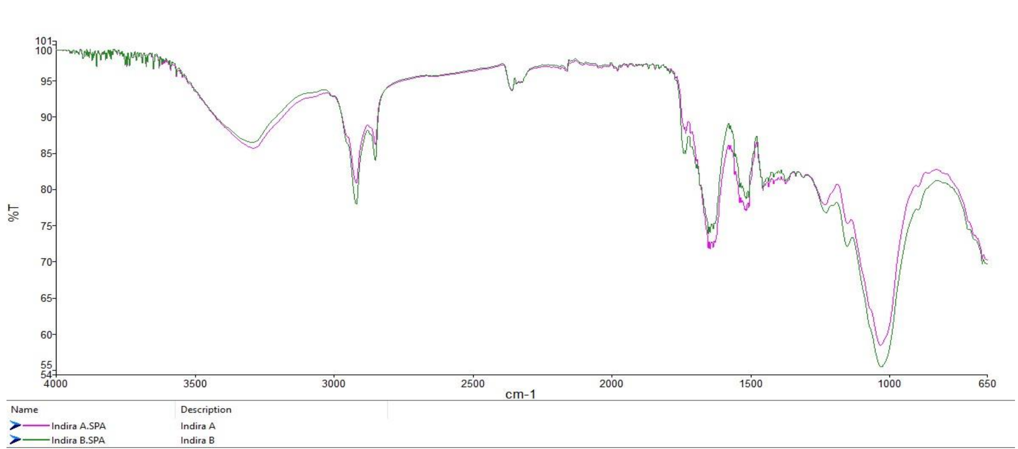

Fig. 3. Comparing FTIR analysis before and after the adsorption process

3.1.3 Influence of pH values

The influence of the pH values for the adsorption process of Cu^{2+}, Ni^{2+} and Cr^{2+} ions was examined using brewer's grain as adsorbent at different pH values. From the results shown, it can be noticed that at all pH values a high degree of sorption

efficiency is achieved, and that with the increase in time the removal efficiency is increased, depending on the type of metal, which is in correlation with the physical and chemical properties of the metal.
It can be noticed that brewer's grain has much better adsorption properties for copper ions (Cu^{2+}) in the tested ranges of pH values compared to other metals. The copper ions adsorption efficiency is the lowest at pH value of 1.25 (Figure 4), while the highest at pH 4 and keeps the approximate values at pH 5 and 6. At pH 4, the copper values achieve the removal efficiency of around 99.97 %, and moves into direction of Cu>Ni>Cr (Figure 5).
This behaviour is explained by the fact that copper ions, depending on the solution pH value, can exist in different forms, where at pH values lower than 5 they are present as Cu^{2+}, while at higher pH values they precipitate in the form of $Cu(OH)_2$ [8], so their removal in these conditions is not a consequence of just adsorption on the brewer's grain.

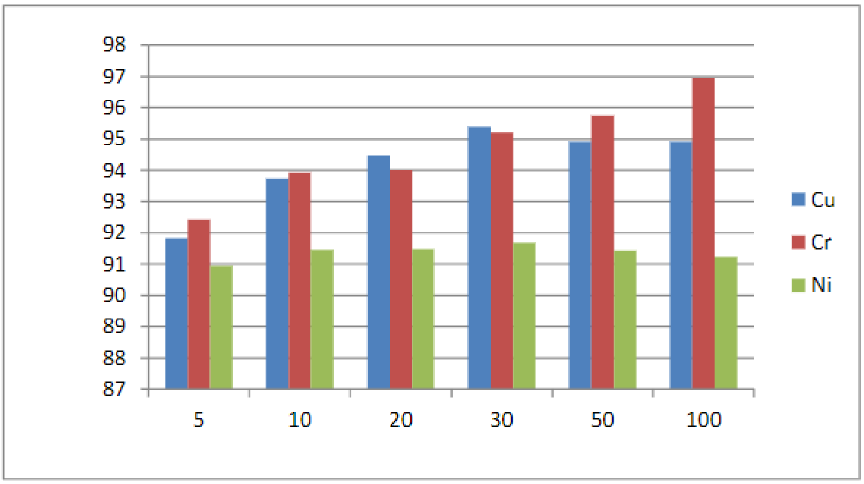

Fig. 4. The adsorption process efficiency using brewer's grain as the adsorbent at pH 1.25

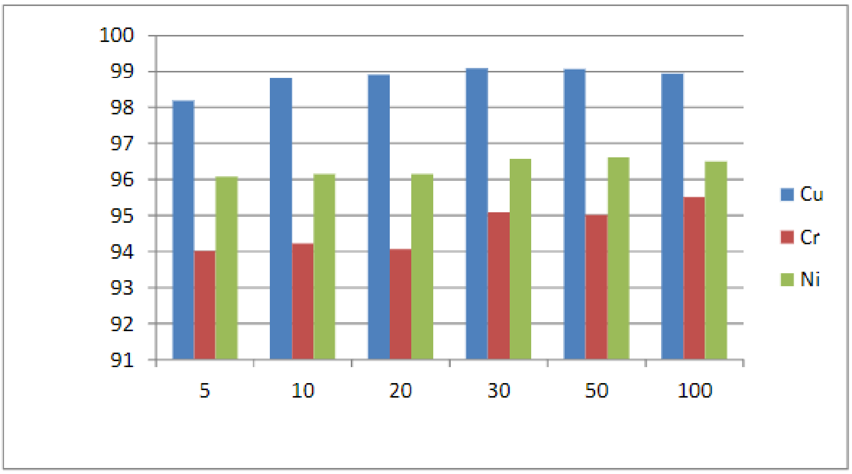

Fig. 5. Adsorption process efficiency using brewer's grain as the adsorbent at pH 4

The adsorption efficiency of Ni^{2+} ions is lower that the adsorption efficiency of Cu^{2+}ions, but it slightly increases with an increase of the pH value to 6, where at that pH value it achieves maximum adsorption. The maximum removal efficiency of Ni^{2+} ions at a concentration of 10 mg/l is 98.88 % (Figure 6). In the conducted analyses, chromium ions are most effectively removed at the lowest pH value (pH 1.25) 96.96 %. With further increase of the pH value the efficiency is reduced, and reaches its minimum at pH 6 - 91.92 %. The chromium ions can be found in several forms in aqueous solutions, depending on their concentration and the solution pH value. In the range of pH from 2 to 6, chromium is the form of $HCrO^{4-}$ or $Cr_2O_7^{2-}$ (9), and adsorption of weak anions is based on the formation of complexes with protonated active groups on the adsorbent surface, whereby a high affinity occurs for negatively charged ions in water, so the adsorption efficiency of these ions is higher with lower pH values (Figure 4).

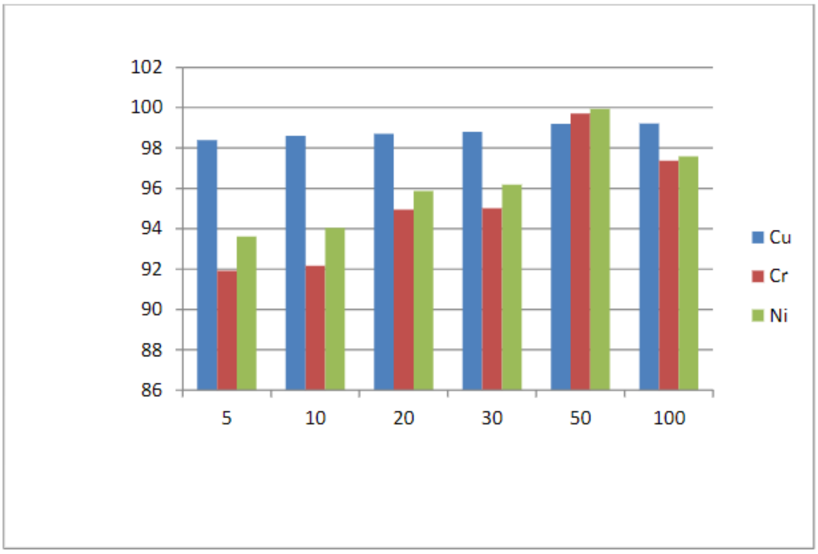

Fig. 6. Adsorption process efficiency using brewer's grain as the adsorbent at pH 5

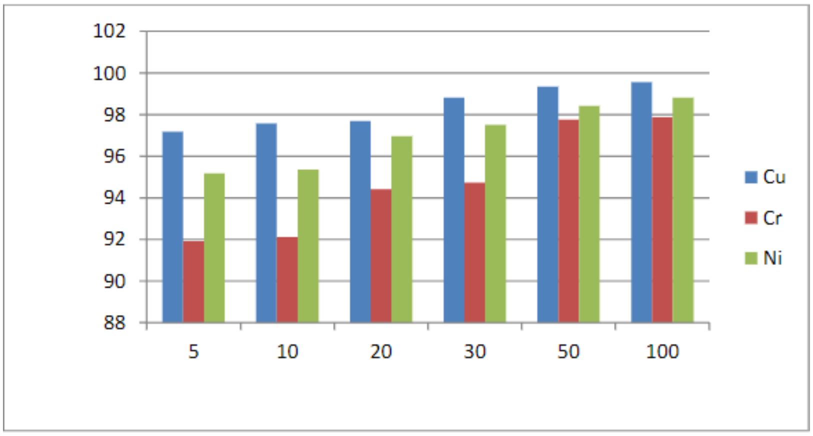

Fig. 7. Adsorption process efficiency using brewer's grain as the adsorbent at pH 6

It can be noticed from the obtained result that the metal ions binding efficiency by brewer's grain as the adsorbent at pH 4 to achieve the best efficiency provided the following order: Cu^{2+}> Ni^{2+} > Cr^{2+}. Although this is the same type of adsorbent, it must be taken into consideration that it is a biological material whose structure and composition can vary depending on the conditions of cultivation and technological process of sugar production, which can cause different adsorption characteristic.

4. Conclusion

Based on the conducted analyses it has been shown that the brewer's grain, resulting from the wort production for light beer, can be used as adsorbent for removing metal ions from galvanization wastewater. The moisture and ash analysis have shown that this biosorbent does not retain a large amount of water in itself, and as such can be used in wastewater treatment. The conducted FTIR analysis has also shown presence of numerous functional groups, and that replacement of metal ions occur. The results have shown that a high degree of removal is achieved at all pH values, and at pH 4 all metals have high degree of removal, and that removal takes place in the Cu^{2+}> Ni^{2+} > Cr^{2+} direction, indicating that brewer's grain can be used as adsorbent in galvanization wastewater treatment at different pH values.

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