

Wastewater treatment from heavy metals using extracts of wood processing waste (oak bark)

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Abstract. The paper considers the issues of using extracts from wood processing industry waste (oak bark) for wastewater treatment from heavy metal ions (Cr^{+6}) are considered. The principle of purification is the formation of aggregates, formed by the contact of organic colloidal compounds (tannins) with positively charged heavy metal ions. It is established that the maximum formation of a precipitate is observed in acid media ($\text{pH} = 2.5$). This is due to the fact that during the oxidation of the substance the compounds of hexavalent chromium pass to the salts of trivalent chromium, which forms a precipitate. To improve the efficiency of treatment, oak bark was crushed on a shredder and a hammer mill with the subsequent production of an alkaline extract.

1. Introduction

Heavy metals have the ability to concentrate in the ecosystem and enter the human body with drinking water and food. One of the most dangerous from the point of view of biological activity and toxic properties are compounds of chromium, copper, nickel, which present a serious danger to surface and ground waters, possess the properties of toxicants of cumulative and additive character, and can have mutagenic and carcinogenic effects on living organisms [1].

Traditionally used methods of wastewater treatment from heavy metals are reagent treatment, ion exchange, and membrane purification methods. Sorption methods are the most effective ones. At the same time, the main disadvantage of sorbents is its rather high cost. In this case, the production of sorbents based on waste products is an urgent task [1,2].

In recent years, of great interest is the development of sorbents based on many-tonnage products of plant origin [3-8]. The main selection criteria are the amount of waste, the technical and economic efficiency of the developed materials, and the reduction of the technogenic load on the environment by economically viable methods of wastewater treatment, high sorption characteristics. The use of wood bark as a promising material for the removal of heavy metal ions from wastewater is of particular interest [9-12].

2. Materials and methods

In the work waste oak bark, formed during wood processing, was used. Mechanoactivation of the bark was carried out using a shredder and a hammer mill of the DKR type.



The pH of the aqueous extract from the waste of crushed bark was 5.48 – 5.51. The fractional composition of the shredded sawdust of the oak bark is presented in Table 1. In the work on the extraction of chromium (VI) ions, an extract of the oak bark was used. For this purpose, the extract was prepared at a ratio of bark : distilled water (pH = 12.32) = 1: 10. The bark was boiled for 1 hour, followed by settling for 12 hours. Alkaline extraction was carried out for the most complete extraction of the organic component into the aqueous medium. The precipitate was then filtered off, and the extract was used for treatment of the model solution. The pH of the extract was 6.52.

Table 1. Fractional composition of crushed oak bark.

Cell size, mm	Sieve residue, %
> 2.5	0.12
1.25 – 2.5	48.34
0.63 – 1.25	37.18
0.315 – 0.63	8.96
0.25 – 0.315	3.78
0.14 – 0.25	0.45
0.08 – 0.14	0.67
0.05 – 0.08	0.38
<0.05	0.12

Table 2 shows the data of experimental studies on the determination of the physical and chemical properties of the oak bark.

Table 2. Physical and chemical properties of the oak bark.

Characteristic	Unit	Oak bark shredded
Moisture	%	15
True density	kg·m ⁻³	897
Bulk density	kg·m ⁻³	451
Particle packing density	–	0.50
pH of water extract	–	7.8
Solubility in distilled water (pH = 7.0).	%	0.18
Solubility in concentrated hydrochloric acid (36.0 % HCl, $\rho = 1.18 \text{ g}\cdot\text{sm}^{-3}$)	%	95.6
Solubility in concentrated sulfuric acid (98.0 % H ₂ SO ₄ , $\rho = 1.83 \text{ g}\cdot\text{sm}^{-3}$)	%	93.2

The bark contains 10 – 20% of tannins; 13 – 14% of pentosans; up to 6% of pectin substances; quercetin and sugar [13,14]. Analysis of the composition of the oak bark for the content of basic metals is performed by atomic-adsorption and flame-emission methods and is presented in Table 3. Chlorides were determined by titrimetric method, sulfates – by turbidimetric method of analysis [15].

For the preparation of the extract, shredded oak bark sawdust was used. The initial concentration of chromium (VI) ions in the model solution was 205 mg·l⁻¹. The studies were carried out by adding to the 100 ml model solution the oak bark extract in the ratios of 10 : 0.5 – 5, respectively.

Table 3. The chemical composition of the crushed oak bark.

Substance	Concentration, mg·m ⁻³
Zinc	11.25
Manganese	8.05
Copper	0.35
Chromium	0.96
Cadmium	0.11
Lead	1.75
Iron	156
Nickel	0.04
Potassium	33.3
Sodium	197.70
Calcium	20040
Chlorides	21270
Sulphates	122.20

3. Results and discussion

The effectiveness of using oak bark extracts for wastewater treatment from heavy metal ions is due to the presence of tannins. Tannins are divided into 2 groups [13, 14, 15]:

1) hydrolysable tannins (add water under the influence of acids), are esters of saccharides and phenol carboxylic acids, which are hydrolyzed by enzymes or dilute acids to form simpler phenolic compounds (pyrogallol derivatives);

2) condensed tannins (not capable of hydrolytic cleavage) are mainly represented by polymers of catechins (flavanol-3) or leucocyanidins (flavandiol-3,4) or copolymers of these two types of flavonoid compounds (Figure 1).

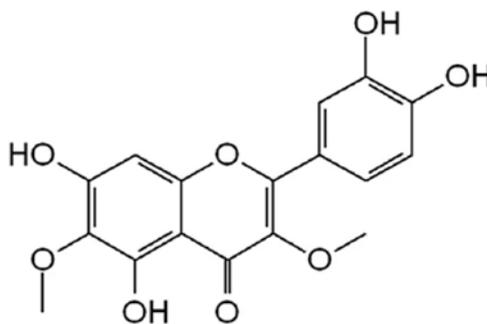


Figure 1. Polymers of catechins (Flavanol-3).

Tanning agents are weak acids that behave like negatively charged colloids, when it come in contact with positively charged heavy metal ions, aggregates precipitate in the form of precipitation [16-20].

The kinetic curves of wastewater treatment are shown in Figure 2. When the extract was added for 60 min, precipitate flocs were formed in the entire volume of the liquid at a purification pH of 2, and 3.5, which indicates the reaction of oxidation of organic substances in an acid medium in the presence of bichromate. In this case, a precipitate is formed, with which the Cr (VI) ions are precipitated.

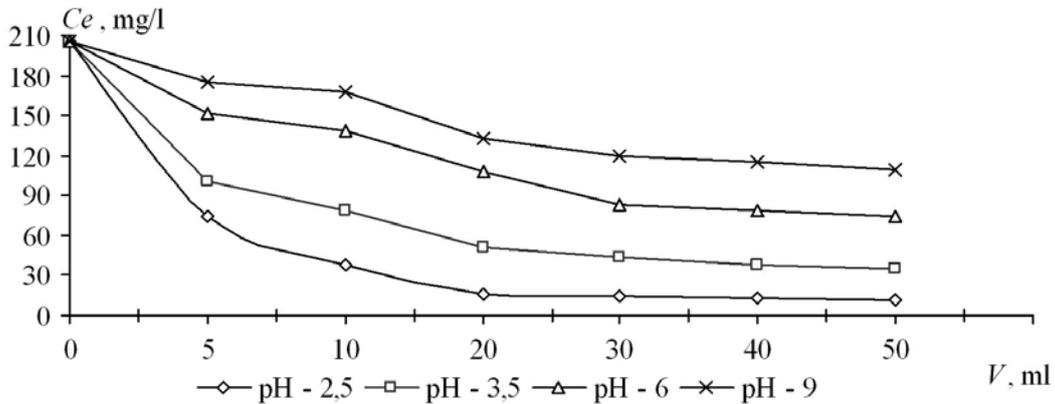


Figure 2. Kinetic curves for reducing the concentration of chromium (VI) ions at different pH values in model solutions; C_e – equilibrium concentration of chromium (VI) ions in solution, mg/l; V – volume of added extract, ml.

Mathematical processing of the results of the experiments made it possible to establish polynomial models describing the waste water treatment process using oak bark extracts as a function of the pH values of model solution [20]:

For the pH=2.5:

$$y = 10.207x^2 - 107.54x + 279.53$$

For the pH=3.5:

$$y = 7.5107x^2 - 83.961x + 264.67$$

For the pH=6:

$$y = 3.6143x^2 - 50.079x + 248.01$$

For the pH=9:

$$y = 2.2143x^2 - 33.857x + 237.43$$

The root-mean-square values of the reliability of the approximation were, respectively: for the pH=2.5 $R^2 = 0.9233$, for the pH=3.5 $R^2 = 0.9446$, for the pH=6 $R^2 = 0.9848$, for the pH=9 $R^2 = 0.9768$.

In Table 4 and Figure 3 the values of the volumes of the formed sediment from the purification module are shown. The purification module is the ratio of the volume of the model solution to be cleaned to the volume of the extract to be added. The sediment in the model solutions at a purification pH of 6.0 and 9.0 was not formed. More complete precipitation occurs at a pH of 2.5.

Table 3. Values of sediment volume in model chromium-containing solutions from the purification module.

The purification module	Volume of sediment, sm^3	
	pH = 2.5	pH = 3.5
10:0.5	8.0	5.0
10:1	18.0	16.0
10:2	38.0	22.0
10:3	44.0	34.0
10:4	48.0	38.0
10:5	51.0	38.0

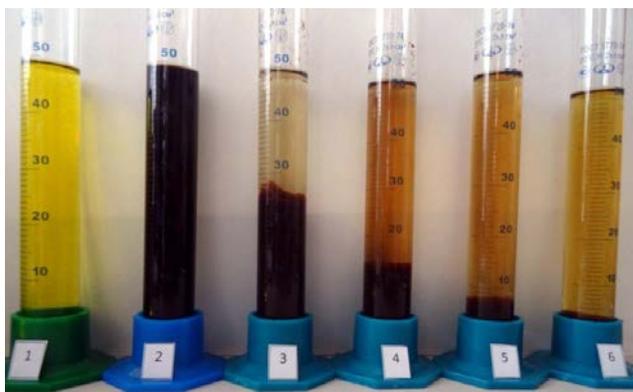
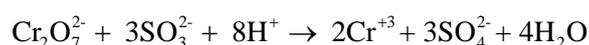


Figure 3. Samples of model solutions with the addition of oak bark extract with purification modules, respectively: 1 – 10:0.5; 2 – 10:5; 3 – 10:4; 4 – 10:3; 5 – 10:2; 6 – 10:1

As it can be seen from the data in Table 3, with increasing volume of added extract, the volume of precipitation formed increases. The maximum formation of a precipitate is observed in acid media, which is due to the fact that oxidizing substances, hexavalent chromium compounds are converted to salts of trivalent chromium, which precipitates. Thus, the presence of an organic component (an extract of the oak bark) contributes to the removal of chromium (VI) ions from acidic effluents. Traditionally, at local treatment plants, the reduction of Cr^{+6} in Cr^{+3} is done by adding sodium sulphite to the reactor with constant stirring with compressed air. The reduction of Cr^{+6} to Cr^{+3} by sodium sulphite occurs by reaction at $\text{pH} = 2 \div 3$:



4. Conclusion

It is shown that waste of the woodworking industry can be used for sewage treatment from heavy metal ions. Organic colloidal compounds (tannins) in contact with positively charged heavy metal ions form aggregates, settling in the form of precipitation. It is shown that the oak bark extract is effective for purifying model chromium-containing solutions from Cr^{+6} ions. When applying mechanoactivation (crushing waste of the oak bark) the efficiency of wastewater treatment from chromium ions significantly increases.

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