Alternative Sorbents for the Cobalt-Containing Wastewater Treatment

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Abstract. Electroplating industry cobalt-containing wastewater treatment solutions have been found. We have opted for the reactant method of chemical treatment. We have precipitated cobalt (2+) as cobalt stearate, which we propose to use in lubricants mixed with paraffin, high-pressure polyethylene and ultrafine polytetrafluoroethylene, thus resulting in a material, possessing lower rolling friction coefficient than polytetrafluoroethylene. We have resorted to the ion-exchange method as a means of physico-chemical treatment. This method has made it possible to lower the wastewater cobalt (2+) ion concentration to the MPC h.h. (Maximum Permissible Concentration for Households). We propose the use of waste products of timber-processing (lignin) and power-producing (ash, fly ash) industries as sorbents. The mix of slag, fly ash and hydrolised lignin has been found to be the most efficient cobalt ion sorbent for the sorption method. Upon the sorbent treatment, it can be burnt in a furnace, while the ash can be stored in a sludge collector without any heat treatment.

1. Hydrolised lignin, fly ash, ultrafine polytetrafluorethylene
Hazard class 2 cobalt-ion containing waste water to be treated is the waste product at mining-, metallurgic-, machine-building-, metal-working-, chemical-, pharmaceutical-, dye-, and textile plants, etc.. Cobalt ions concentration in the waste water is extremely low as compared to that of other heavy metals cations. The solubility product of cobalt hydroxide is $6.3 \times 10^{-15}$, the medium's pH upon cobalt hydroxide precipitation is 6.7-7.7. Wastewater treatment with alkaline reagents reduces the content of heavy metals in the solution to values comparable to the MPC for sanitary/household water reservoirs. However, when a much thorough treatment is required, e.g. in case of wastewater discharge directly into fishery reservoirs, alkaline reagents treatment doesn't produce the needed result [1].

Thus, development of more ecologically friendly ways to treat cobalt-containing waste water, as a result of electroplating steel items with cobalt, is of importance.

The objective of the study was to research the possibility of heavy metal ions (e.g. cobalt) extraction by various methods, including multistage ones, through the use of industrial waste as sorbents.

The cobalt ions content in solutions and wastewater was determined by the complexometric method. After cobalt plating, the Co²⁺ content in the wash water of a static capture bath should not exceed 0.01 g/l. However, in case of two sequentially installed traps, there is a possibility of excessive cobalt content in the first trap of the two.

We extracted cobalt ions from wastewater by means of reagent-, ion-exchange-, and sorption methods.
Due to the fact that lime-milk recovery resulted in large amounts of hard-to-dehydrate pulp, we used carboxylic acid salts (sodium stearate) to perform reagent treatment of waste water. Previously, such salts were used to dispose of solutions left after chemical nickel- and cobalt plating [2]. The KU-2-8 (Rus. КУ-2-8) cationite was used for the further post-treatment.

Additionally, we used waste products of the hydrolysis wood processing (lignin) and the power production (slag and fly ash) to adsorb cobalt ions.

Figure 1 demonstrates the results of the sodium stearate reagent treatment of cobalt containing waste water. As it is evident, with the increasing reagent concentration, the residual cobalt content in wastewater decreases. For lower concentrations of cobalt in wastewater, the reagent concentration increase is not so effective.

![Figure 1. Correlation between treated wastewater Co\textsuperscript{2+} concentration and the sodium stearate content.](image)

The resulted cobalt stearate precipitate was separated, dried and then mixed in the following ratio: 70 % paraffin, 28 % high-pressure polyethylene waste, 1.5 % ultrafine polytetrafluoroethylene, and 0.5 % cobalt stearate. To homogenize and dye the mix, it was melted at 190-230 °C. The cooled solid was used as a lubricant (its rolling friction coefficient was 0.0165-0.0221, while for polytetrafluoroethylene the average value was 0.0381).

Upon the KU-2-8 cationite post-treatment, the wastewater Co\textsuperscript{2+} recovery was 98.8 %.

Due to the high cost and difficulty of regenerating the KU-2-8 cationite, we tested sorbents based on waste products of power-manufacturing- (slag and fly ash), and biochemical (hydrolyzed lignin) industries.

According to Russian federal classification, ash and slag waste is class five hazard, in other words, it is practically safe to handle, as such, it is used in civil engineering, road building, agriculture, etc. However, the use of ash and slag waste in Russia is not wide-spread and does not exceed 5-7%. The need to process ash/slag waste is quite obvious. Being spread over large potentially valuable but decommissioned agricultural areas, the ash dumps are a threat to the environment and to human health. Infiltration of ash-dump pollutant solutions (heavy metals, radioactive elements, etc.) into the ground water, and, later, into rivers and water bodies can result in their contaminating human food sources [3].

Due to the fact that wood processing results in a large amount of waste, that is not used in further production, the waste re-use is environmentally sound [4, 7-14].
Adsorption of metals with bio-sorbents (lignin), which are renewable waste products of wood processing, is possible, since such materials contain, as a rule, natural biologically active substances, that can react to heavy metal ions.

When wood sawdust is used as a sorbent, the heavy metal ions recovery from solutions within a single extraction cycle reaches approximately 70% [5]. The low sorption characteristics of the material cause certain difficulties in the treatment of high heavy metal-ions concentration water [6], however, cobalt-infused wastewater contains, as it has been mentioned above, low concentration of cobalt.

The correlation between the efficiency of cobalt-containing wastewater treatment and the volume of wastewater passed through the sorbents is given in Figure 2. The wastewater $\text{Co}^{2+}$ initial concentration is 825 mg/l.

![Figure 2. Sorbents' efficiency in treating cobal-containing wastewater: 1 – slag, fly ash (1:1); 2 – lignin; 3 - lignin, slag, fly ash (1:1:1); 4 – double amounts of lignin, slag, and fly ash (1:1:1).](image)

The figure clearly demonstrates, that the treatment efficiency increases in the sequence (slag, fly ash) $\rightarrow$ (lignin) $\rightarrow$ (lignin, slag, fly ash) $\rightarrow$ (double amounts of lignin, slag, and fly ash). Doubling the amount of the lignin, slag, and fly ash mix in the filtering column increases the recovery efficiency by 9-27 %.

Upon the recovery cycle completion there is no need in the sorbent regeneration. The resulting waste can be burnt in a furnace, while the ash can be stored in a sludge collector without any heat treatment.

2. Conclusion
The research has resulted in the technological solutions for cobalt ions recovery treatment from the cobalt-containing wastewater. The recovery solutions call for the use of reagent-, ion-exchange-, and sorption methods, and the further use of solid cobalt stearate as a lubricant component.

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