Wastewater purification from copper and nickel ions by means of thermally modified organo-mineral wastes and their combinations

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Abstract. Wastewaters, which contain heavy metals, are one of the main sources of environment pollution. This paper presents the data of research findings concerning the combined use of thermally modified organo-mineral waste products of sugar production and brewing industry for purifying test solutions from copper and nickel ions. The most efficient is the sorption material, obtained by heat treatment of brewing industry's kieselguhr sludge KS450 (94% for nickel ions and 95% for copper ions); the next efficient is the material, obtained from sugar industry's carbonaceous sludge CS600; the application of combined sorbents showed no increase in wastewater purification efficiency.

Over The presence of heavy metals ions from the family of transition d-elements in environmental media poses a serious threat due to their high toxicity to many life forms. Unlike organic pollutants, most of which are prone to biodeterioration, metal ions are not transformed into safe end products. The industrial effluents of enterprises, involved in electroplating production, contain the ions of such heavy metals, as Cu(II), Pb(II), Zn(II), Ni(II) etc. [1, 2].

The industrial wastewaters of electroplating sites are usually divided into two types: those formed in the process of plating coating and those formed after rinsing [3].

The current research considerably expands our understanding of the toxic hazard of heavy metals. Discharge of sewage waters, containing such pollutants, to water bodies, can be hazardous for both people and aquatic organisms. There is evidence in literature that the presence of heavy metals in water can cause mutagenic and carcinogenic effects. Besides, they can induce disfunctions of kidneys, reproductive system, liver, brain and central nervous system [4, 5].

Nickel is an essential microelement for some species of living organisms, but consuming too small or too large amount of it can cause deficiency symptoms or toxic poisoning, respectively. Nickel exists in various mineral forms, which are used for manufacturing nickel-based alloys, catalysts and pigments for metal, chemical and food industries [6].

Copper has been mined since ancient times for many industrial purposes. It is also an essential microelement in living organisms’ metabolism, though its excessive amount results in various health issues, such as nausea, headache, dizziness, labored respiration, anemia, major gastrointestinal bleedings, renal and hepatic failures and death. Among heavy metals it is considered the third in terms of toxicity after mercury and cadmium [7].
In developed countries heavy metals are usually removed from wastewaters by means of such advanced technologies as ion exchange, crystallization, extraction and using membranes [8, 9].

At the same time, in many countries these purification methods can’t be used due to low technological level and the high cost of equipment. So, it is desirable to develop simple and economically-efficient methods of wastewater treatment for using them in various economic conditions.

Many researchers strive to find an alternative material, which could be used for wastewater treatment. It should be low-cost, easy-to-work and high-efficient. An example of such materials is sorbents, obtained on the basis of agricultural and industrial waste [10].

At processing agricultural products, such as sunflower seeds and sugar-beet, the raw stuff is subject to multistage treatment. These technological processes include clarification stages, in which mineral sorbents and reagents are used. Thus, at beet juice clarification the lime milk is used, which in the course of chemical transformations forms calcium carbonate, carboxylic acids salts and amino acids salts [11, 12]. For beer filtering they use diatomite (its main component is SiO2), also called kieselguhr, which adsorbs the components of malt and related substances, brewing yeast cells, proteins and other compounds, which can impair the consumer qualities of the end product [13, 14]. As a natural result, this generates waste products in form of sludge with various moisture contents, which contains chemically inert mineral substances and absorbed organic compounds of various natures.

Nowadays there are no conventional methods of recycling such sludge wastes. In most cases they are dumped at landfills, which creates economic problems for enterprises and causes an adverse impact on the environment [14, 15].

It is known that thermally modified organo-mineral wastes can be used for wastewater purification [16, 17].

This paper presents the research findings concerning the combined usage of thermally modified organo-mineral wastes of sugar production and brewing industry for purifying test solutions from copper and nickel ions.

As sorbents the following waste products were used: carbonaceous sludge of beet-root sugar production and kieselguhr sludge of the brewing industry. Both materials were heat-treated in a muffle furnace, and then used for purifying test solutions both individually and as part of mixes (Table 1).

**Table 1.** Variants of sludge modification, sorbents combination and conventional notations

| Waste product and heating temperature | Ratio  | Notation        |
|--------------------------------------|--------|-----------------|
| Carbonaceous sludge, 600             | -      | CS600           |
| Kieselguhr sludge, 450               | -      | KS450           |
| Kieselguhr sludge, 550               | -      | KS550           |
| Carbonaceous sludge, 600 and kieselguhr sludge, 450 | 1:1    | CS600+KS450    |
| Carbonaceous sludge, 600 and kieselguhr sludge, 550 | 1:1    | CS600+KS550    |

In Figure 1 micrographs of the used sorption materials – CS600, KS450 and KS550 – are presented, and in Table 2 – the content of chemical elements in the materials under study. The data were obtained by using a microscope TESCANMIRA3 LMU.

The pH values of suspensions and filtrates of sorbents in the water were measured with a pH-meter I-500 «Akvilon».

As test solutions the solutions of NiCS₄*7H₂O, CuCS₄*5H₂O salts were used.

The concentration of Cu²⁺ and Ni²⁺ ions was determined by a spectrophotometer «KFK-3».

The solutions were treated in static conditions, by adding a weighed sample of sorption material to the test solution of the known concentration. The content of flasks was stirred for 20 minutes, and then filtered through «Blue ribbon» paper filter.
Figure 1. Micrographs of used sorption materials.

Table 2. Chemical elements content in sorption materials.

| Chemical element | Amount, wt% | Chemical element | Amount, wt% | Chemical element | Amount, wt% |
|------------------|-------------|------------------|-------------|------------------|-------------|
| O                | 42.9        | O                | 46.5        | O                | 49.0        |
| Ca               | 35.1        | Si               | 40.9        | Si               | 38.1        |
| C                | 12.8        | C                | 8.7         | C                | 3.7         |
| Mg               | 4.2         | Fe               | 1.2         | Al               | 3.1         |
| Si               | 2.4         | Al               | 1.2         | Na               | 2.2         |
| P                | 1.8         | Na               | 0.5         | Fe               | 1.6         |
| Al               | 0.5         | Ca               | 0.4         | K                | 1.2         |
| Fe               | 0.1         | Mg               | 0.2         | Mg               | 0.3         |
| Na               | 0.1         | Other            | 0.1         | Other            | 0.1         |

The solutions purification efficiency by means of the obtained sorbents was determined by the formula (1):

$$\eta = \frac{(C_1 - C_2) \cdot 100\%}{C_1}$$

where $C_1$ – initial concentration of substance in the solution, mg/l; $C_2$ – its final concentration in the solution, mg/l.

The experiments were carried out simultaneously for all sorption materials, in triplicate. The arithmetic mean of the obtained findings is presented in Figures 2 and 3. The amount of sorbent was 1 g/100 ml; the initial concentration of copper and nickel ions was 25 mg/dm$^3$.

As we can see from the presented data, the carbonaceous sludge contains 25 % of organic matter, and diatomite sludge – 21 %. The oxides, which compose the mineral part of the waste diatomite, are silicon oxide and, to a lesser extent, calcium oxide; the carbonaceous sludge is presented with calcium carbonate, expressed as oxides – 49% of calcium oxide and 38.24 % of carbon dioxide.

As sorbents in this research the materials of the following thermal modifications were used (Table 3).
As we can see from the obtained data, the most efficient for copper and nickel ions is the sorption material KS450, and the second efficient is the material CS600.

The combined use of materials in mentioned ratios didn’t improve the water purification efficiency. It should be noted that all the sorption materials are good at extracting ions of the selected metals from test solutions – the lowest purification efficiency value is 86% for nickel and 88% for copper. It is interesting to note that the suspending effect of KS450 is lower than of KS550 (Table 3), and, consequently, its surface charge amount is also lower.

Table 3. The filtrate-suspension pH difference of sorption materials.

| Sorbent         | ΔpH  |
|-----------------|------|
| CS600           | 0.35 |
| KS450           | 0.27 |
| KS550           | 0.51 |
| CS600+KS450     | 0.39 |
| CS600+KS550     | 0.51 |

Probably in this case the higher efficiency is explained by carbonized materials’ presence on diatomite surface, which provides more pores and more possible active sites. At higher baking temperature part of organic substances is decomposed (Table 2), reducing the amount of pores, available for filling.

The saturation sludge shifts the medium pH to alkaline, which should promote the better extraction of heavy metals ions from the solution [14]. But at the combined usage of CS600 and KS450 the
purification efficiency doesn’t increase. This can occur due to the change of surface charge of KS450 at the pH change, which weakens the intensity of heavy metals ions attraction to the sorbent surface.

In general, the suspending effect of all sorption materials and their mixes is rather low (as well as their surface charge amount), so it’s safe to assume that the interaction of adsorbate and adsorbent takes place due to orientation and dispersion interactions.

It has been determined that the most efficient for copper and nickel ions extraction is the sorption material KS450, the next efficient is the material CS600, and the application of combined sorbents showed no positive effect. The measured suspending effect value is small for all sorption materials and their mixes, so we can assume that the interaction of adsorbate and adsorbent takes place due to orientation and dispersion interactions.

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References
[1] Pandová I, Panda A, Valicek J, Harnícárová M, Kusnerová M and Palkov Z 2018 Use of Sorption of Copper Cations by Clinoptilolite for Wastewater Treatment Int. J. Environ. Res. Public Health 15 1364
[2] Sverguzova S V, Sapronova Zh A and Svyatchenko A V 2016 Production technology of iron-containing coagulant from steelmaking waste for storm-waters treatment Bulletin of BSTU named after V.G. Shukhov 12 160-4
[3] Abdel-Raouf M E, Maysour N E, Farag R K and Abdul-Raheim A-R M 2019 Wastewater Treatment Methodologies Review Article. Int J Environ & Agri Sci 1 25
[4] Baktyaeva Z B, Suleymanov R A, Yamalov S M, Kulagin A A, Valeev T K and Rakhatullin N R 2016 Assessment of heavy metals content and migration in components of stream ecosystems at ore-mining territories of the Republic of Bashkortostan Hygiene and Sanitation 9 822-7
[5] Borisov P O 2019 The influence of heavy metals on human organism Bulletin of Science 3 6-8
[6] Hoseinian F S, Irannajad M and Nooshabadi A J 2015 Ion flotation for removal of Ni(II) and Zn(II) ions from wastewaters International Journal of Mineral Processing 143 131-7
[7] Siao P C Li, Engle G C, Ilao H L and Trinidad L 2007 Biosorption of Cu(II) ions from synthetic and actual wastewater using three algal species J Appl Phycol 19 733-43
[8] Al-Saydeh S A, El-Naas M and Zaidi J 2017 Copper Removal from Industrial Wastewater: A Comprehensive Review Journal of Industrial and Engineering Chemistry 56 35-44
[9] Wan Ngah W S and Hanafiah M A K M 2008 Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review Bioresource Technology 99 3935-48
[10] Chirkova V S, Sobaida N A and Rzazade F A 2015 Sorbents based on agro-industrial complex waste products for sewage waters purification Bulletin of Kazan Technological University 20 263-6
[11] Sapronova Zh A, Sverguzova S V and Svyatchenko A V About a Possibility of Usage of Sugar Beet Industrial Carbonate Containing Byproducts in Dry Construction Mixtures and Oil Paints Manufacturing Solid State Phenomena 284 899-904
[12] Reshetova R S, Bgantseva O Yu and Gamanchenko M A 2020 Types of returns to preliminary defecation, their influence on non-sucrose sediment formation and purification efficiency of diffusion juice Sugar 9 18-23
[13] Mathias Th R dos Santos, Moretzsohn de Mello P P and Servulo E F C 2014 Solid wastes in brewing process: a review Journal of Brewing and Distilling 1 1-9
[14] Rudenko E Yu, Bakharev V V, Mukovnina G S et al 2016 Possibility of using waste kieselguhr for wastewater purification from copper Izvestia of Samara Research Center of the RAS 5-1 24-8
[15] Hergert G W, Darapuneni M K, Abdullah Aqeel M, Wilson R G, Harveson R M, Bradshaw J D and Nielsen R A 2020 Agronomic Potential of Using Precipitated Calcium Carbonate on Early Plant Growth and Soil Quality in the Intermountain West - Greenhouse Studies Journal of Sugar Beet Research 4 537

[16] Sapronova Zh A and Sverguzova S V Peculiar 2020 Properties of Temperature Modification of Carbonate Precipitate Materials Science Forum Trans Tech Publications Ltd 989 365-71

[17] Starostin a I V, Stolyarov D V, Anichina Ya N and Porozhnyuk E V 2018 The carbonaceous sorbent based on the secondary silicapcontaining material from oil extraction industry IOP Conf. Series: Earth and Environmental Science 107 012075