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Alkali-activated metallurgical slag as a sustainable adsorbent

This paper is devoted to obtaining a zeolite-containing sorbent based on metallurgical waste — slag. The synthesis of zeolite adsorbent from ash and slag was carried out by hydrochemical and thermal treatment. The initial object and the obtained material were characterized using following methods: Fourier-transform infrared spectroscopy, scanning electron microscopy, energy dispersive analysis, X-ray phase analysis, titrimetry. The way of converting solid-phase waste into a beneficial product has been demonstrated. The study results showed that the surface of the obtained material is saturated with functional groups (hydroxy-, carboxy-, lactone), which predetermine the ability to bind metal ions during adsorption. The adsorption capacity of the product has been estimated for iodine and methylene blue. A thermodynamic analysis of the process of sorption of copper (II) ions from an aqueous solution has been conducted. It has identified that the sorbent can also be used for the adsorptive concentration of ions of rare-earth elements by the example of lanthanum and erbium. Laboratory testing of the possible use of the sorbent to purify industrial water was carried out using the example of wastewater from a chromium plating shop.

Keywords: metallurgical slag, recycling of slag, sorbents, sorption, absorption capacity, d-, f-metals ions, wastewaters purification, sorption isotherms, thermodynamics of adsorption.

Introduction

Zeolite materials are of great fundamental and industrial importance and widely used as commercial adsorbents and catalysts. All the unique properties of zeolites are specified with their structure based on porous aluminosilicates formed by a combination of tetrahedral $[SiO_4]_4^-$ and $[AlO_4]_5^-$. One way to obtain them is to converse metallurgical wastes into zeolites; however, the phase composition of the material obtained by the hydrochemical pathway is controlled by various factors such as temperature, type of modifying agent and its concentration, pH of the media, etc. [1–5].

The purification of natural and industrial water bodies from copper ions is a significant environmental issue due to its relatively high toxicity. The threshold limit value (TLV) for copper ions in drinking and sanitary waters for domestic and industrial use is 1 mg/L, then 0.001 mg/L is for reservoirs of fish economic purpose. Thus, practice shows the residual concentration of Cu in water purified at pH level from 8 to 9 is 0.1–0.2 mg/L generally, which conforms to theoretical calculations on the solubility of copper hydroxide in aqueous solutions [6, 7]. This issue may be solved by applying sorption methods of purification with inorganic sorbents. However, even though a considerable amount of research focused on an in-depth investigation of how to turn slag into a beneficial material (in this case, adsorbent), many open questions should be answered to clarify this mechanism [7–13].

This paper aims to demonstrate the behavior of the alkali-treated metallurgical slag in the water purification by testing it for both model metal-containing solutions and in industrial multi-component water system.

Experimental

The solid-phase waste of the metallurgy plant "ArcelorMittal Temirtau" was applied as a raw material. The technique that consists of two stages is used to design the adsorbent. Firstly, the initial material has been washed with distilled water for 48 h, then has been dried at room temperature. The ratio of S/L was one to ten (by weight). The intermediate was treated thermally in the muffle furnace at the temperature of 600 °C for 90 min. in the presence of sodium hydroxide solution (2 mol/L) used as a modifying agent. The ratio of S:L was the same. The final product has been tested for the adsorption properties.

The following methods have been applied to characterize the material synthesized: X-ray Powder Diffraction (XRD) analysis was conducted using the DRON-4-07 diffractometer. The scanning electron microscope Hitachi TM3030 with microanalysis system Bruker X Flash MINSVE (accelerating voltage of 15 kV) has been used to determine the elemental composition and structural features of the adsorbent. Finally, the IR-spectra of the samples have been taken by FTIR-spectrometer FSM-1201.

The concentration of functional groups concentrated on the adsorbent's surface has been determined by the Boehm method described in [14]. In addition, the material capacity in the adsorption toward iodine and methylene blue has been estimated by well-known procedures [15, 16]. Regarding the adsorption tests, samples of industrial multi-component waters have been taken to purify by the adsorption in a static mode at a temperature of 298 K. The duration of this treatment was 30 minutes. The analyte's volume of each portion was 20 ml, the mass of adsorbent for each test was 0.5 g. Both spectrophotometry and titration methods have been used to detect initial and residual concentrations of metal ions. The chemical composition of the water taken from industry has been detected by the XRF method (on the X-MET 8000 GEO portable X-ray fluorescence analyzer) before and after the adsorption tests.

The adsorption experiments with the wastewater taken from the industry were carried out at the following conditions: temperature was 293 K, mass of each portion of the sorbent was 0.5 g, the duration of the adsorbent/adsorbate contact was 19 h in the static mode. The stirring frequency with a magnetic router was 500 rpm. Three parallel series of purification experiments were performed.

Results and Discussion

It is known that the bulk of solid wastes like ashes and slags consists of both macroelements (Al, Fe, Ca, Si, Mg, S, C), which are significant constituents of mineral rocks, and microelements as minor components [17].

Experimentally (based on XRD analysis), the phase composition of the slag has included $Ca_5Al_2(OH)_4Si_3O_{12}$, Fe_2O_3, $Mg_3Al_4TiO_{25}$, MnS, and $KOH \cdot H_2O$ that are likely to be products of the coal agglomeration. However, after the thermal treatment experienced by the slag sample, which had dried before, there was a radical change in color that turns from greyish to light blue (Fig. 1), which can be caused by phase transformations.

| I | II |

Figure 1. The slag dispersed of the metallurgical enterprise "Arcelor Mittal Temirtau" (I);
sorbent obtained after alkaline treatment (II)

The elemental composition of the material has been determined by the energy dispersive X-Ray analysis (EDXRA) (Fig. 2, 3); the ratio of Si/Al is 20.62 approximately, which is consistent with high-silica zeolites (Si/Al ratio for them is from 10 to ∞) [18].

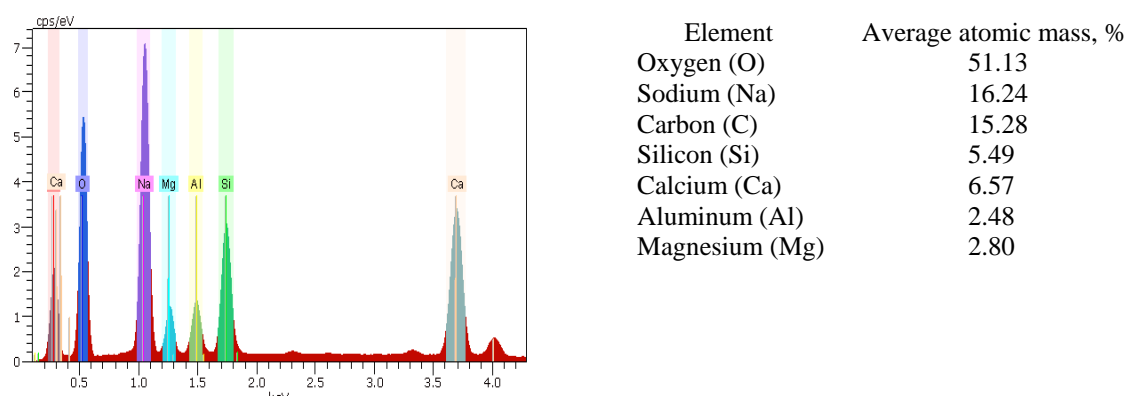| Element	Average atomic mass, %
Oxygen (O)	51.13
Sodium (Na)	16.24
Carbon (C)	15.28
Silicon (Si)	5.49
Calcium (Ca)	6.57
Aluminum (Al)	2.48
Magnesium (Mg)	2.80

Figure 2. The EDXRA spectra and elemental composition of alkali-treated metallurgical slag
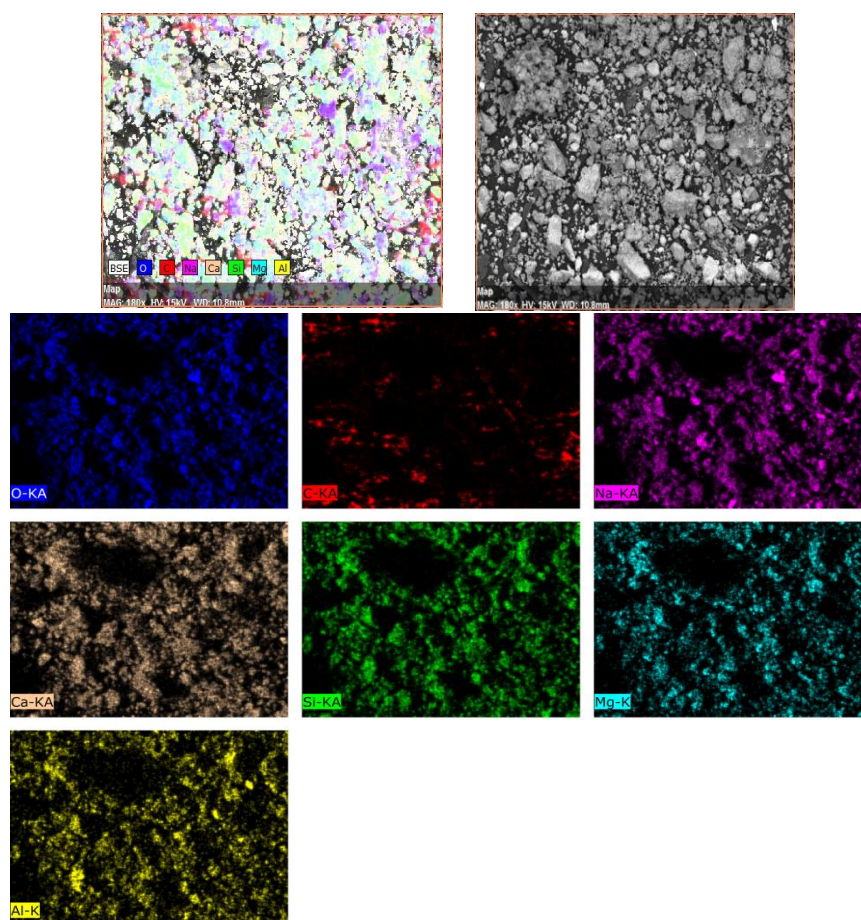
Figure 3. EDXRA pictures of alkali-treated metallurgical slag

The FTIR spectra of the studied samples can be conditionally divided into three frequency regions <470–1600, 1600–2900, and >2900 cm^{-1} (Fig. 4).
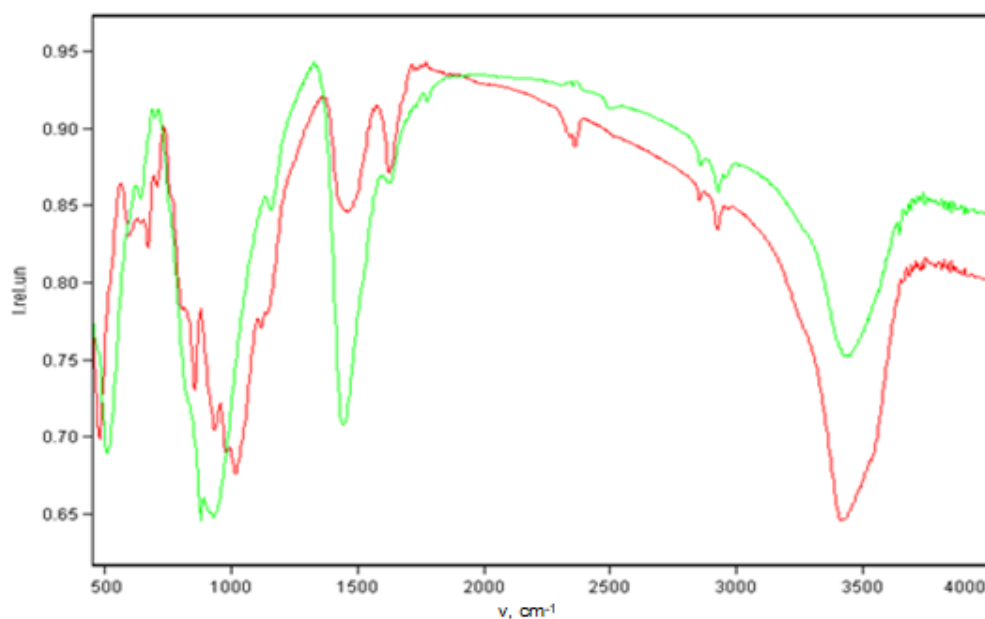

Figure 4. FT-IR spectra of the initial slag (green) and the alkali-treated sample (red)

The first region (<470–1600 cm^{-1}) includes vibration bands of Si-O (Si), SO_4^{2-}, Al-OH, Si-O groups. The prominent absorption bands present in all spectra are rather intense bands at 777 cm^{-1}. Since the Si-O

bond is common for all silicates and clay materials, it may be assumed that the absorption bands in the region of 777–1135 cm^{-1} are mainly due to the stretching vibrations of Si-O.

Because of alkaline treatment, changes occur on the material surface, which are observed in the FTIR spectrum in the form of a shift of absorption bands in one direction or another. For example, the absorption band at 509 cm^{-1} is shifted to the left by 19 cm^{-1}. The absorption band at 928 cm^{-1} has shifted to the right by 155 cm^{-1}. The intensity of the absorption band at 1442 cm^{-1} due to alkaline treatment decreases by a 0.15 relative unit (a.u.).

It can be seen from the above spectra that in the second region (1600–2900 cm^{-1}), the intensity of the absorption band at 2350 cm^{-1} as a result of alkaline treatment of the material increases by 0.05 a.u. The intensity of the absorption band at 2800–2900 cm^{-1} due to alkaline treatment increases by 0.02–0.03 relative units.

The third region > 2900 cm^{-1} is mainly associated with the stretching vibrations of OH-groups its presence can be seen at absorption band 3435 cm^{-1}. Absorption in the region of 3440–3738 cm^{-1} is presented as bands associated with vibrations of free O-H groups. An absorption band at 3435 cm^{-1} increases by 0.07 a.u. in the intensity after the alkali treatment.

In addition, there is a growth in the intensity of the absorption band at 3647–3738 cm^{-1} by 0.04 a.u. after the treatment.

The results of the Boehm method based on acid-base titration have revealed that there are carboxyl, hydroxyl and lactone groups on the adsorbent surface (Table 1).

T a b l e 1

Content of carboxyl-, hydroxyl and lactone functional groups in the sorbent sample

Functional group	Total	Hydroxyl groups	Carboxyl groups	Lactone groups
Concentration [mmole/g]	1.06	0.44	0.30	0.32

According to [14], the adsorbent samples were examined for the adsorption concentration of iodine and methylene blue (MB) (Table 2).

T a b l e 2

Adsorption capacity of the sorbent synthesized toward iodine and MB

Adsorbate	Adsorption capacity	
	Carbon sorbent [17–18]	Synthesized sorbent
Iodine X, %	25.00	13.65
Methylene blue A, mg/g	40.00	55.00

It is found that sorbent has an adequate sorption capacity towards both substances. Nevertheless, compared to the carbon sorbent, the slag-based one works better for MB, while the former one is approximately twice efficient for iodine. Generally, it should be assumed zeolite-templated sorbent is applicable for the capture of organic and inorganic pollutants.

As for the capture of metal ions, copper was chosen for the adsorption tests. Figure 5 demonstrates the dependence of the adsorption capacity (a_e) on pH, and the highest a_e values have been achieved at pH 4,6–7.

However, these high indexes in the pH range 6–7 are likely to be related to the impact of hydrolysis that foster copper (II) hydroxide to form and precipitate. At pH 4, the deprotonation of hydroxyl groups increases the number of negatively charged centers on the sorbent surface. Since a negative charge raises the electrostatic gravitational force on the surface of sorbent and metal ions, the latter ones begin to concentrate on the sorbent surface quickly. Thus, further experimental tests were carried out at pH 4.

The adsorption isotherms for the pair consisting of alkali-treated slag as adsorbent and Cu^{2+} ions as adsorbate (at 318 K, under static conditions) are presented in Figure 6.
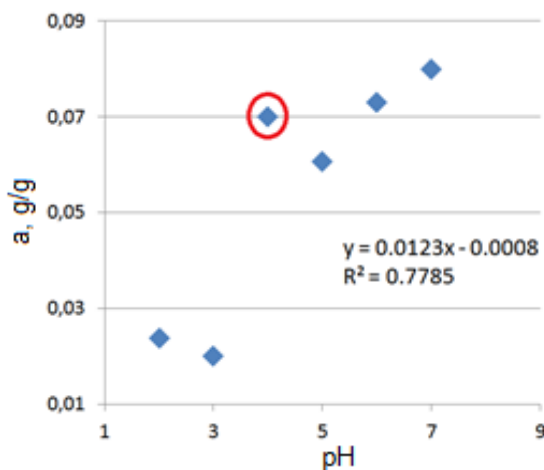
Figure 5. Effect of pH on the adsorption of copper (II) ions by the slag-based sorbent in aqueous solutions
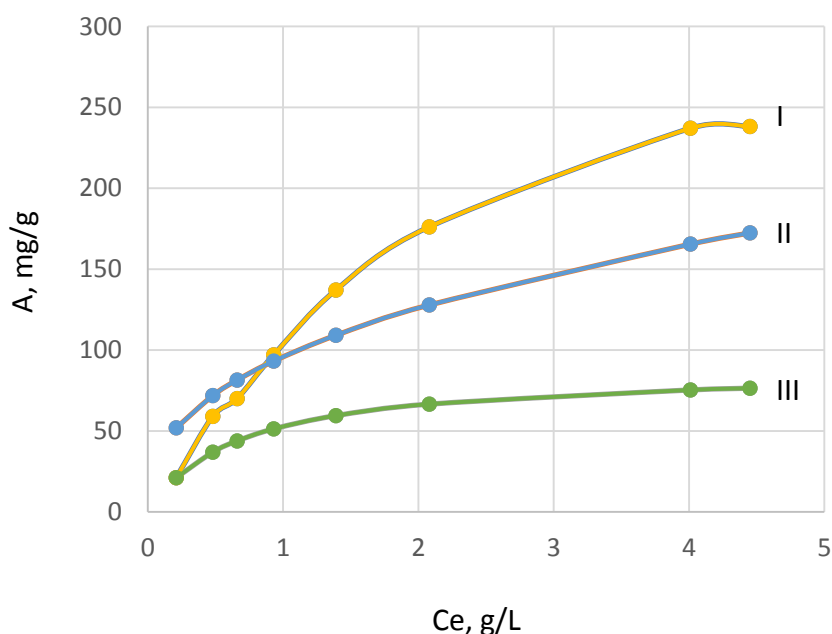

Figure 6. Adsorption isotherms Cu(II) onto sorbent at 318 K and pH 4: plotted from experimental data (I).
Theoretical isotherms Freundlich (II) and Langmuir (III)

There is a level off at 4 g/L with the degree of purification of ≈88.72 % (Fig. 6(I)). In [19], authors have compared the adsorption capacities of copper (II) ions on various low-cost adsorbents: diatomite (27.55 mg/g) and modified diatomite (55.56 mg/g) [20], cassava waste (56.82 mg/g) [21], dehydrated wheat bran (51.51 mg/g) [22]; around low concentrations up to 1 g/L the sorbent investigated is likely to be the alternative to them. If the metal concentration is higher than 1 g/L, the adsorbent behaviors likely the materials based on citric acid modified soybean hulls (154.90 mg/g) [23], modified orange peel (289 mg/g) [24] or nanoporous metal-organic framework MOF-5 (290 mg/g) [24].

Next, the experimental adsorption isotherm was processed using the Langmuir and Freundlich equations. By comparing the approximation coefficients and the location of isotherms on the diagram can be concluded Freundlich's model is more suitable for this case. Finally, the thermodynamic parameters that describe Cu(II) adsorption onto the slag-based sorbent from aqueous solutions have been calculated (Table 3).

**The adsorption constants for the Freundlich model and thermodynamic parameters
of the adsorption of Cu(II) ions onto the sorbent**

Value	298 K	318 K
1/n	0.41	0.39
$K \cdot 10^{-3}$	0.096	0.090
Correlation coefficient	0.97	0.99
$-\Delta H$, kJ/mole	2.29	
$-\Delta G$, kJ/mole	11.16	12.06
ΔS, J/mole·K	29.77	30.73

The values of the isobar-isothermal potential have a negative sign that indicates the spontaneous character of the adsorption. The higher temperature is, the higher are the Gibbs energy values. The chemisorption type of adsorption can be predicted on the basis of the change in enthalpy equal to -2.29 kJ/mole. The positive value of the change in entropy is likely to correspond to the feasibility of adsorption and the randomness that is raised at the sorbent/solution interface due to the adsorption of metal ions onto the slag-based material.

Besides that, the zeolite-templated sorbent is used to concentrate rare metals ions from aqueous solutions on the example of lanthanum (III) and erbium (III) (Table 4).

Concentration of La^{3+}, Er^{3+} ions on the sorbent surface

Metal ions	r_{ion}, pm	a, mole/g	X, %
La^{3+}	101	$5 \cdot 10^{-4}$	99.80
Er^{3+}	226	$5 \cdot 10^{-5}$	99.90

Thus, the results demonstrated that the level of extraction is high for both La and Er. The literature review of the La(III) sorption capacities of different sorbents, illustrated that though the different experimental conditions, the reported materials has comparable sorption capacities: SnO_2–TiO_2 NCs nanocomposites [26] and polydopamine/nanofibrous mats [27], showing 0.473 and 0.429 mmole/g, respectively. That is close to the sorbent with 0.50 mmole/g in this work (Table 4), whilst grapefruit peel has an adsorption capacity of 1.233 mmole/g [28]. As for Er(III) ions, the sorbent based on rice husk demonstrates the monolayer capacity of 250 mg·g^{-1} for Er(III) [29] that is higher than the material developed has.

Regarding the purification of industrial waters, the investigated sorbent has been tested toward the wastewater that is oversaturated with metals ions from the chromium plating shop of the metallurgical plant "ArcelorMittal Temirtau". The following diagrams (Fig. 7–9) provides the results obtained by comparing the total content of metals before and after the purification (the conditions are presented in *Experimental*).

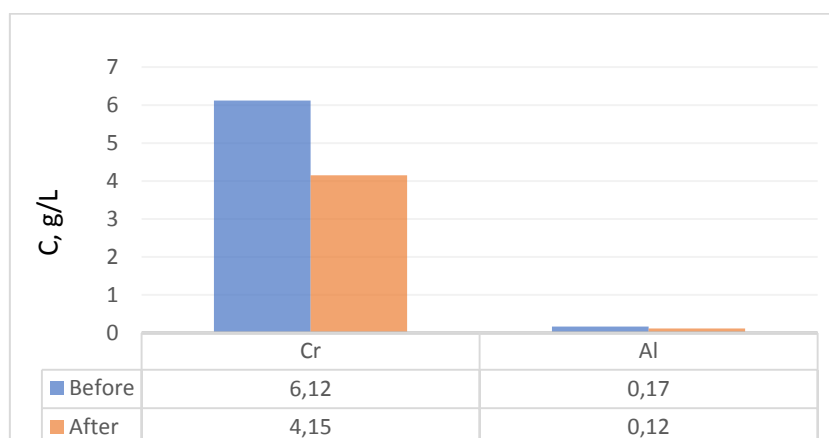|	Cr	Al
Before	6,12	0,17
After	4,15	0,12

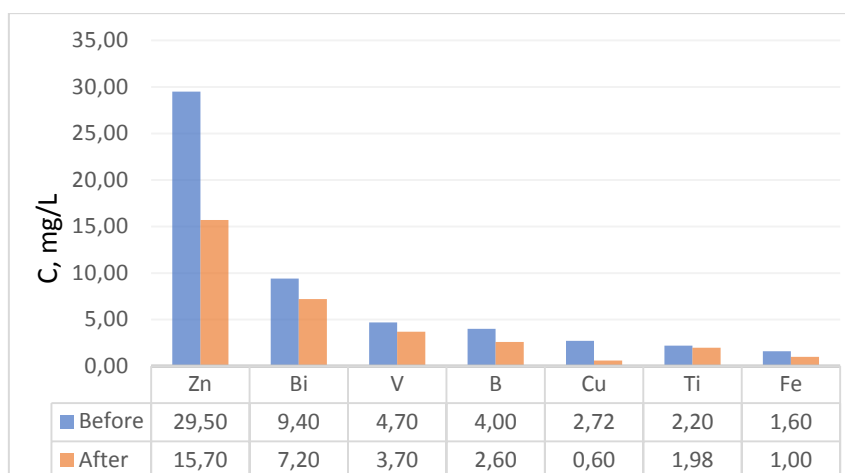Figure 7. The change in the content of Cr and Al in the wastewater before purification and after

Figure 8. The change in the content of Zn, Bi, V, B, Cu, Ti, and Fe in the wastewater before and after purification
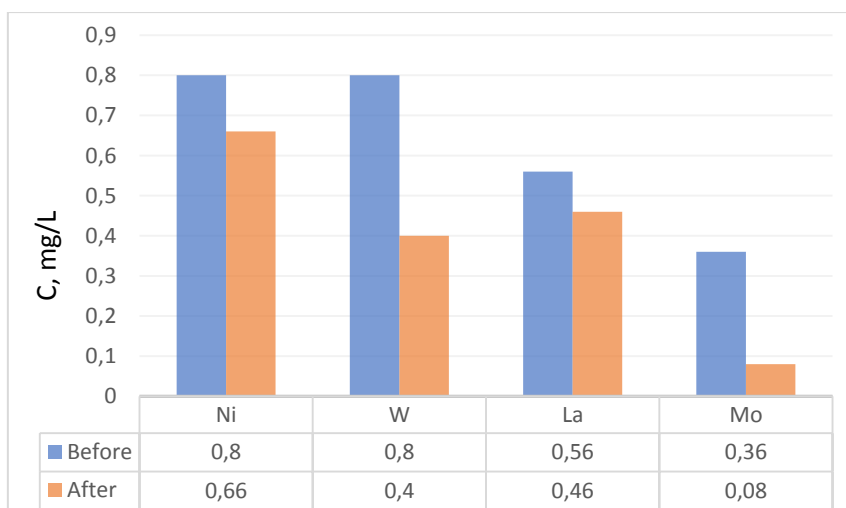
	Zn	Bi	V	B	Cu	Ti	Fe
■ Before	29,50	9,40	4,70	4,00	2,72	2,20	1,60
■ After	15,70	7,20	3,70	2,60	0,60	1,98	1,00

Figure 9. The change in the content of Ni, W, La, and Mo in the wastewater before and after purification

	Ni	W	La	Mo
■ Before	0,8	0,8	0,56	0,36
■ After	0,66	0,4	0,46	0,08

There is an overall trend of decreasing the concentrations for all metals tested. Turning to the details, the amounts of chromium and aluminon as main components have been down by 32.19 and 29.41 %, respectively. Likewise, the concentrations of zinc and wolfram have halved after the adsorption. As for copper and molybdenum, their amount in the wastewater has declined by four times approximately.

Conclusion

To sum up, it may be concluded that zeolite-templated adsorbent obtained by two-stage hydrochemical and thermochemical treatment from metallurgical slag has been influential in wastewater purification based on adsorption.

The possibility of using the sorbent obtained in water purification has been evaluated on the examples of model solutions that contains copper (II) ions and rare metal ions. Besides that, the adsorbent's capacity toward industrial wastewater from the metallurgical enterprise "ArcelorMittal Temirtau" has been estimated. Therefore, it can be assumed that obtained sorbent may be used in the sewage treatment.

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Сілтімен белсендендірілген металлургиялық қож тұрақты сорбент ретінде

Мақала металлургиялық қалдықтар — шлактар негізінде цеолит бар сорбент алуға арналған. Күл мен қождан цеолит адсорбентінің синтезі гидрохимиялық және термиялық өңдеу арқылы жүргізілген. Бастапқы объект және алынған материал келесі талдау әдістерін қолдану арқылы сипатталды: ИҚ-Фурье спектроскопия, сканерлейтін электронды микроскопия, энергия дисперсиялық анализ, рентгендік фазалық талдау, титриметрия. Қатты фазалық қалдықтарды пайдалы өнімге айналдыру тәсілі берілген. Зерттеу нәтижелері көрсеткендей, алынған материалдың беті адсорбция кезінде металл иондарын байланыстыру қабілетін алдын-ала анықтайтын функционалды топтармен (гидрокси-, карбокси-, лактон) қаныққан. Өнімнің адсорбциялық қабілеті йод пен метилен көгіне қатысты бағаланады. Мыс (II) иондарының сулы ерітіндіден сорбциялану процесіне термодинамикалық талдау жасалған. Сорбентті лантан мен эрбий мысалында сирек-жер элементтерінің иондарының адсорбтивті концентрациясы үшін де қолдануға болатындығы көрсетілген. Өндірістік суды тазарту үшін сорбентті қолдану мүмкіндігінің зертханалық сынағы хромдау цехының ағынды суларының мысалында жүргізілді.

Кілт сөздер: металлургиялық қож, қожды өңдеу, сорбенттер, сорбция, сорбция қабілеті, *d*-, *f*-металл иондары, ағынды суларды тазарту, сорбциялық изотермалар, адсорбцияның термодинамикасы.

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Металлургический шлак, активированный щелочью, как устойчивый адсорбент

Статья посвящена получению цеолитсодержащего сорбента на основе отходов металлургического производства — шлака. Синтез цеолитного адсорбента из золошлака проводился посредством гидрохимической и термической обработки. Исходный объект и полученный материал охарактеризованы следующими методами анализа: ИК-Фурье спектроскопия, сканирующая электронная микроскопия, энергодисперсионный анализ, рентгенофазовый анализ, титриметрия. Продемонстрирован путь превращения твердофазных отходов в полезный продукт. Результаты исследования показали, что поверхность полученного материала насыщена функциональными группами (гидрокси-, карбокси-, лактоновые), предопределяющими способность связывать ионы металлов при адсорбции. Адсорбционная емкость продукта оценена по йоду и метиленовому голубому. Проведен термодинамический анализ процесса сорбции ионов меди (II) из водного раствора. Показано, что сорбент может быть использован и для адсорбционного концентрирования ионов редкоземельных элементов на примере лантана и эрбия. Кроме того, произведена лабораторная апробация возможного применения сорбента для очистки промышленных вод на примере сточной воды цеха хромирования.

Ключевые слова: металлургический шлак, переработка шлака, сорбенты, сорбция, сорбционная емкость, ионы *d*-, *f*-металлов, очистка сточных вод, изотермы сорбции, термодинамика адсорбции.

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