СОРБЦИОННАЯ ОЧИСТКА СТОЧНЫХ ВОД ОТ ОРГАНИЧЕСКИХ КРАСИТЕЛЕЙ С ПОМОЩЬЮ ГРАНУЛИРОВАННОГО ДОМЕННОГО ШЛАКА

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Определены свойства гранулированного доменного шлака «АрселорМиттал Кри вой Рог», обусловливающие его сорбционную активность. В составе фракций шлака идентифицированы минералы: окерманит Ca₂MgSi₂O₇, геленит Ca₂Al(Al,Si)₂O₇, ранкинит Ca₃Si₂O₇, псевдоволластонит CaSiO₃, микроклин КАlSiO₃, кальцит CaCO₃, ольдгами CaS с содержанием алюмосиликатов кальция и магния > 50%. Некоторые фазы находятся в аморфном сорбционно-активном состоянии. Показана целесообразность активации шлака водой в течение 1 сут, в результате которой на поверхности образуются и диссоциируют гидроксильные и силанольные группы с формированием отрицательного заряда поверхности шлаковых частиц, что характерно для алюмосиликатов Ca и Mg, а также минералов кальцита и ольдгамина. Форма изотермы адсорбции свидетельствует об образовании полимолекулярных слоев органического красителя метиленового синего (МС), что увеличивает эффективность шлакового сорбента. Величина адсорбции МС не менее 2 мг/г. Показано отсутствие десорбции МС из шлака, что обеспечивает безопасность как захоронения отработанного сорбента, так и его утилизации в качестве наполнителя строительных материалов. Доказана радиационная безопасность шлака. Удельная эффективная активность фракций шлака не превышает 370 Бк/кг, что разрешает их использование в качестве технических материалов без ограничений. Показана радиационная безопасность шлака. Удельная эффективная активность фракций шлака не превышает 370 Бк/кг, что разрешает их использование в качестве технических материалов без ограничений. Предложена технологическая схема адсорбционной очистки сточных вод предприятий органического синтеза и текстильной промышленности, содержащих органические красители, с помощью шлакового сорбента. Стадии технологического процесса: поступление шлака из отвала, анализ минерального состава шлака, водная активация шлака, статическая сорбция красителей в отстойнике, дальнейшая утилизация шлака, поступление очищенных вод в первичное производство. Технология предусматривает удаление органических красителей из сточных вод и их повторное использование, что обеспечивает замкнутость цикла оборотного водопотребления, отсутствие расхода химических реагентов на активацию шлакового сорбента, улучшение экологической ситуации в местах расположения шлаковых отвалов за счет использования шлаков в качестве сорбентов.

Ключевые слова: сорбция, гранулированный доменный шлак, органические красители, величина адсорбции, активация шлака, адсорбционный процесс, очистка раствора

SORPTION PURIFICATION OF WASTEWATER FROM ORGANIC DYES USING GRANULATED BLAST-FURNACE SLAG

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The properties of granulated blast-furnace slag from “ArcelorMittal Krivoy Rog”, which stipulate its sorption activity, have been determined. The following minerals were identified in the slag fractions: akermanite Ca$_2$MgSi$_2$O$_7$, helenite Ca$_2$Al(Al,Si)$_2$O$_7$, rankinite Ca$_2$Si$_2$O$_7$, pseudowollastonite CaSiO$_3$, merwinite Ca$_2$MgSi$_2$O$_8$, microcline KAlSi$_3$O$_8$, calcite CaCO$_3$, aldhahmite CaS with > 50% of calcium and magnesium aluminosilicates. Some phases are in an amorphous sorption-active state. The expediency of activation with water for 1 day is shown, due to which hydroxyl and silanol groups are formed and dissociated on the surface with the formation of a negative charge on the surface of slag particles, which is typical for Ca and Mg aluminosilicates as well as minerals calcite and aldhahmite. The shape of the adsorption isotherm indicates the formation of polymolecular layers of the methylene blue (MB) organic dye, which increases the efficiency of the slag sorbent. The adsorption value of MB is not less than 2 mg/g. There is obviously no desorption of MB from the slag, which ensures the safety of both the disposal of the waste sorbent and its utilization as a filler for construction materials. The radiation safety of the slag has been proven. The specific effective activity of slag fractions does not exceed 370 Bq/kg, which allows using them as technical materials without restrictions. A technological scheme of adsorption purification of wastewaters from organic synthesis enterprises and textile industry containing organic dyes, is suggested using a slag sorbent. The stages of the technological process are the following: receiving the slag from the dump, analysis of the mineral composition of the slag, water activation of the slag, static sorption of dyes in the sump, further utilization of the slag and the inflow of purified water into the primary production. The technology provides for the removal of organic dyes from wastewater and its repeated usage, which ensures the closed cycle of water reuse, no need for chemical reagents for the activation of the slag sorbent, improvement of the environmental situation in the locations of the slag dumps due to the use of slags as sorbents.

**Key words:** sorption, granular blast-furnace slag, organic dyes, adsorption value, slag activation, adsorption process, solution purification

**INTRODUCTION**

In adsorption technologies, it is possible to use various materials of natural and industrial origin [1]. The introduction of low-waste technologies makes it necessary to identify the resource value and useful properties of industrial waste, to substantiate the expediency of their disposal as technical materials and sorbents when purifying industrial wastewater. The efficiency of wastewater treatment with the help of technogenic sorbents can reach 95% [2]. The possibilities of using various types of industrial waste are shown: sorption of phosphate ions has been proven on red mud [3], the modified waste of cellulose textile waste is used to purify wastewater from metal ions [4], thermally modified carbon-containing shungite in combination with Al oxychloride is used in combined wastewater purification from Fe (III) [5]. Materials of inorganic origin can also be used for the sorption of organic compounds, for example, oil products [6] or phenol [7] in a batch adsorption mode using modified industrial solid waste in the presence of cationic and anionic surfactants. Sorption of the cationic surfactant [CH$_3$(CH$_2$)$_3$N(CH$_3$)$_3$]Cl with an adsorption value of 12.8 mg/g was carried out on slag cement [8]. It has been shown that the textile dye Reactive Blue 19 is absorbed by bentonite modified with a cationic surfactant [9]. Coal fly ash is successfully used for sorption of organic dyes [10-12]. The sorption of Acid Brown 75 and Direct Yellow 162 dyes onto unmodified and modified by surfactant Hexadecyltrimethylammonium Bromide granules developed from coal fly ash was carried out [13]. Layered silicates modified with cationic polyelectrolytes adsorb anionic organic dyes [14]. An ecological-chemical assessment of metallurgical slags as sorbents was carried out with the determination of the direction of practical use [15,
The sorption of methylene blue (MB), Congo red (CR) and methyl violet (MV) by metallurgical slag from Fe-Ni alloy production with the main mineral diopside CaMg(Si₂O₆) was studied [17, 18].

Objective of the research. To substantiate the possibility of using granulated blast-furnace slag from “ArcelorMittal Krivoy Rog” as a sorbent for organic dyes with the development of a technological scheme for adsorption wastewater purification with ensuring the closed cycle of water reuse. To achieve the goal, it is necessary to determine the mineralogical composition of the slag, prove its radiation safety, characterize the slag surface (specific surface area, particle charge), determine the sorption activity of the slag in relation to MB, prove that there is no desorption of MB from the slag.

Methods of the research. The mineralogical composition of the slag was determined using X-ray phase analysis carried out on a Siemens D500 powder diffractometer in copper radiation with a graphite monochromator. The primary search for phases was carried out using the PDF-1 card index [19], the calculation of X-ray patterns was performed by the Rietveld method using the FullProf program [20].

Micrographs of the surface of slag particles were obtained using a JSM-6390 LV scanning electron microscope.

Specific activities of natural slag radionuclides (At) were determined by gamma-spectrometric method using a scintillation gamma-spectrometer SEG-001. Based on the results of the gamma-spectrometric study, the values of the specific effective activities of the slag fractions \( A_{ef} \) were calculated using the formula [21]:

\[
A_{ef} = A_{Ra} + 1.31A_{Th} + 0.085A_K, \text{ Bq/kg.}
\]

The organic dye MB sorption by slag was studied spectrophotometrically using SPEKOL 11. The slag adsorption value \( a \) was calculated by the formula:

\[
a = \frac{(C_1 - C_2) \cdot V}{m} \text{, mg/g}
\]

where \( C_1 \) and \( C_2 \) are sorbate (MB) concentrations before and after the sorption respectively, mg/dm³; \( V \) – is the solution volume, dm³; \( m \) – is the mass of the sorbent, g. Initial dye concentrations were 10-20 mg/dm³, which is comparable to the concentration ranges of dyes in the washings of the textile industry.

The specific surface area \( S \) of the slag, determined by the air permeability method on the TQD-G1 device, is 1625 cm²/g for the slag fraction < 0.63 mm. The small value of \( S \) indicates insufficient development of the slag surface to be the main reason for its sorption activity.

The charge of particles and the magnitude of the electrokinetic potential are determined during macroelectrophoresis of slurry suspensions. Granulometric slag fraction < 0.63 mm was used. The presence on the surface of the slag of silanol groups dissociating with the cleavage of \( H^+ \) determines the negative charge on the surface of the slag particles. The electrokinetic potential was calculated by the formula that takes into account the movement of the suspension border to the positive electrode \( (h = 2.633 \text{ mm}) \) and the time of movement of the suspension border (659.5 s). The value of \( \xi \)-potential 11.7 mV corresponds to the average \( \xi \)-potential for mineral suspensions with conditionally spherical particles.

RESULTS AND DISCUSSION

Mineralogical composition of the slag. X-ray phase analysis of the slag showed the presence of mineral phases (fraction > 10 mm), %: calcite CaCO₃ (33.2), akermanite Ca₂MgSi₂O₇ (5.5), helenite Ca₃(Al(Si₃)O₇) (24.6), rankinite Ca₃Si₂O₇ (4.8), pseudowollastonite CaSiO₃ (4.3), merwinite CaMgSi₂O₈ (6.1), microcline KAlSi₃O₈ (6.5), oldhamite CaS (15.1). The wavelike nature of the slag diffraction patterns is associated with the presence of amorphous phases. X-ray diffraction patterns of slag fractions < 0.63 mm and 1.25-2.5 mm show a diffuse maximum against the background in the range of angles 20-40°. The glassy structure is visible on micrographs of slag particles belonging to different fractions (Fig. 1). With rapid cooling, granular slags do not have time to completely crystallize, therefore they possess a chemical, sorption and hydraulic activity. Thus, the sorption properties of the slag can be explained by the high concentration (> 50%) of Ca and Mg aluminosilicates and the presence of amorphous compounds.

Slag radionuclide composition. When using slags as sorbents, their radiation safety must be ensured. The most probable mechanism for the accumulation of natural radionuclides is heterovalent isomorphic substitution in the structures of slag minerals [22]. Table 1 shows the results of gamma spectrometric analysis of slag fractions. The radionuclide composition of the fractions differs from each other, especially in the \(^{40}\)K isotope. The \(^{232}\)Th activity does not change significantly. \( A_{ef} \) increases by 1.35 times with increasing dispersion of fractions and reaches a maximum value of 91 Bq/kg. The highest \( A_{ef} \) values were recorded for fine fractions < 1.25 mm. Coarse fractions > 5 mm are the most radiation-pure. However, the \( A_{ef} \) value of the average sample and all slag fractions does not exceed 370 Bq/kg; therefore, slag fractions can be used without restrictions as a technical material [21].
**Fig. 1**. Micrographs of the surface of granulated blast-furnace slag particles at a magnification of 300, fraction, mm: a – 1.25–2.5; b – > 10

**Fig. 2**. Isotherm of MB adsorption by granular blast-furnace slag activated with water for 1 day \((T = 298 \text{ K}, C_{\text{MB}} = 20 \text{ mg/g})\)

**Sorption characteristics of the slag.** The main quantitative characteristic of the slag sorption activity – the adsorption value \((a)\) – was determined in a static mode. Chemical activation with water and solutions of 0.5 M H$_2$SO$_4$ and 1 M NaOH, tested to increase the sorption activity of the slag, showed that the value of adsorption \(a_{\text{MB}}\) for a certain period of time does not depend on the type of activator. Within 24 h, \(a\) reaches a value of 0.2 mg/g. With a slight variation in the rate of sorption after the effect of various activators, in order to save chemical reagents and eliminate the stage of washing the slag from the activator, water pre-treatment for 24 h is recommended. An adsorption isotherm was constructed according to the experimental data (Fig. 2).

The adsorption value does not reach the limiting value with an increase in the equilibrium concentration of MB \((C_{\text{eq}})\). This indicates a high efficiency of adsorption with the formation of a polymolecular layer of organic dye on the surface of the sorbent.

The efficiency of cleaning wash water with an MB concentration of 20 mg/dm$^3$ was tested within 5 days and was, \%,: 97.5 (1 day), 99.9 (3 days); 99.95 (5 days).

The slag, which was sorbing MB until the maximum \(a\) was reached, was stored in water for 30 days, after which MB was not detected in the control water samples. Thus, the efficiency of adsorption is confirmed by the absence of MB desorption from the slag.

Earlier in [18], it was shown that a slag sorbent based on the diopside mineral adsorbs organic dyes MB, Congo red (CR), and methyl violet (MV). The common feature of this sorbent with the sorbent based on granular blast-furnace slag studied in this work is the presence of hydroxyl and silanol groups formed upon contact with water and causing a negative surface charge. The dyed ion of MB is positively charged and is adsorbed mainly on electronegative (acidic) adsorbents. Polar adsorption is accompanied by ion exchange between the sorbent and the solution. The retention of the large ion of the dye on the surface of the sorbent is facilitated by dispersion forces. The adsorbed aromatic compounds have a sufficiently large constant dipole moment due to which induction electrostatic interaction with the sorbent surface occurs. The nature of the interaction of slag adsorbents and organic compounds indicates the occurrence of specific, irreversible activated adsorption, which is confirmed by the virtual absence of desorption of organic compounds from the waste sorbent. The chemical inertness of slag minerals exhibits with a simultaneous manifestation of sorption activity.

<table>
<thead>
<tr>
<th>Granulometric fraction, mm</th>
<th>(A_{\text{cl}}), Bq/kg</th>
<th>(A_{\text{c}}), Bq/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average sample</td>
<td>127±15</td>
<td>116</td>
</tr>
<tr>
<td>&gt; 10</td>
<td>117±17</td>
<td>209</td>
</tr>
<tr>
<td>5-10</td>
<td>119±18</td>
<td>244</td>
</tr>
<tr>
<td>2.5-5</td>
<td>131±18</td>
<td>269</td>
</tr>
<tr>
<td>1.25-2.5</td>
<td>153±19</td>
<td>369</td>
</tr>
<tr>
<td>0.63–2.5</td>
<td>157±19</td>
<td>368</td>
</tr>
<tr>
<td>&lt; 0.63</td>
<td>161±19</td>
<td>391</td>
</tr>
</tbody>
</table>

Table. Results of gamma-spectrometric analysis of granular blast-furnace slag fractions

**Fig. 2.** Isotherm of MB adsorption by granular blast-furnace slag activated with water for 1 day \((T = 298 \text{ K}, C_{\text{MB}} = 20 \text{ mg/g})\)

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Technological scheme of adsorption purification of wastewater from organic dyes with ensuring the closed cycle of water reuse. The scheme (Fig. 3) can be used at organic synthesis enterprises and textile industries. Granular blast-furnace slag from dump 1 goes to block 2 for mineral composition analysis. If the mineral composition meets the necessary requirements, the slag is activated by water in reservoir 3. The water can be used repeatedly to activate the portions of the slag sorbent. Periodic adjustment of the water volume is provided. After activation, the slag sorbent enters tank 4 of the adsorption wastewater purification, where the dyed wastewater from enterprise 5 enters. When the process is carried out under static sorption conditions on the slag, the concentration of organic dyes in industrial wastewater is significantly reduced. The holding period is 3 days. After the end of the cycle in adsorber 4, the purified water enters the technological process at the consumer enterprise. The cycle of water reuse is closed.

For the purification of 1 m$^3$ of wash water with an MB concentration of 10-20 mg/dm$^3$, taking into account the value of slag adsorption for 1 day $a = 0.2$ mg/g, 50-100 kg of slag will be required.

CONCLUSIONS

The sorption activity and efficiency of granulated blast-furnace slag from “ArcelorMittal Krivoy Rog” as a sorbent is determined by the aluminosilicate composition of the slag, the presence of compounds in the amorphous state, the negative charge of the slag particles surface, the adsorption value of $\geq 2$ mg/g, the formation of a polynuclear molecular layer of MB on the surface of the slag, the absence of MB desorption, radiation safety.

The proposed adsorption purification of wastewater from organic dyes will offer to saving water resources and solving the environmental problems of the accumulation of solid waste from metallurgy when used as sorbents. The absence of MB desorption from the waste slag sorbent ensures the efficiency of the adsorption process.

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