АДСОРБЦИЯ ОРГАНИЧЕСКИХ КРАСИТЕЛЕЙ НА МЕТАЛЛУРГИЧЕСКОМ ШЛАКЕ ПРОИЗВОДСТВА СПЛАВА Fe-Ni

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Определены оптимальные параметры адсорбции органических красителей на металлургическом шлаке производства сплава Fe-Ni Побужского ферроникелевого комбината, Украина: рН, массовое соотношение «краситель: шлаковый адсорбент», вид химической активации в зависимости от режима адсорбционного процесса. Сорбция шлаком органических красителей (метиленового синего МС, Конго красного и метилвиолета MB) изучена спектрофотометрическим методом. Показано, что на поверхности шлака при кислотной и щелочной активации формируются поверхностные адсорбционные центры: гидроксильные и силанольные группы, диссоциация которых обусловливает отрицательный заряд поверхности частиц. Наиболее целесообразно использование соотношения «МС : шлак» = 1 мг/г, при котором величина адсорбции а = 0,92 мг/г регистрируется при эффективности очистки 92%. Максимальная эффективность адсорбции МС шлаком на основе диопсида зарегистрирована в области рН 4,8–10,4. Определена зависимость вида химической активации шлака от режима сорбции органических красителей. Кислотная активация шлака целесообразна при статическом режиме сорбции МВ; щелочная — в условиях динамической сорбции MB с невысокой скоростью прохождения раствора через слой сорбента. Шлаки на основе диопсида целесообразно использовать в качестве адсорбента органических красителей на уровне их низких концентраций при локальной очистке сточных вод, образующихся при определенных технологических операциях.

Ключевые слова: металлургический шлак, адсорбционный процесс, активация шлака, очистка раствора, органические красители, величина адсорбции, эффективность очистки, рН

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ADSORPTION OF ORGANIC DYES ON METALLURGICAL SLAG OF Fe-Ni ALLOY PRODUCTION
The optimal parameters of organic dyes adsorption on the metallurgical slag of the Fe-Ni alloy production of the Pobuzhsky Ferronickel Plant, Ukraine: pH, the mass ratio “dye: slag adsorbent”, the type of chemical activation depending on the mode of the adsorption process were determined. Sorption of organic dyes (methylene blue MB, Congo red and methyl violet MV) by slag was studied spectrophotometrically. It is shown that after acid and alkaline activation the surface adsorption centers are formed on the surface of the slag: hydroxyl and silanol groups, whose dissociation causes a negative charge of the particles surface. The most appropriate ratio is “MB : slag” = 1 mg/g, at which the adsorption value a=0.92 mg/g is recorded at a treatment efficiency of 92 %. The maximum efficiency of MB adsorption by slag based on diopside was recorded in the pH range of 4.8-10.4. The dependence of the type of chemical activation of slag with basic mineral – diopside on the sorption mode of organic dyes was determined. Slag acid activation is advisable in the static mode of MV sorption; alkaline – under conditions of MV dynamic sorption with a low rate of solution passage through the sorbent layer. Diopside-based slag is expedient to use as an adsorbent of organic dyes at the level of their low concentrations at the local treatment of wastewater generated during the certain technological operations.

Key words: metallurgical slag, adsorption process, slag activation, solution purification, organic dyes, adsorption value, purification efficiency, pH

INTRODUCTION

The adsorption process with industrial waste as adsorbents solves a number of problems: stimulation of efficient use of resources, elimination of dumps and wastewater treatment [1]. The physical and chemical properties of artificial sorbents used for the treatment of wastewater from oil products have been studied [2]. Heavy metal ions can be extracted from the liquid phase using cellulose-based textile waste [3]. Blast furnace slags and their modifications obtained by treatment with a dilute HCl solution showed high sorption activity for Cu(II) and Pb(II) ions [4]. It was proposed to use red sludge as a waste from Al production for sorption of F- ions with an adsorption efficiency of 97.5% [5]. The authors of [6, 7] proved the possibility of phosphorus sorption from aqueous solutions by red sludge, crystalline and amorphous blast furnace slags. For phenol sorption, it was suggested to use steel slag with preliminary acid treatment of their surface [8].

Sorbents from recycled materials are particularly relevant in treatment and bleaching of the textile industry wastewater containing several types of dyes [9-12]. In [13], the influence of the parameters of the adsorption removal of Ostantren blue textile dye from water using a sorbent obtained by burning brown coal was studied. To increase the sorption efficiency of the methylene blue dye (MB), coal can be activated from sewage sludge of a treatment plant using ZnCl2 [14]. Lignocellulose waste biosorbents are effective for removing MB from aqueous media with cleaning efficiency of 98.5% [15]. The prepared starch-g-polyacrylamide was an effective adsorbent for removal of MB from aqueous solution [16]. The powder of electrostatic precipitators of the cement industry can be used as an inexpensive material for removing Astrazone blue dye from aqueous solutions [17].

Metallurgical slag of the production of the “iron – nickel” alloy from the dump of the Pobuzhsky Ferronickel Plant (PFP), Ukraine, was used as the sorbent. We have previously demonstrated the sorption activity of the slag basic mineral – diopside CaMg(SiO3)2 with respect to the methylene blue dye after preliminary acidic or alkaline activation of the slag. It was shown that the highest adsorption value and the efficiency of MB adsorption from the solution are achieved upon preliminary activation of the slag in a 0.5 M sulfuric acid solution at 20 °C [18, 19].
Objective of the research is to substantiate the expediency of acidic and alkaline activation of slag and to determine the optimal parameters of organic dyes adsorption on the metallurgical slag of the Fe-Ni alloy production: pH, the mass ratio “dye : slag adsorbent”, the type of preliminary chemical activation depending on the mode of the adsorption process.

Methods of the research. The organic dyes (MB, Congo red CR and methyl violet MV) 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 concentrations before and after the sorption respectively, \(\text{mg/dm}^3\); \(V\) – is the solution volume, \(\text{dm}^3\); \(m\) – is the mass of the sorbent, \(g\).

Initial dye concentrations were 10 mg/l, which is comparable to the concentration ranges of dyes in the washings of the textile industry.

The efficiency of the activation methods was evaluated by comparing the infrared absorption spectra of the slag surface. IR spectra were obtained in KBr tablets on a Fourier IR-spectrophotometer SPECTRUM ONE (Perkin Elmer) (Fig. 1).

The charge of particles and the magnitude of the electrokinetic potential are determined during macroelectrophoresis of slurry suspensions. Granulometric slag fractions \((1.0-6.3) \cdot 10^{-4} m\) were used.

RESULTS AND DISCUSSION

Chemical modification of the surface of PFP slags. With the chemical activation of slags the change in the nature and the number of functional groups is observed.

The initial slag (Fig. 1a) is characterized by absorption bands in the area of 1063 cm\(^{-1}\), which are related to the valence asymmetric vibrations of the Si–O–Si siloxane bond [20, 21]. The valence vibrations of water molecules and the main valence vibrations of OH of Si–OH silanol groups [21] cause absorption in the area of 3430 cm\(^{-1}\). In conditions of slag clinkering, thermal dehydroxylation occurs: siloxane groups are formed from silanol when water is cleaved (2).

\[
\text{Si} \overset{\text{OH}}{\text{O}} \text{Si} + \text{Si} \overset{\text{O}}{\text{O}} \text{Si} \rightarrow \text{Si} \overset{\text{O}}{\text{O}} \text{Si} + \text{H}_2\text{O} \quad (2)
\]

The presence of amorphous substances and the strong tension of the siloxane bonds make possible the transition of the molecular adsorption of water into the chemical reaction of re-hydroxylation [20], which is manifested in some increase in the band intensity of the free Si–OH groups in the IR spectra (3).

Fig. 1. IR spectra of PFP slag samples treated with various reagents: a – initial slag; b – water; c – solution of 1 M NaOH; d – solution of 0.5 M H\(_2\)SO\(_4\). Vertical axis – transmittance with respect to air \(T, \%\); horizontal axis – wave number \(v, \text{cm}^{-1}\).
Incomplete re-hydroxylation of PFP slag surface reduces the efficiency of this type of slag activation when treated by water (Fig. 1b).

In the sample treated with sodium hydroxide solution (Fig. 1c), there is an increase in the deformation vibrations of water molecules in the area of 1629 cm\(^{-1}\) and the appearance of a peak in the range of 1583 cm\(^{-1}\), which can be attributed to the deformation vibrations of the hydroxide ion [21]. The peak value of 3430 cm\(^{-1}\) is slightly larger than for the samples previously considered.

Three peaks of 1698, 1635, and 1585 cm\(^{-1}\) were recorded for the sample aged in sulfuric acid (Fig. 1d) in the area of deformation vibrations of water molecules [20, 21]. It can be assumed that the appearance of an additional peak is caused by a change in coordination of water molecules with the crystal lattice of the diopside. The peak value of 3430 cm\(^{-1}\) is the largest compared to the other samples. On this basis, it can be concluded that the treatment with sulfuric acid is the most effective method of activation of the slag, which causes intense hydration of the slag and the implementation of the re-hydroxylation. This confirms the previously obtained data [18, 19].

The charge of the surface of the slag particles and the magnitude of the electrokinetic potential. 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 (\(h = 1.317.10^{-3}\) m) and the time of movement of the suspension border (173.8 s). The value of \(\xi\)-potential corresponds to the average \(\xi\)-potential for mineral suspensions with conditionally spherical particles.

The influence of the ratio “MB: slag” factor on the adsorption of the dye by PFP slag. As can be seen from Fig. 2, with an increase in the slag mass, the adsorption efficiency increases. For the initial period, a 5000-fold excess of the slag mass over the amount of MB is necessary to achieve sufficient adsorption efficiency (\(\geq 80\%\)). The most appropriate ratio is “MB: slag” = 1 mg/g (Fig. 3, curves 2, 2’), at which during the first 12 days \(a\) and purification efficiency (\(Ef\)) increase at the highest rate. A sufficiently high \(a = 0.92\) mg/g is recorded at a high \(Ef\) of 92%. Within 30 days, desorption was not observed, which ensures the safety of the disposal of slag and their disposal in the production of building materials.

The efficiency of adsorption of CR and MV with PFP slag. The dependences of \(a\) and the \(Ef\) from CR and MV dyes are presented in Fig. 4. Diopside-based slag is activated for 1 day by solutions of \(\text{H}_2\text{SO}_4\) and NaOH. As can be seen from Fig. 4, the sorption characteristics of acid-activated diopside are higher, than those activated by alkali. For the CR dye, this is true for the entire time interval. For MV, \(a\) and \(Ef\) is initially higher for adsorption on alkali activated slag, however, after 7 days, MV desorption begins (Fig. 4, curve 4). Thus, the adsorption of various sorbates requires individual selection of the type of chemical activation of the slag sorbent.

With acid activation, the slag can maintain a sufficient sorption capacity for the MV dye without its desorption into the solution for a long time. The maximum value of \(a = 0.192\) mg/g, corresponding to 96% of MV extraction from the solution, is reached on day 11. For 3 days, \(Ef\) is 71%. Thus, it is impractical to activate the slag with acid if it is necessary to carry out adsorption within a short time.

Slag activation with alkaline has the advantage of high \(Ef\) from MV in a short time. When the ratio is \(m_{\text{MV}}: m_{\text{slag}} = 0.2\) mg/g, then 90% of the MV sorbate is absorbed within 3 days. Halving the slag mass causes a slight decrease in \(Ef\) from MV to 87% within 1 day. The process of MV desorption into the solution begins.

Fig. 2. The dependence of \(Ef\) from MB using slag adsorbent on the ratio of “MB:slag” in various sorption intervals, days: 1 – 3; 2 – 5; 3 – 10; 4 – 20; 5 – 30

Рис. 2. Зависимость эффективности очистки раствора от МС шлаковым адсорбентом от соотношения «МС : шлак» в различные интервалы сорбции, сут.: 1 – 3; 2 – 5; 3 – 10; 4 – 20; 5 – 30.

Fig. 3. Temporal dependences of \((1-4)\) and \(Ef\) from MB (1’-4’) with the ratios “MB : slag”, mg/g: 1 – 0.8; 2 – 1.0; 3 – 1.33; 4 – 2.0

Рис. 3. Временные зависимости \((1-4)\) и эффективности очистки воды от МС (1’-4’) при соотношениях «МС : шлак», мг/г: 1 – 0.8; 2 – 1.0; 3 – 1.33; 4 – 2.0.

Thus, the acid and alkaline activation of the slag adsorbent can be used in Various modes of MV adsorption. Acid activation can be used in static conditions, when the technological process provides for a
long-term contact of the solution being purified with the adsorbent. Alkaline activation is advisable in conditions of dynamic sorption with a low rate of solution passage through the sorbent layer.

Fig. 4. Temporal dependences of $a$ (1–4) and $E_f$ (1′–4′) from organic dyes CR (1, 2) and MV (3, 4) with the “dye : slag” ratios, mg/g: 1 – 0.8; 2 – 1.0; 3 – 1.33; 4 – 2.0 and the preliminary activation of slag in 0.5 M H$_2$SO$_4$ (1, 3) and 1 M NaOH (2, 4).

**The effect of the liquid phase pH on the process of organic dyes adsorption by the PFP slag.** Adsorption from very acidic and alkaline solutions is less intense than from the neutral media. Complete extraction of MB from solutions is possible in the range of pH from 4.8 to 10.4 for a time interval of at least 7 days. The efficiency of MB extraction for this interval is 89-97%, and the value of $a$ is equal to 90-93% of its limit. Thus, in this range of acidity of the solutions, the cleaning efficiency of adsorption and adsorption value are very high and practically unchanged. Increase in the pH of the sorbate solution until 10.4 promotes the formation of a gel-like layer of silicic acid H$_2$SiO$_4$ on the surface of the slag, which should have good sorption properties [18]. At pH < 4.8 the dissociation of silanol groups and hydrolysis of silicates are suppressed, and the silicic acid gel layer is destroyed [19].

**Prospects for using PFP slag in sorption technologies.** Using slag in water treatment in the textile industry can be a preliminary practical recommendation. The concentration of acid bright blue dye in the wash water is 15-400 mg/dm$^3$ [22]. Taking into account the maximum value of $a$ of the PFP slag of 0.92 mg/g, 160-4300 kg of slag will be required to purify 10 m$^3$/day of wash water. Preliminary research is necessary to develop recommendations for the use of slag in sorption treatment technologies for sewage waters with high concentration of organic dyes.

**CONCLUSIONS**

It is shown that after acid and alkaline activation surface the adsorption centres are formed on the surface of the slag: hydroxyl and silanol groups, whose dissociation causes a negative charge of the particles surface.

Slag acid activation is advisable in the static mode of MV sorption; alkaline – under conditions of MV dynamic sorption. The maximum efficiency of MB adsorption by slag based on diopside was recorded at the ratio “MB: slag” = 1 mg/g in the range of 4.8 ≤ pH ≤ 10.4 with a variation of 97% ≥ $E_f$ ≥ 89%.

Diopside-based slag is expedient to use as an adsorbent of organic dyes at the level of their low concentrations at the local treatment of wastewater generated during the certain technological operations.

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107