Recycling of red mud in iron-containing catalyst for oxidizing organic impurities in waste water

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Red mud is a solid waste of the industrial process of natural bauxite processing in aluminum production by the Bayer method. Currently, there is no effective and profitable technology for industrial red mud processing, and most of it is placed for permanent storage in specialized sludge storage facilities, and therefore development of the recycling technologies for this man-made waste into functional materials for various purposes is extremely relevant, since it will allow both to use its potential raw material resource and to solve environmental problems. This paper presents the results of investigations of the red mud recycling possibility at the Bogoslovsky aluminum plant into an iron-containing catalyst for waste water purification with removal of organic impurities by their oxidizing destruction using hydrogen peroxide.

Identification of the initial and obtained samples was carried out by methods of energy dispersive X-ray spectroscopy, scanning electron microscopy, low-temperature nitrogen adsorption, atomic absorption spectroscopy. It is shown that use of hydrochloric acid treatment of red mud with subsequent precipitation of dissolved compounds with ammonium carbonate and calcination of the precipitate allows to obtain the material with the iron content 55.17 wt. %. The sample has a developed specific surface area of 98.4 m^2/g and porosity of 0.174 cm^3/g, and consists of particles having a shape close to spherical with an average size of about 0.2−0.3 μm. The obtained material showed high catalytic activity and stability in the oxidation reaction of organic substances (on the example of the azo dye carmoisine) in an aqueous solution with hydrogen peroxide. The degree of discoloration of the dye solution during 30 minutes of contact was at least 94 % during 20 cycles of using the catalyst.

Key words: red mud, processing, recycling, iron-containing catalyst, waste water, dye, organic substances, aluminium, bauxite.

Introduction

Red mud is a solid waste of the industrial process of natural bauxite processing in aluminum production by the Bayer method. Amount of red mud per ton of produced aluminium depends on quality of used raw materials and varies from 1.6 t (during processing of tropical bauxites) to 3.7 t (during processing of European bauxites) [1]. Red mud composition includes mainly compounds of iron, aluminium, silicon, titanium, calcium; however, they also can contain such valuable elements as rare-earth metals (totally about 2 kg per ton of wastes) [2, 3], including scandium (80−120 g/t of red mud) [4].

Currently, there is no effective and profitable technology for industrial red mud processing, and most of it is placed for permanent storage in specialized sludge storage facilities, what creates essential difficulties due to large volumes of these wastes and can lead to emergency accidents and eco-logical catastrophe (e.g. 2010, aluminium plant in Hungary). In this case, the researches aimed on development of the recycling technologies for this man-made waste into functional materials continue worldwide, what will allow to prevent environmental problems and to use its potential raw material resource. Complex processing of red mud with extraction of valuable components from it is rather actual, but difficult task, because both pyro- and hydrometallurgical technological methods ore often realized together [5, 6]. Red mud is often suggested to use for building operations as additive to cement or as fluxing material of iron-containing concentrate in metallurgy [1, 3]. Technical literature presents researches on red mud processing in complex coagulants for water purification processes [7−10], in adsorbents [11−14] and in catalysts [15−26] for cleaning of gas emissions and waste water with removal of different impurities during solving both environmental and technological problems. When red mud is processed into functional materials, in several cases it can

be used individually (in mono-component mode) [12, 16, 21−23], however, more often it plays the role of carrier of catalysts, e.g. of copper [16], gold [17], cobalt [18], nickel [19], manganese [20] or as composites with other man-made wastes or substances, such as graphene oxide [13], carbon nanotubes [14], rice hull ash [20], zinc oxide [24], mesoporous silicon oxide MCM-41 [25], polyethylen terephthalate [26].

The aim of this research is study of possibility of red mud processing in order to obtain a catalyst for waste water purification with removal of organic impurities via their oxidizing destruction using hydrogen peroxide, as well as analysis of activity and stability of obtained material.

Materials and methods of the research

Red mud of bauxites processing at Bogoslovsky aluminium plant was chosen for the research. A weigh of waste was preliminarily comminuted, sieved through 0.2 mm screen, dried at the temperature 110 °C during 6 hours. To process red mud in a catalyst, acidic leaching of soluble components was conducted. These components are presented in a waste with consequent re-deposition of low-soluble compounds from the obtained solution. The procedure was carried out in the following way. Red mud was dissolved in 4M solution of hydrochloric acid during 4 hours at the temperature 80 °C, correlation between red mud mass and volume of hydrochloric acid solution was 1:40. Solution, which was formed as a result of acidic processing, was separated from insoluble remainder via vacuum filtration. 2M solution of ammonium carbonate was added to obtained filtrate as a depositing agent. The formed deposit was separated from the liquid phase via centrifugal processing, using OPN-8 centrifuge, then dried at the temperature 110 °C, and afterwards calcinated at the temperature 500 °C during 4 hours.

Morphology of samples was examined via scanning electron microscopy, using the microscope JSM-6510 LV JEOL. Micro-pictures of material particles were obtained at accelerating voltage 15 kV using detector of secondary electrons.

Elementary composition of materials was determined via the method of energy dispersive X-ray spectroscopy, using the analyzer X-MAX Oxford Instruments in the Research equipment sharing center in the Mendeleev University of Chemical Technology. Powder for examination was formed in pellets using hydraulic press Crush IR PIKE Technologies. X-ray phase analysis was implemented by diffractometer Olympus BTX III.

Content of Fe ions in acidic exhaust was determined via the method of atomic absorption spectroscopy with flame ionization using spectrometer Quant 2A.

Parameters of porous structure of materials were calculated on the base of isotherms of nitrogen adsorption-desorption at the temperature −196 °C, which were obtained at the unit Nova 1200e Quantachrom. Specific surface S_{sp} was calculated via the BET method, summarized sorption volume of pores V_Σ was determined by nitrogen adsorption isotherm for the value of relative pressure equal to 0.99. Average diameter of mesopores D_{me} was determined via BJH method

by desorption isotherm branch. Activation of samples at the temperature 300 °C and residual pressure $10^{−3}$ mm Hg at 4 hours was carried out before measuring isotherms.
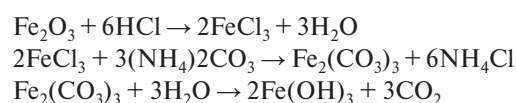
Catalytic activity of materials was examined by the reaction of oxidizing destruction of organic mono azo-dye carmoisine in an aqueous solution with hydrogen peroxide. Carmoisine (azorubine, E 122) is a food dye which is widely used in manufacture of dairy, confectionary and meat products. This dye was selected as an object for research, because it is one of the most hardly oxidized compound in comparison with other organic substances (including dyes). We can evaluate activity of samples by discoloration of the dye solution due to destruction of chromophoric azo-group and decrease of optical density of solution for the wave length 517 nm, using spectrophotometer SF-2000 made by the experimental designing bureau "Spectr". Initial concentration of carmoisine in the solution was 20 mg/l, catalyst content − 3 g/l, experience temperature −60 °C, pH value − 3. The amount of hydrogen peroxide with concentration 3 % (mass.) was twofold in comparison with stoichiometric amount, until the complete carmoisine oxidation according to the reaction:

$$C_{20}H_{12}N_2Na_2O_7S_2 + 51H_2O_2 = 20CO_2 + 55H_{2O} + 2HNO_3 + 2NaHSO_4$$
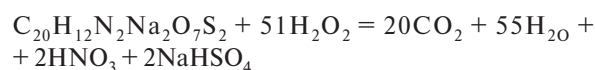
Examination of catalyst stability in relation of activity value, as well as resistance to washout of the active component in the solution, was carried out in cyclic tests. For this case, after realization of catalytic oxidation of carmoisine, purified solution was drained by decanting, then new portion of solution was added and dye oxidation was conducted. Thus, 20 cycles of examination of obtained catalyst activity were carried out.

Results and discussion

Interaction of red mud with hydrochloric acid at the leaching stage leads to dissolution of its main component (iron oxide) and forming of iron chloride. When adding amonium carbonate to iron chloride solution, iron carbonate is extracted, which is then subjected to hydrolysis in the aqueous solution, with consequent dorming of iron hydroxide and gaseous carbon dioxide. The reminder is decmposed during further heat treatment with forming of iron oxides:

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$
$$2FeCl_3 + 3(NH_4)2CO_3 \rightarrow Fe_2(CO_3)_3 + 6NH_4Cl$$
$$Fe_2(CO_3)_3 + 3H_2O \rightarrow 2Fe(OH)_3 + 3CO_2$$

According to the data of energy dispersive X-ray spectroscopy, content of the aimed component (Fe in the red mud) makes 35 % (mass.) and is maximal relating to other metals (**Table 1**). Sodium is presented in non-processed waste in the amount appr. 2 % (mass.), what is stipulated by the features of processing technology of natural bauxite. Conduction of acidic treatment of red mud is accompanied by partial material dissolution, resulting in transition of metal

Table 1. **Elementary composition of the samples, % (mass.)**									
Sample	Fe	Al	Si	Ca	Ti	S	Cl	Na	O
Initial	35.20	4.06	6.65	2.21	3.33	0.51	5.42	1.93	40.69
Catalyst	55.17	2.50	1.58	0.86	0.82	0.20	0.87	0	38.00

ions in the liquid phase. After deposition of iron ions from the leaching solution by ammonium carbonate with consequent heat treatment, iron content in the obtained catalyst sample increases by 1.5 times in comparison with initial mud and is equal to 55.17 % (mass.), while aluminium content, unlike this, decreases by 1.6 times. Amount of other elements in the obtained catalyst lowers more than by 2 times, sodium is not revealed. According to the temperature of final metal treatment and the data of the Table 1, all elements are presented in the form of oxides. Based on the results of X-ray diffraction, identification of phases, which are included in composition of the obtained material, seems to be impossible due to forming of X-ray amorphized structure. However, estimating material colour (black and brown) and in accordance with the data [16], we can suggest presence of the mix of iron oxides (magnetite and hematite).

Owing to prevailing iron content in the material composition and presence of impurities in the amount not exceeding 6 % (mass.), it is possible to suggest its use as a secondary raw material in the iron and steel industry as an additive for iron making and steelmaking.

According to the results of atomic absorption spectroscopy, the degree of iron extraction in the solution as a result of hydrochloric treatment of red mud makes approximately 75 % (mass.).

Comparison of morphology of initial red mud samples, as well as a catalyst obtained during processing in accordance with the data of scanning electron microscopy (**Fig. 1**), displayed the following results. Presence of fine-dispersed spherical particles with their size $0.1-0.2$ μm in average is typical for non-processed red mud. These particles are located on the surface of large agglomerates with average size about $50-100$ μm and having relatively dense structure. It is seen from micro-pictures of the obtained catalyst that material dispersity practically did not vary; presence of particles with larger average size $(0.2-0.3$ μm) and the form close to spherical (however, with more loose and less aggregated structure are observed.

Based on the results of low-temperature nitrogen adsorption, it can be seen that isotherms of nitrogen adsorption-desorption for initial and finished materials (**Fig. 2**) and, respectively, the features of porous structure and its parameters,
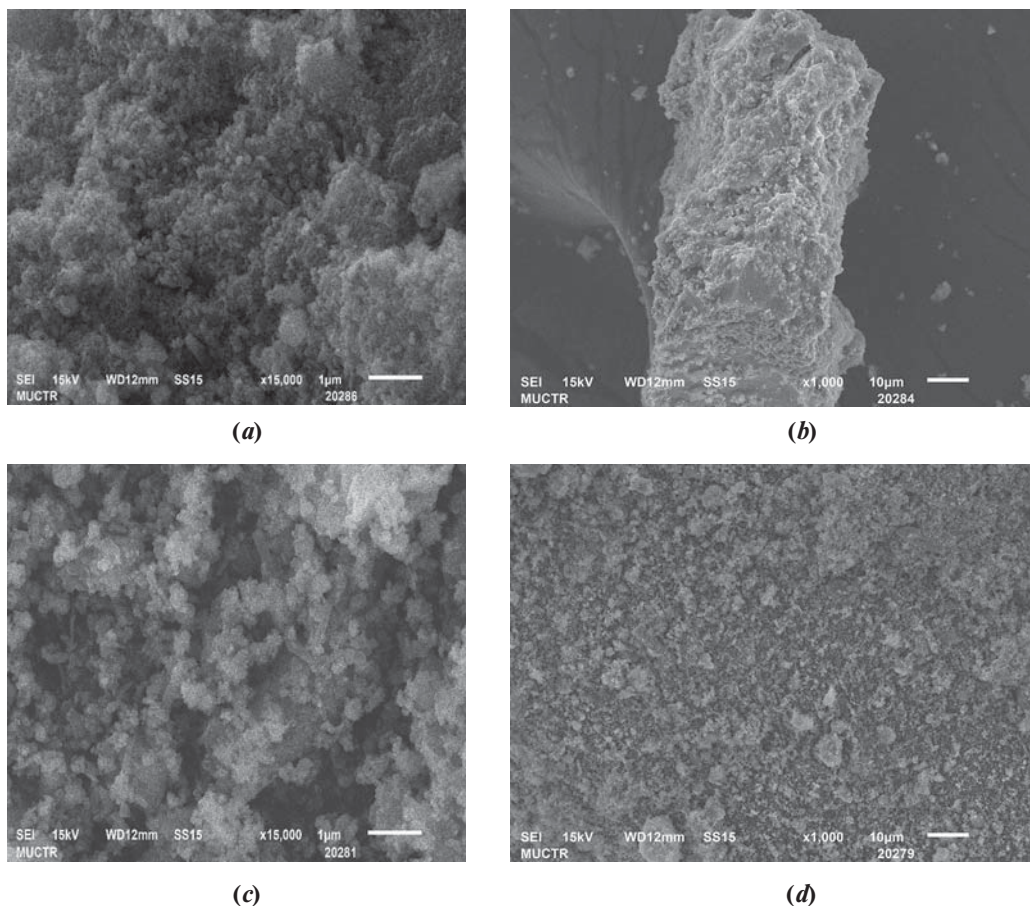

(*a*)

(*b*)

(*c*)

(*d*)

Fig. 1. Micro-pictures of the red mud initial sample (*a, b*) and the obtained catalyst (*c, d*) with various magnification

are varied essentially (**Table 2**). As a result of processing, specific surface of the obtained catalyst increased by more than 5 times in comparison with initial red mud. Summarized sorption volumes of pores increases almost by 1.5 times, typical widening of the hysteresis loop is observed; this loop is typical for meso-porous materials, in this case the average size of meso-pores varies slightly from 3.65 to 4.76 nm. Increase of the values of texture parameters of the catalyst is caused by forming of essential number of meso-pores, as a result of removal of gaseous products in the process of its heat treatment.
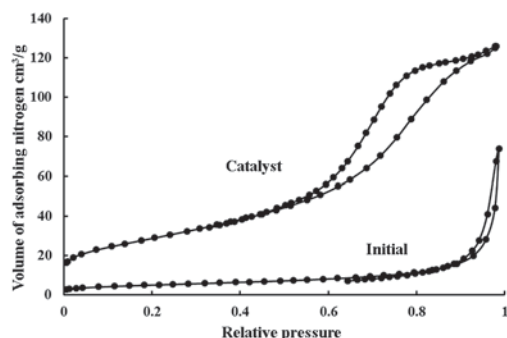

Fig. 2. Isotherms of nitrogen adsorption-desorption by the samples of initial red mud and by the catalyst

Table 2. **Parameters of porous structure of red mud and the obtained catalyst**			
Sample	S_{sp}, m²/g	V_{Σ}, cm³/g	D_{Me}, nm
Initial	18.1	0.119	3.65
Catalyst	98.4	0.174	4.76

Kinetic curves of oxidizing destruction of carmoisine dye in aqueous solution (**Fig. 3**) testify that discoloration degree of a dye solution in presence of the obtained catalyst made 97 % during 30 min contact. Non-processed red mud also displays slight activity, however its value is rather smaller, and discoloration degree of a dye solution does not exceed 18 % during the same contact time. Low activity of the initial mud is connected with the worse parameters of porous structure and smaller iron content.
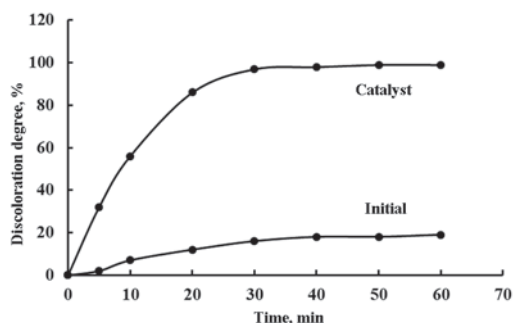

Fig. 3. Kinetic curves of discoloration degree of carmoisine solution by hydrogen peroxide in presence of initial mud and the catalyst obtained from this mud

The material (iron oxide) plays in this case the role of the catalyst of a heterogeneous Fenton-type process, it can be explained in the following way. Hydroxyl and peroxide radicals are forming during interaction of hydrogen peroxide and iron ions, which are localized on the catalyst surface. These radicals, in their turn, oxidized organic impurities in the aqueous solution:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + HO^-$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\cdot + H^+$$
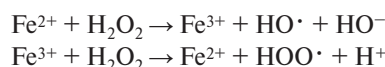
The obtained catalyst displayed high activity during 20 cycles of secondary use (**Fig. 4**), in this case discoloration degree of dye solution did not decrease below 94 %. The tendency to lowering of purification efficiency of the solution was caused by slight entrainment of catalyst particles with solution in the process of purified solution separation from the catalyst after finishing the carmoisine oxidation operation.
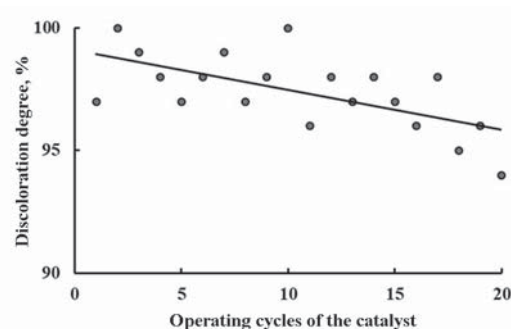

Fig. 4. Efficiency of carmoisine solution discoloration in dependence to the number of operating cycles of the catalyst

Based on the data of atomic absorption spectroscopy, the catalyst stability (in relation to washout of active iron component in the solution) remained at high level. Concentration of Fe ions in aqueous solution after oxidizing dye destruction was 0.12−0.27 mg/l and did not exceed the intimate allowable concentration. Total iron loss from the catalyst due to transition of Fe ions in the solution made approximately 0.8 % (mass.) during 20 cycles of catalyst use.

Conclusion

Thus, based on the conducted researches, we can conclude that acidic leaching of soluble components with consequent re-deposition of low-soluble iron compounds and heat treatment of obtained deposit should be carried out to provide red mud recycling in catalysts, for oxidation of organic substances in waste water. As a result of waste processing, high-dispersive material with average size of spherical particles 0.2−0.3 µm was obtained; in contains mainly iron oxide (Fe content makes 5.17 % (mass.), in calculation for metal). Total amount of the rest impurities (mainly presented by aluminium oxide) does not exceed 6 % (mass.). The obtained material displays high catalytic activity and stability during long time of use in oxidation process of organic carmoisine

dye and is considered as prospective material as a catalyst for purification of waste water with removal of organic impurities. So, discoloration degree of the dye aqueous solution during 30 min of its processing was within the range 94−99 % during 20 cycles of the catalyst operation, while summarized iron loss from the catalyst due to washout of Fe ions in the solution during the catalysis process did not exceed 1 % (mass.). High material activity was caused by the parameters of porous structure (S_{sp} 98.4 m²/g, V_{Σ} 0.174 cm³/g), which increased by several times, and its composition. Owing to advantageous iron content in the material composition, it is possible to use this material as an additive in ironmaking and steelmaking. **CIS**

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