Method of wastewater treatment from emulsified petroleum products

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Abstract. The authors developed the composition of integrated adsorbent for the disposal of wastewater containing cutting fluids and consisting of decaying steel slag and iron ore concentrate at a weight ratio of 1:1.5. It was identified that the maximum degree of cleaning from emulsified petroleum products (EOP) is observed at the size of adsorbent particles (d) in the range of 80>d>50 um. The values of the process hydrogen ion exponent $\text{pH} \leq 3$ while the ratio between solid and liquid phases at the separation of water and emulsified petroleum products is equal to 0.6-0.7. The authors managed to set the parameters of the magnetic processing of a suspension consisting of complex adsorbent and water&oil emulsions with subsequent separation of the aqueous and oil phases. At this, the magnetic field intensity was equal to 180 kA/m and the magnetic field processing time - 120 seconds.

1. Introduction

The environmental situation in cities is significantly aggravated by machining workshops of mechanical engineering and other companies. Most modern industrial processes of metal processing are conducted with the application of cutting fluids. When such fluids are used, the key source of pollution are discharge cutting fluids (CF). They represent a special kind of wastewater which are very dangerous for the environment because of a large number of stable emulsified petroleum products, mechanical impurities, free oils, de-structured organic components formed at additive decomposition - sulfur-, chloro-, phosphorus and nitrogen containing organic compounds as well as alkyl-phenolic additives [1-4]. The content of mineral oils, emulsifiers and grease lubricates in discharge cutting fluids sometimes reaches 50g/l, and up to 15g/l of them belong to the emulsified ones. The share of such wastewaters reaches 40-60% of the total amount of plantwide discharge waters.

The removal of cutting fluid decomposition products to the values of maximum admissible discharge is possible by means of destructive methods applying natural or synthetic adsorbents to extract dissolved materials. The application of natural materials in the cleaning of wastewaters is more acceptable in economic terms but such materials will not have necessary sorption and filtration properties. Using synthetic adsorbents involves the problems in their manufacture and obtaining as well as significant expenses for their acquisition. Meanwhile, utilizing industrial plant wastes allows obtaining adsorbents with a high sorption capacity in relation to the organic and non-organic substances and decrease the expenses for their acquisition.

It was believed that for hydrocarbon absorption it is more reasonable to use carbon foamed materials - active carbons, semicoke, coke, synthetic polymeric resins, etc. [5]. However, recently the
prices for carbon adsorbents have been quite high. Use of synthetic adsorbents involves the problems in their manufacture and obtaining.

At present, adsorption cleaning of wastewaters from petroleum products is frequently conducted with the help of cheap non-organic adsorbents, including metallurgical production wastes having quite high adsorption properties [6-8].

In this connection the research on highly efficient cleaning of wastewaters of metallurgical plants, containing discharge cutting fluids, with the help of affordable adsorbents on the basis of industrial plant wastes from the same production is a relevant scientific and practical problem [9-12].

The present paper considers the material which combines the achievements both in the area of metallurgical waste utilization technologies and in the area of environmental technologies of oil containing discharge processing with the application of physical methods facilitating the achievement of high ultimate results [13,14].

The authors pay special attention to the environmental safety aspects, in particular, to the development of adsorbent and technology of disposal for wastewaters containing discharge cutting fluids and emulsified petroleum products at metallurgical plants.

2. Experimental part
The discharge cutting fluid “Emulsol T”, grade A, was subject to research. It is a mix of triethanolamine salt of oleic acid, grade OM, and mineral oil. Emulsol T is intended for the preparation of 3-10% water emulsions applied during cold metal rolling at metallurgical plants and at metal cold cutting at metal processing plants.

During the process cycle cutting fluids are subject to biological destruction which is explained by quite a long time of their usage (they can be replaced once in 3 months and up to once a year). For this purpose the authors conducted the tests to assess funginertness of the discharge cutting fluid. The results show the absence of the funginertness area (Figure 1). One can observe the development of mushroom spores Aspergillus Niger covering the surface under test. The intensity of mushroom spores development on the material surface was equal to 4 points.

![Figure 1. Results of studying fungicidal properties of discharge cutting fluid.](image)

It is known that preliminary magnetic processing of various emulsions changes the water structure, provide conditions for coagulation and aggregation of water suspended particles, decrease hydratation of the interface “liquid-liquid”, “liquid-solid body”, “liquid-gas” thus reducing their hydrophylic properties [15-20].

The research on discharge cutting fluids’ disposal were conducted with the adsorption method in the magnetic field using complex adsorbents based on ferrous oxides. Disintegrating electric steelmaking slag and iron ore concentrate were used as the components.

Approximately a half of a total output of electric steelmaking slags in our country are subject to spontaneous decomposition during cooling because of polymorphic transition of dicalcium silicate (C2S) characterized by the transformation of the β-phase C2S into the γ-phase C2S accompanied by the increase of the crystalline lattice absolute volume. The density β-C2S is 3,280 kg/m³, the density γ-C2S
– 2,970 kg/m³. One can suggest that this process is associated with significant plastic deformations and, consequently, intense defect formation increasing slag activity. To specify this hypothesis, the research were conducted on the slag of arc steelmaking furnaces of Oskol Electrometallurgical Plant; this slag belongs to self-decomposed substances.

To define the nature of the slag structure, the authors conducted microscopic analysis. The slag contains well-defined crystals of the size 5-50 μm. Analyzing the micro-photos of particles of slag obtained by air cooling (Figure 2a) one can find out a whole range of structural damages at the mesoscopic level - presence of micro-cracks, possibly, the presence of dislocation clusters in slide planes forming long-range stress patterns. This proves a high sorption capacity of slag [21].

The predominant size of iron ore concentrate particles is less than 0.5 mm. In addition, there are also small (10 μm) magnetized particles (Figure 2b) facilitating the increase of the specific surface.

At research conduct the authors found out the dependences of the wastewater cleaning degree from dispersity and percentage ration of complex adsorbent components. The degree of impurities’ extraction was controlled by the solution transparency defined by means of the optical density with the help of a photocolorimetric method.

Experimental data showed that the maximum degree of cleaning from emulsified petroleum products (EOP) is observed at the size of adsorbent particles (d) in the range of 80>d>50 μm. In case the fractions are smaller than 50 μm the process efficiency decreases as the vacuum filter operation deteriorates at the separation of saturated adsorbent and water. When using fractions with d > 80 μm the cleaning degree decreases because of the insufficiently developed adsorbent specific surface.

The optimal percentage ratio of adsorbent components by weight slag/magnetite concentrate = 40/60 %. If less than 40% of slag are used, the cleaning degree of the emulsified petroleum product extraction decreases as the amount of main absorbing substance decreases as well. When the slag amount is more than 50% the cleaning degree also decreases because the amount of OH- groups increases due to the growth of the concentration of calcium oxides the slag consists of (2CaO+H₂O=2Ca(OH)₂), while the discharge cutting fluid having a negative charge at the collision with a negative group OH- leads to the particle repulsion which decreases the cleaning degree.

The research of change in the degree of emulsified petroleum product extraction from wastewaters with cutting fluids was conducted by means of introducing adsorbent into wastewaters in various ratios. The obtained results make it clear that the optimal adsorbent-cutting fluid ratio is 0.7. The use of the ratio with lower values significantly decreases the cleaning degree due to an insufficient adsorbent amount. When the ratio is higher than 0.7 at good cleaning from organics the suspension loses its fluidity and is hardly subject to filtering.

Magnetic processing influence was studied at the electromagnetic unit for labs where suspension was located in the area of the magnetic field action. At magnetic processing, in case the ratio of slag-
magnetite concentrate is 40% - 60% by weight and with the size of particles 50…80 μm, the cleaning degree increases virtually twice.

The optimal time of suspension presence in the magnetic field was 120 seconds at the magnetic field intensity of 18 kA/m.

The conducted research showed that, at the magnetic processing of oil-containing water in the magnetic field, the field and charged and polar particles of the suspension interact with the force connected with change of magnetic induction flux at liquid entry in the magnetic field and at leaving the field, which causes the change in its structure and properties.

The process of defining the action the pH medium of the discharge cutting fluid has on the cleaning efficiency showed that the processed water cleaning degree increases simultaneously with the decrease in the hydrogen index. The acid action triggers the destruction of the structural & mechanical barrier. I.e., the emulsion system, which makes the difference in magnetic properties of oil particles and water more obvious, is subject to destructuring, and the system viscosity also reduces as, in its turn, provides for more favorable conditions for oil particle motion from the interpolar area in the magnetic field.

In this connection the adsorbent allows for more efficient cleaning at pH ≤ 5. To study the dependence of the emulsified petroleum products extraction from wastewaters, the discharge cutting fluid, which had been preliminary acidified to pH = 3–5, was held for 3-7 days. At the 3d and 4th day of the discharge cutting fluids increases up to 80% and reaches 99% after 5 days of hold.

Therefore, to increase the cleaning efficiency before magnetic processing, it is necessary to hold suspension for 3-5 days – with preliminary reaching pH = 3. The lower is the hydrogen exponent of the medium subject to cleaning, the faster is the sedimentation due to division of the discharge cutting fluid into layers. As the slag contains free CaO, at processing of the discharge cutting fluid its hydrogen exponent can reach the values 6–8.

Adsorbent capacity was studied with the help of methylene blue widely applied at researching of powder materials’ porosity. Methylene blue sorption was conducted with the solution with the initial concentration of 1.5 g/l. Adsorption properties were defined by the spectrophotometric measurements of optical density. The obtained results demonstrated that the sorption capacity of each separate component is virtually the same (54 and 61 mg/g) while as a whole the sorption capacity increases up to 78 mg/g (without magnetic field action) and up to 104 mg/g (with magnetic field action), Figure 3.

![Figure 3. Sorption capacity of adsorbents: 1 – iron ore concentrate; 2 – electric steelmaking slag; 3 – slag+iron and ore concentrate green – without magnetic field action blue – at the action of magnetic field.](image)

To explain this phenomenon, the authors conducted the measurements of the complex adsorbent bulk density which was lower than the estimated one by 10%.

On the basis of the obtained data the conclusion can be drawn that after mixing the components the mixture bulk weight decreases due to the occurrence of cohesion forces facilitating the increase in the free package volume and formation of intergranular spaces which conditions the increase in the sorption capacity.
In addition, after magnetic processing, due to the increase in the active centers of ferromagnetic particles, adsorption properties of iron ore concentrate and adsorption complex increase because of magnetic saturation (81 and 104 mg/g).

To recover adsorbent properties and its reuse in the process of wastewater cleaning, the authors studied the possibility of its regeneration after full saturation. Regeneration was conducted by drying the adsorption complex at 105 °C to the constant weight and further tempering at 400 °C for half an hour. After the third cycle of regeneration the cleaning level from petroleum products decreases to 67%. Decreasing of adsorbent sorption capacity facilitated the pore filling with the products of absorbed substances’ thermal decomposition.

Therefore, it is reasonable to use adsorbent not more than 3 times with double regeneration.

As the considered adsorbent contains the metallurgical production components, it is more profitable and economically viable for metallurgical plants to dispose discharge adsorbent as a part of raw materials used for steel production.

3. Conclusion
On the basis of the obtained data the authors found out the characteristics of the suggested complex adsorbent with magnetic properties for processing oilwater containing wastes under the magnetic field action to intensify the destruction of emulsified petroleum products.

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