Artículo de investigación

Investigation of the sorption properties of pyrolysis product of sludge after treatment with ashing

Investigación de las propiedades de sorpresión de la pirólisis producto de lodo después del tratamiento con ashing

Investigação das propriedades de sorção do produto de pirrolise do lodo depois do tratamento com a cinza

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Abstract

In this paper the properties of potential sorption materials obtained by the pyrolysis method from sludge and treated with ashing were investigated. The moisture content and bulk density of the solid product of the pyrolysis of the biological wastewater treatment sludge are studied. The indices of water extract are determined. The content of heavy metal ions is studied. The sorption ability of the obtained solid product of pyrolysis of sludge by iodine was studied using the titrimetric method and methylene blue on a spectrophotometer UNICO 2800.

The sorption properties of the pyrolysis product of silt sediments treated with ashing with respect to iron, copper, chromium, nickel and zinc ions under static conditions using atomic emission spectrometry on the Agilent 720-OES spectrometer were studied. Degree of sorption of heavy metal ions is calculated.

Data on the coal sorbent BAU and the degree of sorption of solid pyrolysis products without treatment for comparison are given. It has been established that after treatment with "dry" ashing for the product of pyrolysis of sludge the sorption capacity with respect to chromium ions increases.

The degree of purification from ions of heavy metals: iron, copper and chromium, using a solid product of pyrolysis of sludge treated with ashing, reaches 52.7-99.6 %.

Keywords: Pyrolysis, sorption, sludge, waste, heavy metal ions, ashing.

Resumen

En este trabajo se investigaron las propiedades de los materiales de sorción potenciales obtenidos por el método de pirólisis de los lodos y tratados con ceniza. Se estudia el contenido de humedad y la densidad aparente del producto sólido de la pirólisis del lodo biológico de tratamiento de aguas residuales. Los índices de extracto de agua están determinados. Se estudia el contenido de iones de metales pesados. La capacidad de sorción del producto sólido obtenido de la pirólisis del lodo por yodo se estudió utilizando el método titrimétrico y azul de metileno en un espectrofotómetro UNICO 2800. Se estudiaron las propiedades de sorción del producto de pirólisis de los sedimentos de limo tratados con cenizas respecto a los iones de hierro, cobre, cromo, níquel y zinc en condiciones estáticas utilizando espectrometría de emisión atómica en el espectrómetro Agilent 720-OES. Grado de sorción de iones de metales pesados se calcula.

Se proporcionan datos sobre el sorbente de carbón BAU y el grado de sorción de productos de pirólisis sólidos sin tratamiento para comparación. Se ha establecido que después del tratamiento con ceniza "seca" para el producto de la pirólisis del lodo aumenta la capacidad de sorción con respecto a los iones de cromo.

El grado de purificación de iones de metales pesados: hierro, cobre y cromo, utilizando un producto sólido de pirólisis de lodo tratado con ceniza, alcanza el 52.7-99.6%.

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Palabras claves: Pirólisis, sorción, lodo, desechos, iones de metales pesados, cenizas.

Resumo

Neste trabalho foram investigadas as propriedades dos potenciais materiais de sorção obtidos pelo método de pirólise do lodo e tratado com cinza. O teor de umidade e a densidade aparente do produto sólido da pirólise do lodo biológico do tratamento de águas residuárias são estudados. Os índices do extrato de água são determinados. O conteúdo de íons de metais pesados é estudado. A capacidade de sorção do produto sólido obtido da pirólise da lama pelo iodo foi estudada pelo método titulométrico e azul de metileno em um espectrofotômetro UNICO 2800.
as propriedades de adsorção do sedimento produto de pirólise de lodo tratado calcinação em relação aos iões de ferro, cobre, crómio, níquel e zinco em condições estáticas utilizando espectrometria de emissão atómica no espectretro Agilent 720-OES estudado. Grau de sorção de íons de metais pesados é calculado. Os dados são fornecidos no sorvente de carbono BAU e o grau de sorção de produtos de pirólise sólidos sem tratamento para comparação. Foi estabelecido que após o tratamento com cinza "seca" para o produto da pirólise do lodo a capacidade de sorção em relação aos íons de cromo aumenta.
O grau de purificação de íons de metais pesados: ferro, cobre e cromo, usando um produto sólido de pirólise de lama tratada com cinza, atinge 52,7-99,6%.

Palavras-chave: Pirólise, sorção, lodo, resíduos, íons de metais pesados, cinzas.

Introduction

Disposal of production and consumption wastes is an important environmental problem at present. A lot of such wastes accumulated. Dumps for production and consumption waste occupy huge areas. Legislation introduced strict standards for the disposal and neutralization of such waste.
An alternative way of processing such waste is storing pyrolysis. When pyrolyzed, a number of useful products are formed. Such as gaseous, liquid pyrolysis fuel and solid pyrolysis product. With the help of pyrolysis, most carbon-containing waste can be disposed of. For example, sawdust, used car tires, chicken manure, etc. The composition of the solid pyrolysis product depends on the qualitative composition of the pyrolysis waste or mixture of waste. For the most part, a solid pyrolysis product contains carbon in the composition. This allows us to predict the sorption properties of the final product. Sorption properties of the final product can be improved by a special procedure - "dry" ashing (Abo-El-Enein et al, 2009).
The use of pyrolysis, unlike conventional incineration of waste, reduces the negative impact on atmospheric air and allows us to obtain valuable products.

Sorption materials from solid products of pyrrole can be effective and relatively cheap, because this provides an increase in the volume of processed waste. To create highly effective sorption materials, it is necessary to investigate the initial sorption characteristics. This will allow you to choose the optimal method of modification.

Methods

The moisture content of the solid pyrolysis product of the sludge after treatment with ashing was determined using a moisture analyzer of the ML-50 grade. It implements the principle of thermogravimetric analysis (Nasyrov et al, 2017). With this analysis, the sample dries and the moisture content is determined in%.

The bulk density of the sample was investigated in accordance with GOST 4453-74. To determine the bulk density, the sample with the product was pyrolyzed into a pre-weighed cylinder of 20 ml volume. Shake the cylinder with the sample for 1 minute. Next, the volume occupied by the sample before and after shaking was measured.

The adsorption capacity of the solid product of pyrolysis of sludge with respect to methylene blue was studied using a spectrophotometer UNICO 2800 in the 393 nm spectral range. The adsorption capacity of the solid product of pyrolysis with respect to iodine was investigated using the titrimetric method (Fazullin et al, 2014).
To prepare the aqueous extract, 30 g of a solid product of pyrolysis of sludge in 150 ml of

distilled water was dissolved. The resulting suspension was shaken for 30 minutes on a stirring device, allowed to stand and filtered (Nasyrov et al, 2007).

Ionomer anion 4100 was used to measure the pH of the solutions. The mineralization and specific electrical conductivity were measured with an ANION-7020 conductometer (Nasyrov et al, 2016).
Determination of the content of heavy metal ions in the aqueous extract of the pyrolysis product of the sludge and the sorption properties with respect to heavy metal ions was carried out by the atomic emission method on an spectrometer Agilent 720-OES (Minori et al, 2011; Zaini et al, 2009).

To study the sorption properties of the solid product of pyrolysis of sludge, 1 g of a crushed sample was placed in a series of conical flasks. 250 ml of a model solution of the corresponding heavy metal ion with a concentration of 5-20 mg/dm ^ 3 were added, covered with a lid and stirred on a shaker for 30 min under thermostatting conditions (20 ± 0.1 ° C). The filtrate was separated from the pyrolysis product and the initial and final concentrations of heavy metal ions were determined by atomic emission spectrometry (Nasyrov et al, 2016).

Results and Discussion

As a research object, a sample of the product of pyrolysis processing of a sludge of biological sewage treatment (sludge) is taken. The sample was obtained by low-temperature pyrolysis under production conditions. Subsequently, the resulting pyrolysis product of the sludge was subjected to a dry ashing treatment in a muffle furnace at t = 800 ° C. The treated pyrolysis product was investigated for sorption properties.

The solid product of pyrolysis of sludge treated with dry ashing is presentedin.

Figure 1. It is a powder of dark brown color without foreign inclusions.

Figure 1. Solid product of pyrolysis of sludge treated with dry ashing

The results of a study of the moisture content and bulk density of the pyrolysis product of the sludge after treatment with ashing are presented in Table 1.

Table 1 – Moisture of solid pyrolysis products after ashing

Sample	Moisture, %	Bulk density, g/dm3
solid pyrolysis product of sludge after ashing	2.9	919.5
activated carbon	2.5	229.2 [6]
standard	10 [4]	240 [4]

According to the obtained data, the moisture content of the pyrolysis product under investigation after ashing does not exceed the normative value of 10% according to GOST 4453-74 "Charcoal active clarifying wood powder".

For comparison, in Table. 2 shows the values of the bulk density of known adsorbents (Nasyrov et al, 2016).

Table 2 – Bulk density of adsorbents

Parameters	Silica gel		Aluminosilicate	Activated carbon
	fine-pored			
bulk density, g/dm3	800	700	700	200-600

The obtained results allow to draw the following conclusion: the bulk density of activated carbon of the BAU grade was 229.2 g/dm^3. Normative value according to GOST 6217-74 "Active charcoal charcoal" - 240 g/dm^3. The bulk density of the pyrolysis product of sludge after ashing is not inferior to that of known adsorbents. And they are 919.5 g/dm^3 (Table 1).

The results of a study of the water extract of pyrolysis products of sludge after ashing are presented in Table 3.

Table 3 – Indices of water extract

Sample	pH, unit pH	Mineralization, mg/l	Specific electric conductivity, μS/cm
solid pyrolysis product of sludge after ashing	7.1	147	307

As a result of mixing 30 grams of the solid product of pyrolysis of sludge on a shaker in 150 ml of distilled water for 30 minutes, mineralization and specific electric conductivity increase. The assumption in connection with the increase in mineralization of water by the pyrolysis product about the possibility of emission of heavy metal ions from it into the water was confirmed by the results of the atomic emission determination (Agilent 720-OES) of metals in water extract. The results are shown in Table 4.

Table 4 – Heavy metals content (water soluble form)

Sample	Concentration (water soluble form), mg / kg				
Solid pyrolysis product of sludge after ashing	Fe	Cu	Cr	Ni	Zn
	<0.05	0.010	<0.002	<0.001	1.75

The adsorption capacity of the sample depends largely on the amount and size of the pores. The results of the study of the sorption activity of the solid product of pyrolysis of sludge by the indicators - methylene blue and iodine are presented in Table 5.

Table 5 – Sorption activity on methylene blue and iodine

Index	Solid pyrolysis product of sludge after ashing
methylene blue, mg/g	12
iodine, %	7.6

When iodine is used as an adsorbent, the presence of pores with a diameter of 1 nm is established. This value is expressed as a percentage. Sorption activity on methylene blue indicates the presence of pores with a diameter of more than 1.5 nm.

The sorption properties of the solid product of pyrolysis of sludge after treatment with ashing were studied in model solutions containing metal ions Fe, Cu, Cr, Ni, Zn, which are often found in sewage waters of galvanic plants (Table 6)

The results of the determination of sorption properties with respect to heavy metal ions are presented in Table 7.

The degree of sorption (R, %) was calculated from formula (1):

$$R = \frac{C_0 - C_1}{C_0} * 100 \qquad (1)$$

Where C0 – initial concentration of ions of heavy metals, mg/dm ^ 3;
C1 – concentration of ions of heavy metals after sorption, mg/dm ^ 3.
The results of calculating the degree of sorption are presented in Table 8.

Table 6 – Content of heavy metal ions in model solutions

Heavy metal ions	Model solution of iron ions	Model solution of copper ions	Model solution of chromium ions	Model solution of copper ions	Model solution of zinc ions
Fe	0.025	<0.0001	<0.0001	<0.0001	<0.0001
Cu	0.016	6.13	<0.0003	<0.0003	<0.0003
Cr	4.44	<0.00015	20.5	<0.00015	<0.00015
Ni	0.004	<0.0003	<0.0003	5.51	<0.0003
Zn	0.151	0.071	0.129	0.06	6.01

Table 7 – Mass content of heavy metal ions

Sample	concentration, mg/dm3				
	Fe	Cu	Cr	Ni	Zn
Stock solution	4.44	6.13	20.5	5.51	6.01
Filtrate from pyrolysis Product of sludge after ashing	0.018	1.19	4.50	3.59	2.56

Table 8 – Degree of sorption

Sample	R, %				
	Fe	Cu	Cr	Ni	Zn
Pyrolysis product of sludge after ashing	99.6	80.6	78	34.8	57.4
Pyrolysis product of Sludge without ashing treatment	99.8	77.6	74.6	-	-
activated carbon	99.8	99.9	83.9	-	-

For comparison, the sorption degree for the initial solid product of pyrolysis of sludge (without ashing treatment) and BAU coal , which is a common sorption material, is given in Table 8.

The obtained results indicate a slight increase in sorption capacity with respect to iron, copper and chromium ions after treatment with "dry" ashing for the product of pyrolysis of sludge.
The degree of purification from heavy metal ions: iron, copper and chromium using a solid product of pyrolysis of sludge after treatment with ashing is 78 - 99.6%.

Summary

Primary indicators of the potential sorption material obtained as a result of pyrolysis of sludge and treated with ashing, such as moisture and bulk density are not inferior to known adsorbents and within the limits of the relevant standard.

Half hour mixing on a shaker 30 g sample in 150 ml distilled water leads to a noticeable mineralization. The assumption of the possibility of some emission of heavy metal ions from it into water was confirmed by the results of the atomic-emission determination of metals in aqueous extract.
The sorption activity of the obtained samples was studied by the indicators - iodine and methylene blue.
The sorption properties of the solid product of pyrolysis of the sludge of biological wastewater treatment with respect to iron, copper, chromium, nickel and zinc ions under static conditions are studied.

The pyrolysis product of the sludge after treatment with "dry" ashing showed a relatively high sorption capacity with respect to iron, copper, and chromium ions compared with BAU coal. The degree of purification from heavy metal ions: Fe, Cu, Cr with the use of the test sample after treatment with ashing is 99.6, 80.6, and 78%, respectively.
Treatment with ashing allows a slight increase in the sorption capacity of the solid product of pyrolysis of sludge.

Conclusions

Thus, it has been shown that the method of utilization of carbonaceous waste by low-temperature pyrolysis makes it possible to obtain a complex sorption material. Its sorption properties can be improved by a special procedure - "dry" ashing.
Studies of sorption properties have shown the possibility of using a solid product of pyrolysis of a sludge treated with "dry" ashing as a sorption material designed to remove heavy metal ions from aqueous media.

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