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HEAVY METAL EMISSION FROM PYROLYSIS PRODUCTS OF CARBON-CONTAINING WASTES AFTER ASHING

Ilnar A Nasyrov*, Gennady V Mavrin, Dinar D Fazullin, Aliya R Ahmetshina, Rudel N Safarov

Department of Chemistry and Ecology, Naberezhnye Chelny Institute, Kazan Federal University, RUSSIA

ABSTRACT

In this paper, they studied the emission of heavy metals from a potential sorption material obtained by pyrolysis from silt sediments and treated with "dry" ashing. The use of a solid pyrolysis product after ashing involves the purification of waste water from contaminants. The content of heavy metal ions in aqueous extraction and in the extraction with an acetate-ammonium buffer of a solid pyrolysis product from carbon-containing waste was determined by atomic emission spectrometry. By mass concentration in the order of its value decrease, heavy metal ions in the aqueous extract of the pyrolysis product from mud sediments are arranged in the following series: Si, Sr, V, Mn, Zn, Mo, Ba, Sb, Cu. In the acetate-ammonium extract, heavy metals are in order of value decrease and arranged in the following series: Si, Mn, Zn, Al, Sr, Cr, B, V, Fe, Ba, Ni, Mo, Se, Pb, Sb. They compared the content of harmful ingredients in the aqueous extract of solid pyrolysis products from carbon-containing waste relative to the normative indices of the aquatic environment. They calculated the concentration coefficients compared with the standards for drinking water, fishery water and sewage for the discharge to the centralized system. The obtained results show that the aqueous extracts of the solid pyrolysis products from carbon-containing waste after treatment with "dry" ashing do not exceed the normative indices for sewage by heavy metal content. They determined that the pyrolysis product does not pollute the wastewater after the treatment with ashing, which justifies the possibility of its use from environmental positions with the restriction of wash water discharge from the solid pyrolysis product directly to the fishery water reservoirs.

INTRODUCTION

The protection of the environment from the pollutants entering into it is an important task at the present stage of scientific and technical progress development. With household economic and industrial activity of a person, liquid wastes are formed in the form of sewage, which are discharged into the sewage system. The purification of domestic and industrial wastewater is an urgent problem for urban areas [1].

Various methods are used, including sorption, for the purification of sewage from heavy metal ions (HMI). Activated carbons, zeolites, natural materials, etc. are used as sorbents. Often these materials have a high cost and require the use of natural resources [2]. The technical solutions in the field of cleaning are very useful and relevant, which make it a low-waste. The use of carbon-containing waste (CCW) as a valuable secondary material resource will significantly reduce the environmental burden and will allow to obtain a new type of industrial products. There is no need to develop mining or grow new raw materials, which inevitably leads to new pollution of the environment [3].

CCW contain organic components and often mineral substances that are converted to gaseous pyrolysis fuel, liquid pyrolysis fuel and solid pyrolysis product (SPP) during pyrolysis. SPP, formed at high temperature, is a potential sorbent, the sorption properties of which can be improved by a special procedure - "dry" ashing. [4]

In order to create highly effective sorption materials, a qualitative and a quantitative analysis is necessary to determine the content of mobile and water-soluble forms of the ingredients in their composition.

METHODS

The study of the aqueous extract and the extract by the acetate-ammonium buffer of the pyrolysis products after the treatment with ashing to determine HMI emission volumes was carried out by atomic-emission spectrometry with inductively coupled plasma using Agilent 720-OES spectrometer [5,6].

The water extract for analysis was prepared by the dissolution of 30 g of the sample in 150 ml of distilled water. After that, the suspension was treated for 30 minutes in a laboratory shaker, and then it was settled and filtered. Similarly, the extract with acetate-ammonium buffer was prepared, by the means of which more ions of heavy metals can be transferred to the liquid phase in comparison with a usual aqueous extract [7,8].

The pH values of the solutions were measured with ANION 4100 ionomer. The conductivity meter ANION-7020 was used to measure mineralization and specific electrical conductivity [9].

RESULTS AND DISCUSSION

As a research object, they took the product sample of CCW pyrolysis treatment, obtained by low-temperature pyrolysis under production conditions. The following CCW were subjected to pyrolysis: the sediment of sewage biological treatment. Subsequently, the obtained pyrolysis product of CCW was

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*Corresponding Author
 Email:
 chem_aleb@mail.ru

subjected to ashing in a muffle furnace at $t = 800\text{ }^{\circ}\text{C}$. We studied the emission of HMI from the obtained samples.

SPP treated with "dry" ashing is a dark brown powder [Fig. 1].



Fig. 1: Solid pyrolysis product after ashing.

pH, mineralization and UEP were determined in the aqueous extract of SPP. The results of measurements and normative indices for water bodies are given in [Table 1].

Table 1: Indices of aqueous extract of solid pyrolysis product after ashing

sample	pH, units pH	SEC, μS / cm	mineralization by NaCl, mg / dm^3
sludge	7.05	307	146.5
TLVdrinking water	6.0-9.0	-	1000
TLVopen reservoirs	6.5-8.5	-	1000
LVwaste water	6.0-9.0	-	3000

pH value 7.05 indicates almost a neutral aqueous extract medium and does not exceed the pH standard for the waters of household and cultural value, fishery and sewage waters, which is in the range of 6-9 pH units [Table 1]

The results of HMI content determination in an aqueous extract and in the extraction of acetate-ammonium buffer are given in [Table 2].

[Table 3] indicates, for comparison, the maximum permissible concentration of the ingredient in the water of domestic and cultural facilities (TLVdrinkingwater), the maximum permissible concentration of the ingredient in the water of fishery facilities (TLVopenreservoirs), the permissible concentration of pollutants in wastewater admitted to discharge into a centralized water disposal system (LVwastewater) [10].

Table 2: The content of heavy metal ions in the aqueous extract, the content of heavy metal ions in the extract by ammonium-acetate buffer, standards

element	concentration in aqueous extract, mg / dm^3	concentration in extract by acetate-ammonium buffer, mg / dm^3
Al	<0.1	2.77
Ba	0.079	0.381
Be	<0.01	<0.01
Cd	<0.05	<0.05
Co	<0.2	<0.2
Cr	<0.15	<0.15
Cu	0.001	0.869
Fe	<0.05	0.385
Mn	0.234	9.94
Mo	0.110	0.126
Ni	<0.001	0.150
Pb	<0.001	0.081
Sb	0.007	0.008
Se	<0.005	0.086

Si	0.996	23.7
Sr	0.515	2.32
Ti	<0.1	<0.1
V	0.267	0.846
Zn	0.175	3.08
B	<0.1	0.861
Ag	<0.3	<0.3
As	<1	<1

Table 3: Standards for heavy metals

Element	TLVdrinking water	TLVopen reservoirs	LVwaste water
Al	0.2	0.04	3
Ba	0.7	0.74	-
Be	0.0002	0.0003	-
Cd	0.001	0.005	0.015
Co	0.1	0.01	-
Cr	0.05	0.02	0.5
Cu	1	0.001	0.5
Fe	0.3	0.05	3
Mn	0.1	0.01	1
Mo	0.25	0.001	-
Ni	0.1	0.01	0.25
Pb	0.01	0.006	0.25
Sb	0.05	0.005	-
Se	0.01	0.002	-
Si	10	-	-
Sr	7	0.4	2
Ti	0.1	0.06	-
V	0.1	0.001	-
Zn	1	0.01	1
B	0.5	0.5	-
Ag	0.05	-	-
As	0.01	0.05	0.01

According to the analysis results, the sample of SPP CCW after the treatment with "dry" ashing contains the following metals in the mobile form in the order of concentration decrease [Table 4]

Table 4: Ranks of priority of heavy metals in aqueous extract

sludge	Si, Sr, V, Mn, Zn, Mo, Ba, Sb, Cu
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The acetate-ammonium extract TM has the following series in the order of value decrease [Table 5]

Table 5: Ranks of priority of heavy metals in extract by acetate-ammonium buffer

sludge	Si, Mn, Zn, Al, Sr, Cr, B, V, Fe, Ba, Ni, Mo, Se, Pb, Sb
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In order to evaluate the impact of SPP CCW on water objects of the environment after the treatment by heavy metal ion leaching with water and acetate-ammonium buffer they calculated the concentration coefficients relative to TLVdrinkingwater, TLVopenreservoirs, LVwastewater. according to the following formulae:

a) the concentration coefficient of HMI in SPP extract after the treatment with respect to TLVHMI in the water of domestic and cultural objects.

$$K_{\text{drinking water}} = \frac{C}{\text{TLV}_{\text{drinking water}}} \quad (1)$$

b) the concentration coefficient of HMI in SPP extract after treatment with respect to TLV in the water of fishery reservoirs.

$$K_{\text{open reservoirs}} = \frac{C}{\text{TLV}_{\text{open reservoirs}}} \quad (2)$$

b) the concentration coefficient of HMI in SPP extract after treatment with respect to the permissible concentration of pollutants in the wastewater admitted for discharge to the centralized water disposal system.

$$K_{\text{waste water}} = \frac{C}{\text{LV}_{\text{waste water}}} \quad (3)$$

The calculation results are given in [Table 6 and 7].

Table 6: Coefficient of concentration of heavy metals in aqueous extract relative TLV

element	K_{dw}	K_{or}	K_{ww}
Al	-	-	-
Ba	0,113	0,107	-
Be	-	-	-
Cd	-	-	-
Co	-	-	-
Cr	-	-	-
Cu	0,001	1	0,002
Fe	-	-	-
Mn	2,34	23,4	0,234
Mo	0,440	110	-
Ni	-	-	-
Pb	-	-	-
Sb	0,140	1,40	-
Se	-	-	-
Si	0,100	-	-
Sr	0,074	1,29	0,258
Ti	-	-	-
V	2,67	267	-
Zn	0,175	17,5	0,175
B	-	-	-
Ag	-	-	-
As	-	-	-

Table 7: Coefficient of concentration of heavy metals in extract by acetate-ammonium buffer relative TLV

element	K_{dw}	K_{or}	K_{ww}
Al	13,9	69,3	0,923
Ba	0,544	0,515	-
Be	-	-	-
Cd	-	-	-
Co	-	-	-
Cr	-	-	-
Cu	0,869	869	1,74
Fe	1,28	7,70	0,128
Mn	99,4	994	9,94
Mo	0,504	126	-
Ni	1,50	15	0,600
Pb	8,10	13,5	0,324
Sb	0,160	1,60	-
Se	8,60	43	-

Si	2,37	-	-
Sr	0,331	5,80	1,16
Ti	-	-	-
V	8,46	846	-
Zn	3,08	308	3,08
B	1,72	1,72	-
Ag	-	-	-
As	-	-	-

The use of SPP after ashing involves the purification of waste water from pollutants. The obtained results show that the water extract of SPP after its treatment with "dry" ashing does not exceed the normative indices for sewage by HMI content.

The comparison by K_{ww} series according to all indicators [Table 6] is illustrated by the diagram of [Fig. 2], provided for convenience by the value K_{ww} in logarithmic scale according to the base 10.

[Fig. 2]: the elements whose content in the extract exceeds LVwaste water are located above the horizontal line, and the HMI with the content less than the norm is below the horizontal line.

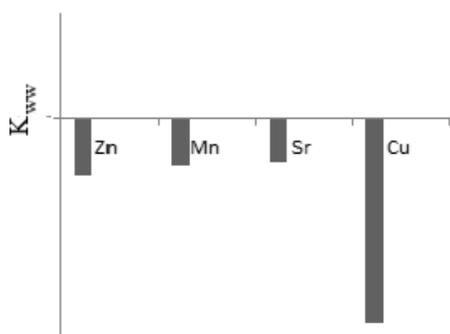


Fig. 2: Coefficient of concentration of ingredients of aqueous extract of solid pyrolysis product after ashing relative to TLVforwaste water in base 10 logarithmic scale.

Thus, in order of K_{ww} decrease HMI in the water extract are located in the following row [Table 8]:

Table 8: Ranks of priority of heavy metals in aqueous extract as reduction of danger to waste water

sludge	Sr, Mn, Zn, Cu
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The absence of HMI normative index exceeding in water bodies indicates a low toxicity of the obtained sample. The use of it as a sorption material is also limited by the possible toxicity. Therefore, there is a need to determine SPP toxicity after ashing experimentally by the mortality of the test object Daphnia magna Straus. The results of the study are shown in [Table 6].

Table 6: Toxicity of solid pyrolysis product after ashing

sample	hazard class	
sludge	1	5

Thus, the studied pyrolysis product of biological wastewater treatment sediment is relatively safe for use as a sorption material.

CONCLUSION

They studied the solid product of carbonaceous waste (sludge) pyrolysis after the treatment with "dry" ashing as the sources of migration into the aqueous phase of harmful ingredients in the form of HMI.

They obtained the values of the observed specific electric conductivity, NaCl mineralization and HMI mass concentration in aqueous extract and in the extraction of the acetate-ammonium buffer of SPP CCW.

HMI subjected to emissions into the water phase are arranged in the order of value decrease according to the following series: Si, Sr, V, Mn, Zn, Mo, Ba, Sb, Cu.

They are arranged in the following series in the acetate-ammonium extract of TM, in the order of value decrease: Si, Mn, Zn, Al, Sr, Cr, B, V, Fe, Ba, Ni, Mo, Se, Pb, Sb.

They compared the content of harmful ingredients in the water extract of SPP CCW relative to the normative indices of the aquatic medium. The concentration coefficients were calculated relative to the standards for drinking water, fishery water, the sewage for discharge to the centralized system.

The obtained results show that in the overwhelming majority the water extract of SPP after the treatment with "dry" ashing does not exceed the normative indices for sewage according to HMI content.

They determined SPP toxicity of the studied CCW after ashing experimentally by the mortality of *Daphnia magna* Straus test object. According to the criteria for hazardous waste classification as a hazard class for the environment [11], the CCW of rubber waste under study belongs to the fifth hazard class.

It has been established that SPP CCW after the treatment with ashing does not have a negative effect on sewage, which justifies the possibility of SPP use from environmental positions with the restriction of SPP wash water discharge into the fishery water reservoirs.

CONFLICT OF INTEREST

There is no conflict of interest.

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None

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