ORIGINAL ARTICLE

Investigation of heavy metals emission from pyrolysis product of rubber wastes treated with ashing

Ilnar A. Nasyrov, Valeriya V. Terentyeva, Gennady V. Mavrin

Department of Chemistry and Ecology, Naberezhnye Chelny Institute of Kazan (Volga Region), Federal University, Russia

Abstract

Aim: In this paper, the emission of heavy metal ions from potential sorption materials is investigated. Samples were obtained by low-temperature pyrolysis from rubber waste (used car tires) and treated with dry ashing. The use of a solid pyrolysis product after ashing involves the purification of wastewater from contaminants. **Methods:** The content of heavy metal ions in aqueous extraction and extraction with an acetate-ammonium buffer of a solid product of pyrolysis of rubber waste was determined by means of atomic emission spectrometry. Of decreasing mass concentration, the heavy metal ions in the aqueous extract of the solid pyrolysis product after treatment with ashing are arranged in the following order: Zn, Si, Mn, Sr, Co, Ba, Mo, Ni, and Sb. In the acetate-ammonium extract of the test sample, the heavy metals are arranged in the following order in the order of decreasing values: Zn, Mn, Co, Fe, Sr, Cu, Al, Ni, B, V, Pb, Cr, Ba, Se, Pb, and Sb. **Results:** The obtained results show that the aqueous extract of the solid pyrolysis product of rubber waste after treatment with "dry" ashing does not exceed the normative indices for sewage by the content of heavy metals. According to the values of the concentration coefficient relative to the permissible concentration of pollutants in the wastewater admitted to discharge into the centralized system of wastewater disposal, the excess of the norm takes place according to Zn. **Conclusions:** It has been established that the solid pyrolysis product of rubber waste treated with ashing does not pollute the wastewater. This implies the possibility of using the processed pyrolysis product from environmental positions with limiting the discharge of wash water directly into fishery water reservoirs.

Key words: Adsorption, ashing, emission, heavy metal ions, pyrolysis, rubber waste

INTRODUCTION

The current task now is to protect the environment from pollutants entering into it. The current task now is to protect the environment from pollutants entering into it, as a result of domestic and industrial activities of man formed waste. Liquid waste in the form of sewage is discharged into the sewer. Wastewater treatment is an urgent problem for urban areas.[1]

Various methods are used to purify sewage from pollutants. One of such methods is sorption. Activated carbons, zeolites, etc., can be used as adsorbents. The sorbents used can be of high cost and require the use of natural resources.[2] A useful solution in the field of environmental protection is the use of waste as a valuable secondary material resource as a sorption material without treatment or with a certain treatment. The use of carbon-containing waste will reduce the burden on the environment and obtain a new type of industrial products. At the same time, there is no need to develop mining or growing new raw materials, which inevitably leads to new pollution of the environment.[3]

In the pyrolysis of carbon-containing waste, a number of valuable wastes are formed: Gaseous or liquid pyrolysis fuel and a solid pyrolysis product. A solid product of pyrolysis of carbon-containing waste is a potential sorbent. Its sorption properties can be improved by special treatment with dry ashing.[4]

To create effective adsorbents, it is necessary to conduct qualitative and quantitative analysis. It is important to determine

Address for correspondence:
Ilnar A. Nasyrov, Naberezhnye Chelny Institute of Kazan (Volga Region), Federal University, Russia.
E-mail: chem_aleb@mail.ru

Received: 13-09-2018
Revised: 24-09-2018
Accepted: 30-09-2018

the content of mobile and water-soluble forms of heavy metal ions in the solid pyrolysis product. The possible emission of these ingredients may limit the use of the pyrolysis product obtained by treatment with the ashing process as a sorption material.

METHODS

A study of the aqueous extract and extraction of the pyrolysis product of the digestion treated with an acetate-ammonium buffer to determine the emission volumes of heavy metal ions was carried out by atomic-emission spectrometry using the Agilent 720-OES spectrometer.[5,6]

The aqueous drawing of the solid pyrolysis product of rubber waste was prepared by dissolving 30 g of the sample in 150 ml of distilled water. The resulting suspension was shaken for 30 min on a stirring device. The sample was then sedimented and filtered. The extraction with acetate-ammonium buffer was prepared in a similar manner. Such an extract allows to transfer more heavy metal ions into the liquid phase in comparison with the usual aqueous extract.[7,8]

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

RESULTS AND DISCUSSION

In this paper, the object of research is the product of pyrolysis rubber waste recycling (used tires). The sample was obtained by low-temperature pyrolysis under production conditions and treated with ashing in a muffle furnace at $t = 800°C$. The emission of heavy metal ions from a pyrolysis-treated rubber waste product was studied.

To study the emission of heavy metal ions, preliminary studies of the primary parameters in the aqueous extraction of a solid pyrolysis product were carried out. The pH, mineralization, and specific electric conductivity were determined. The results of measurements and normative indicators for water bodies are given in Table 1.

The pH value of 6.89 indicates a practically neutral aqueous extracting medium and does not exceed the pH standard for waters of drinking water and cultural and domestic values, fishery and sewage waters, which is in the range of 6–9 pH units [Table 1].

The results of determining the content of heavy metal ions in aqueous extract and in the extraction of acetate-ammonium buffer are given in Table 2. In Table 2, for comparison, the maximum permissible concentration of the ingredient in water of domestic drinking and cultural facilities ($TLV_{drinking\ water}$), the maximum permissible concentration of the ingredient in the water of fisheries ($TLV_{open\ reservoirs}$), and the permissible concentration of pollutants in the wastewater allowed to discharge into the centralized water drainage system ($LV_{wastewater}$).[10]

According to the obtained analysis results, the sample of solid pyrolysis product of rubber waste after treatment with "dry" ashing contains the following metals in mobile form of decreasing concentration: Zn, Si, Mn, Sr, Co, Ba, Mo, Ni, and Sb.

In the acetate-ammonium extraction of the pyrolysis product after treatment with ashing, the ions of heavy metals are arranged in the following series: Zn, Mn, Co, Fe, Sr, Cu, Al, Ni, B, V, Pb, Cr, Ba, Se, Pb, and Sb.

To estimate the effect of the obtained sample on water bodies of the environment by washing out heavy metal ions with water and acetate-ammonium buffer, concentration coefficients were calculated with respect to TLV drinking water, TLV open reservoirs, and LV wastewater. By the following formulas 1-3:

1. Concentration coefficient of the heavy metal ion in the extract relative to TLV in the water of drinking-water and cultural-domestic water objects.

$$K_{drinking\ water} = \frac{C}{TLV_{drinking\ water}} \quad (1)$$

2. Concentration coefficient of the heavy metal ion in the extract relative to TLV in water of open reservoirs.

$$K_{open\ reservoirs} = \frac{C}{TLV_{open\ reservoirs}} \quad (2)$$

3. Concentration coefficient of the heavy metal ion in the extract relative to TLV in wastewater admitted to discharge into the centralized water disposal system.

Table 1: Indices of aqueous extract

Sample	pH, units	Mineralization by NaCl, mg/dm³	Specific electric conductivity, μS/cm
Solid pyrolysis product of rubber waste after ashing	6.89	382	785
$TLV_{drinking\ water}$	6.0–9.0	1000	-
$TLV_{open\ reservoirs}$	6.5–8.5	1000	-
$LV_{wastewater}$	6.0–9.0	3000	-

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	$TLV_{drinking\ water}$	$TLV_{open\ reservoirs}$	$LV_{waste\ water}$
Al	<0.1	1.99	0.2	0.04	3
Ba	0.143	0.220	0.7	0.74	-
Be	<0.01	<0.01	0.0002	0.0003	-
Cd	<0.05	<0.05	0.001	0.005	0.015
Co	0.231	7.89	0.1	0.01	-
Cr	<0.15	0.236	0.05	0.02	0.5
Cu	<0.001	2.24	1	0.001	0.5
Fe	<0.05	5.82	0.3	0.05	3
Mn	0.495	12.7	0.1	0.01	1
Mo	0.010	0.027	0.25	0.001	-
Ni	0.008	1.85	0.1	0.01	0.25
Pb	<0.001	0.492	0.01	0.006	0.25
Sb	0.005	0.019	0.05	0.005	-
Se	<0.005	0.081	0.01	0.002	-
Si	1.64	184	10	-	-
Sr	0.324	3.33	7	0.4	2
Ti	<0.1	<0.1	0.1	0.06	-
V	<0.2	0.557	0.1	0.001	-
Zn	2.05	93.7	1	0.01	1
B	<0.1	1	0.5	0.5	-
Ag	<0.3	<0.3	0.05	-	-
As	<1	<1	0.01	0.05	0.01

$$K_{waste\ water} = \frac{C}{TLV_{waste\ water}} \quad (3)$$

The results of the calculation of the concentration coefficients are given in Table 3.

The use of a solid product of pyrolysis of rubber waste after treatment with ashing involves the purification of wastewater from contaminants, including heavy metal ions. The obtained results show that in the overwhelming majority of the aqueous extract of the solid pyrolysis product after treatment with "dry" ashing does not exceed the normative indices for sewage by the content of heavy metal ions. According to the values of K_{ww}, the excess of the standard is 2.05 times the zinc ion.

A comparison of the concentration coefficient for wastewater (K_{ww}) for all the heavy metal ions to be determined [Table 2] is illustrated by the diagram in Figure 1. The diagram is, for convenience, given by the value of K_{ww} in logarithmic scale on the base 10.

In this diagram [Figure 1], the elements whose content in the extract exceeds $LV_{wastewater}$ are located above the horizontal line. Heavy metals ions with a content lower than the normative index are located below the horizontal line.

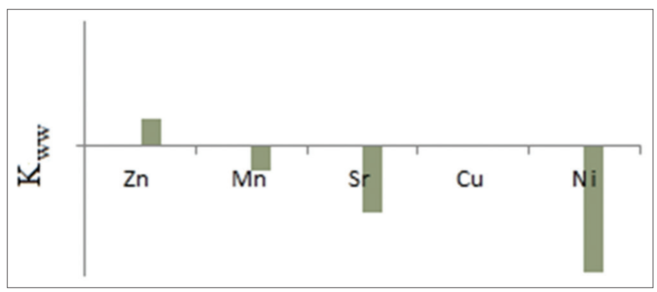

Figure 1: Coefficient of concentration of heavy metals ions of aqueous extract of solid pyrolysis product of rubber waste after treatment with ashing relative to TLV for wastewater in base 10 logarithmic scale

Thus, of decreasing the concentration coefficient relative to wastewater, heavy metal ions in the aqueous extract of the pyrolysis product of rubber waste treated with ashing are arranged in the following order: Zn, Mn, Sr, and Ni.

Summary

A solid product of pyrolysis of V wastes (rubber waste, used car tires) after treatment with "dry" ashing as sources of migration to the aqueous phase of harmful ingredients in the form of heavy metal ions was studied.

Table 3: Coefficient of concentration of heavy metals ions relative TLV

Element	Aqueous extract			Extract by acetate-ammonium buffer		
	K_{dw}	K_{or}	K_{ww}	K_{dw}	K_{or}	K_{ww}
Al	-	-	-	9.95	49.8	0.66
Ba	0.20	0.19	-	0.31	0.30	-
Be	-	-	-	-	-	-
Cd	-	-	-	-	-	-
Co	2.31	23.1	-	78.9	789	-
Cr	-	-	-	4,72	11.8	0.47
Cu	-	-	-	2.24	2240	4.48
Fe	-	-	-	19.4	116	1.94
Mn	4.95	49.5	0.50	127	1270	12.7
Mo	0.04	10	-	0.11	27	-
Ni	0.08	0.80	0.03	18.5	185	7.40
Pb	-	-	-	49.2	82	1.97
Sb	0.10	1	-	0.38	3.80	-
Se	-	-	-	8.10	40.5	-
Si	0.16	-	-	18.4	-	-
Sr	0.05	0.81	0.16	0.48	8.33	1.67
Ti	-	-	-	-	-	-
V	-	-	-	5.57	557	-
Zn	2.05	205	2.05	93.7	9370	93.7
B	-	-	-	2	2	-
Ag	-	-	-	-	-	-
As	-	-	-	-	-	-

The values of the observed values of the specific electrical conductivity, mineralization by NaCl, and the mass concentration of heavy metal ions in the aqueous extract and in the extraction of the acetate-ammonium buffer of the solid product of pyrolysis of rubber waste treated with ashing.

It has been determined that ions of heavy metals undergoing the emission into the aqueous phase of the pyrolysis product are arranged in the order of decreasing values in the following series: Zn, Si, Mn, Sr, Co, Ba, Mo, Ni, and Sb. In the acetate-ammonium extract, ions of heavy metals are arranged in the following order in the order of decreasing values: Zn, Mn, Co, Fe, Sr, Cu, Al, Ni, B, V, Pb, Cr, Ba, Se, Pb, and Sb.

The content of heavy metal ions in the aqueous extract of a solid pyrolysis product of rubber waste treated with ashing relative to the normative indices of the aqueous medium was compared. Concentration factors were calculated with respect to the standards for drinking water, open water, and wastewater for discharge to a centralized system.

The obtained results show that in the overwhelming majority of the water extract of the solid pyrolysis product after treatment with "dry" ashing does not exceed the normative indices for sewage by the content of heavy metal ions. According to the values of the concentration coefficient (K_{ww}) for wastewater, the excess of the norm takes place according to Zn.

CONCLUSIONS

The conducted studies show that the solid product of pyrolysis of rubber waste after treatment with ashing does not have a negative impact on sewage. This fact makes it possible to talk about the possibility of using the obtained sorption material from environmental positions with limiting the discharge of wash water directly into open water reservoirs.

ACKNOWLEDGMENTS

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

REFERENCES

1. Nasyrov IA, Zinnatov RR, Mavrin GV. Pyrolysis of silt Sediments of Sewage Treatment Plants as a Method of Utilization. Belgorod: Modern Trends in the Development of Science and technology: A collection of Scientific Papers on the Materials of the VIII International (correspondence) Scientific and Practical Conference; 2015. p. 19-20.
2. Gulyaev IS, Dyakov MS, Savinova YN, Glushankova IS. Analysis and study of methods of neutralization and disposal of sewage sludge biological treatment plant. Bull PNIPU Prot Environ Transp Saf Life 2012;2:18-32.
3. Minori Uchimiya, Wartelle LH, Klasson KT, Fortier CA, Lima IM. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. J Agric Food Chem 2011;59:2501-10.
4. Nasyrov IA, Ahmetov VM, Miftahov MN, Mavrin GV, Sokolov MP. The problem of disposal sludge treatment plants. Int J Pharm Technol 2016;8:14359-65.
5. Deliyanni EA, Peleka EN, Matis KA. Modeling the sorption of metal ions from aqueous solution by iron-based adsorbents. J Hazard Mater 2009;172:550-8.
6. Zaini MA, Okayama R, Machida M. Adsorption of aqueous metal ions on cattle-manure-compost based activated carbons. J Hazard Mater 2009;170:1119-24.
7. Nasyrov IA, Dvoryak SV, Shaikhiev IG. Sorption properties of carbon waste pyrolysis product for biological wastewater treatment. Acta Technica 2016;61:307-14.
8. Nasyrov IA, Ahmadieva AI, Fazullin DD, Mavrin GV, Sokolov MP. Petroleum containing wastewater products purification by carbon-containing wastes

pyrolysis products. Turk Online J Des Art Commun 2017;7:1713-28.

9. Nasyrov IA, Mavrin GV, Ahmetshina AR, Ahmadieva AI. Sorption properties of pyrolysis products of sludge, wood waste and rubber waste for heavy metal ions. J Fundam Appl Sci 2017;9 S1:1615-25.
10. Bespamyatnov GP. Threshold limit values of harmful substances in air and water. The handbook for the choice and hygienic assessment of methods of neutralization of industrial wastes. 2nd PROD. The Lane and Additional-L.: Chemistry. 2016; 3:673-692..

Source of Support: Nil. **Conflict of Interest:** None declared.