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ANITA STAROŃ, ZBIGNIEW WZOREK, MARCIN BANACH*

ASHES OBTAINED AFTER BURNING OF MBM – PHYSICAL AND SORPTIVE PROPERTIES

POPIOŁY ZE SPALANIA MĄCZKI MIĘSNO-KOSTNEJ – WŁAŚCIWOŚCI FIZYCZNE I SORPCYJNE

Abstract

The paper presents method of utilization of meat bone-meal (MBM) and the results of researches of obtained ashes that can be then used as a sorbent to removal heavy metals ions from the solutions. Physical properties of ashes obtained at 750°C that have influence on sorptive ability, were examinated: specific surface, volume and size of pores, grain-size distribution of material, open and close porosity. The structure of the material was observed. The removal degree of cadmium and zinc from model solutions, that were in contact with the ash, was determined.

Keywords: meat-bone meal, adsorption, ashe

Streszczenie

W artykule przedstawiono metodę utylizacji mączki mięsno-kostnej (MBM) oraz wyniki badań nad możliwością wykorzystania otrzymanych popiołów jako sorbentów do usuwania metali ciężkich. W popiołach otrzymanych w temperaturze 750°C badano czynniki mogące mieć wpływ na właściwości sorpcyjne: porowatość, uziarnienie oraz strukturę materiału. Badano stopień usunięcia jonów kadmu i cynku z roztworów modelowych na otrzymanych popiołach.

Słowa kluczowe: mączka mięsno-kostna, adsorpcja, popiół

* MSc. Eng. Anita Staroń, Prof. PhD. Eng. Zbigniew Wzorek, PhD. Eng. Marcin Banach, Institute of Chemistry and Inorganic Technology, Faculty of Chemical Engineering and Technology, Cracow University of Technology.

1. Introduction

The formation of solid and liquid waste is the result of industrial development and increasing needs arising from the human existence. Solid waste is stored in industrial waste lagoon or storage yard and liquid waste after the removal of these harmful ingredient is discharged to surface waters.

There are many methods used in industrial wastewater treatment: precipitation, oxidation and reduction, ion exchange, filtration and electrochemical methods. These methods have significant disadvantages although advances in technology. These disadvantages are incomplete metal removal, high demand for energy or raw materials, requirements for equipment and advanced monitoring systems, the formation of toxic sludge or other by-products that require utilization [1]. Precipitation is the most popular method of sewage treatment and requires a low financial investment. It consists in carrying out metals to sparingly soluble form of salts, and then separating them from the mother liquors by decantation or filtration. The method of precipitation in many cases does not give a satisfactory result and purified wastewater do not meet the standards for acceptable value of pollution indices for the treated industrial wastewater. Using of an additional cleaning is required. Preliminary treatment of wastewater at its source using adsorption techniques that use inexpensive materials seems to be a reasonable. Such materials are: natural absorbents, waste and by-products from agriculture and industry, characterized by high porosity and large sorption capacity for heavy metals. Because of their ecological safety and ease in obtaining the interest has increased in [2]. The literature data show that biomass can be successfully used in the processes of sorption (walnut shells, algae, fungi, lichens, minerals, eucalyptus bark, pulp obtained from the processing of sugar beets) [3–9]. The aapplication of biosorption process reduces investment costs by 20%, operating costs by 36% and the total cost of cleaning up to 28% compared with the traditional sorptive process [1].

Heavy metals (Pb, Zn, Cd, Hg, Cu, Cr, Ni) are the inorganic pollutants in sewage and require special attention, because of their toxic nature. Heavy metals cause danger to living organisms and permanent damage [10].

Cadmium is one of the most toxic elements. It can occur in water in the form of free ions as well as in the hydrated complex ions and organic chelates. This element is easily taken up by plants and has a high bioavailability [11, 12].

Zinc is an element that occurs widely in the earth's crust. It can occur in ionic form, create complex ions in reactions with inorganic ions, chelate with organic compounds and it depends on pH. Both zinc and cadmium, belong to the elements of motile, migrating from soil to water in an oxidizing environment of acidic reaction [12].

The article presents an attempt to use ashes obtained as a result of burning MBM at temperature 750°C in time of 30 minutes, as an efficient and environmentally sorbent used to remove cadmium and zinc from wastewater.

2. Experimental part

2.1. Methodology of researches

The humidity content of crude MBM was determined with the use of the WPS210S model of a RADWAG weightdryer, at a temperature of 105°C, and the sampling time of 5 seconds. Incineration of the material took place in a rotary kiln. MBM was given co-current, with constant speed of about 2 kg/h by the ribbon feeder and furnace turns 1.3 turns/min. The dwell time of material in the furnace was about 30 minutes. Granulometric composition was determined for the obtained ash using a set of seven sieves with mesh diameter control from 0.063 to 4 mm and the electric shaker (according PN-88/C-97555/01). Intergranular porosity and the open was calculated from the corresponding mathematical relations (1) and (2) between bulk density, real density and density assuming the presence of closed pores of material. The bulk density determined in accordance with PN-C-04532: 1980. Density assuming the presence of closed pores and real density was determined at a constant temperature using a pycnometer with a volume of 50 ml. In both cases, the sample was degassed using a vacuum drier (at a temperature 90°C, pressure 0.8 bar). The ash was crushed in a mortar to a size below 0.063 mm to determine the real density.

Intergranular porosity is given by:

$$P_c = 1 - \frac{\rho_n}{\rho_{rz}} \tag{1}$$

Open porosity:

$$P_o = 1 - \frac{\rho_n}{\rho_p} \tag{2}$$

where:

P_c – intergranular porosity,
P_0 – open porosity,
ρ_n – bulk density,
ρ_{rz} – real porosity,
ρ_p – density with with closed pores.

The specific surface area was determined by the BET method, based on isotherms of nitrogen sorption obtained in the apparatus ASAP2020, model of Micromeritics. The surface structure was observed using a Nikon optical microscope Eklipse LV100. Quantitative analysis of elements in model solutions and in solutions after adsorption were performed on the spectrometer AAnalist 300 from Perkin Elmer. The phase composition of ashes was studied by X-ray diffraction on Philips X'Pert diffractometer equipped with a Philips PW 1752 to 1700 graphite monochromator, and using radiation of CuKα, 2θ angles of 10–60 degrees.

2.2. Discussion of results

The study was conducted in two steps . The first step was to study the physical properties of ash obtained from burning of MBM in a rotary kiln at a temperature of 750°C and time of 30 minutes. The humidity content of raw MBM was 4.5%. The mass decrement amounted to 75.2% during its combustion. Obtained material was light gray and loose (Fig. 1). The X-ray analysis of the ash showed that the one and only crystalline phase is hydroxyapatite. The sieve analysis of the ash has shown that the dominant fraction of a grain size was from 1–2 mm (37.1%) (Table 1). Intergranular porosity was 0.79, the open 0.78. Specific surface area determined by the BET method for ash formed at 750°C was 7.06 m^2/g. Data on the size of the surface of mesopores and micropores, the average pore volume and average pore size have been summarized in Table 2.

Fig. 1. The ash obtained from burning of MBM at 750°C

Rys. 1. Popiół otrzymany w temp. 750°C

Table 1

The mass fraction of individual grain fraction [%]

The mesh size of sieve [mm]	MBM 750
4	0.87
2	20.90
1	37.13
0.5	27.13
0.25	9.20
0.125	2.13
0.063	0.83
0	1.53

Table 2

Results of analysis by the BET method using nitrogen sorption for the ash obtained from burning of MBM at 750°C [%]

The BET method	MBM 750
Specific surface [m^2/g]	7.06
The average pore volume [cm^3/g]	0.02
The average pore size [nm]	10.15
The surface of mesopores [m^2/g]	6.34
The surface of micropores [m^2/g]	1.03

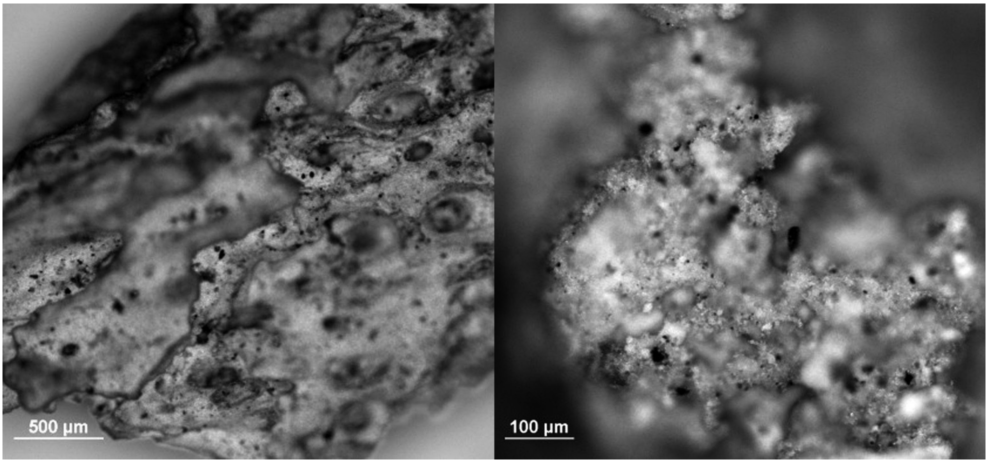

Fig. 2. Microscopic picture of MBM grain after calcination at 750°C

Rys. 2. Obraz mikroskopowy popiołu MBM po kalcynacji w temp. 750°C

The grain structure of ash is heterogeneous, which was observed under an optical microscope (Fig. 2). Grains are probably formed from the inorganic substances, but may contain small amounts of carbon. Their surface has an irregular structure and macropores.

The second step of the research was the realization of the adsorption process using static and dynamic methods. Model solutions used for carrying out the experiments were aqueous solutions of individual metal cations (Cd and Zn) at concentrations to 5000 mg/dm^3 and solutions containing both metals with the same concentrations of each. The solutions were prepared based on analytically pure compounds of metals, containing ions of one type of metal. These solutions were acidified to pH 3.5 before the process of adsorption, to prevent precipitation of metal hydroxides. According to literature data, precipitation of $Zn(OH)_2$ occurs at pH = 6.96, $Cd(OH)_2$ at pH = 9.36 [2]. Samples of solutions containing Zn^{2+} and Cd^{2+} ions with the appropriate amount of sorbent (approximately 8 g weighed to 0.0001 g) were shaken for 24 hours. Measurements were carried out at a constant temperature of 20°C. Clear solutions after filtration were analyzed quantitatively. Next step was to determine changes of the concentration of metal ions in the samples and to determine the removal degree of these ions using equation (3).

$$\text{Removal degree} = [(C_0 - C_1) / C_0] \cdot 100\% \qquad (3)$$

where:

C_0 – initial concentration of metal in solution before sorption, mg/dm^3

C_1 – concentration of metal in solution after sorption

The results for removal of cadmium are shown in Table 3, for zinc in Table 4.

Tables 3 and 4 show the removal degrees of Cd and Zn cations from model solutions having different initial concentrations. Removal of metal is almost complete for the low concentrations.

Table 3

The removal degree of Cd from solution-static method

Concentration of solution before sorption Cd [mg/dm^3]	Concentration of solution after sorption Cd [mg/dm^3]	The difference between the concentration before and after adsorption [mg Cd/dm^3]	Removal degree of Cd [%]	mg Cd/1g ash
54.9	0.0	54.9	99.9	0.4
91.0	0.1	90.9	99.9	0.7
233.0	0.1	232.9	100.0	1.9
566.5	0.8	565.7	99.9	4.5
1133.0	0.5	1132.5	100.0	9.1
5843.8	1143.9	4699.9	80.4	37.6
9887.5	6410.8	3476.7	35.2	27.8

Table 4

The removal degree of Zn from solution-static method

Concentration of solution before sorption Zn [mg/dm^3]	Concentration of solution after sorption [mg/dm^3]	The difference between the concentration before and after adsorption [mg Zn/dm^3]	Removal degree Zn [%]	mg Zn/1g ash
36.1	0.0	36.1	100.0	0.3
68.4	0.0	68.4	100.0	0.5
157.2	0.0	157.2	100.0	1.3
514.1	0.0	514.1	100.0	4.1
782.0	0.0	782.0	100.0	6.3
5950.0	916.3	5033.7	15.4	40.3
9350.0	7763.4	1586.6	17.0	12.7

Sorption in dynamic conditions were carried out using a glass column filled with a defined amount of the deposit, which was the ash. Model solution was given from the top, with a constant flow rate using a metering pump. Model solutions containing one metal, zinc or cadmium with concentration of about 5000 mg/dm^3, and a solution of zinc and cadmium at a concentration of 5000 mg/dm^3 of each metal. It was received in 2 ml effluent.

The relationship between the removal degree of metal from the solution and the volume of model solution, which was passed through the bed is shown on the graphs (Figure 3 and 4).

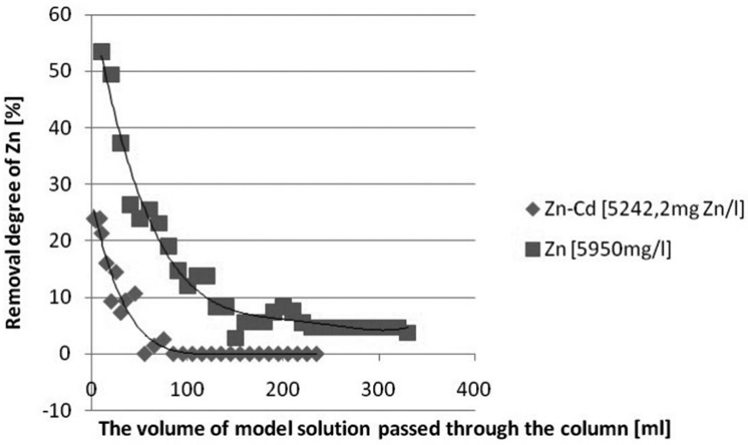

Fig. 3. The relationship between the degree of removal of Zn from the solution and the volume of model solution, which was passed through the bed

Rys. 3. Wpływ objętości roztworów modelowych przepuszczanych przez złoże na stopień usunięcia jonów cynku

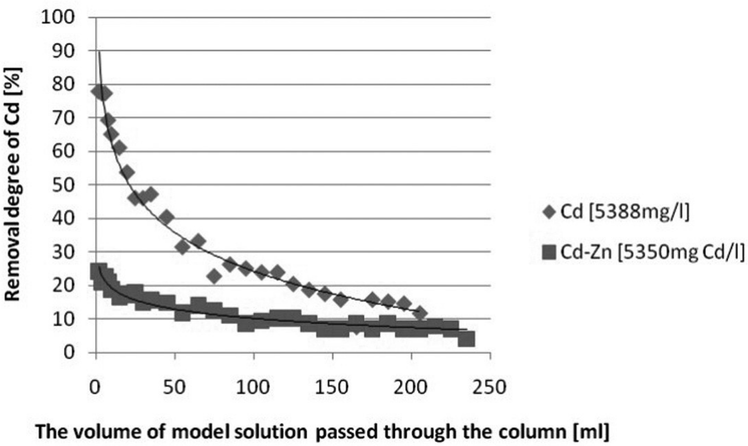

Fig. 4. The relationship between the degree of removal of Cd from the solution and the volume of model solution, which was passed through the bed

Rys. 4. Wpływ objętości roztworów modelowych przepuszczanych przez złoże na stopień usunięcia jonów kadmu

The decrease the concentration of zinc and cadmium in model solutions after passing through the column was observed. It is possible to remove 53% of zinc and 78% of cadmium in the initial stage of the process for solutions with a single metal ion. The decrease of the removal degree of both metals to 24% was seen in solutions containing both metals. The presence of one metal reduces the removal degree of the second metal from the solution. Cadmium is removed better than zinc, which is shown in Fig. 5, presenting the relationship between the removal degrees of both metals from the model solution. The removal degree of zinc was compared with cadmium at the beginning of process but then it decreased rapidly.

X-ray analysis of deposits after the processes of adsorption with cadmium solution has shown that there were identified cadmium in the ash (Fig. 6). The spectrum of ash after the processes of adsorption with zinc solution has shown that only one phase is crystalline hydroxyapatite (Fig. 7). It is assumed that the removal of cadmium is done by exchangingion.

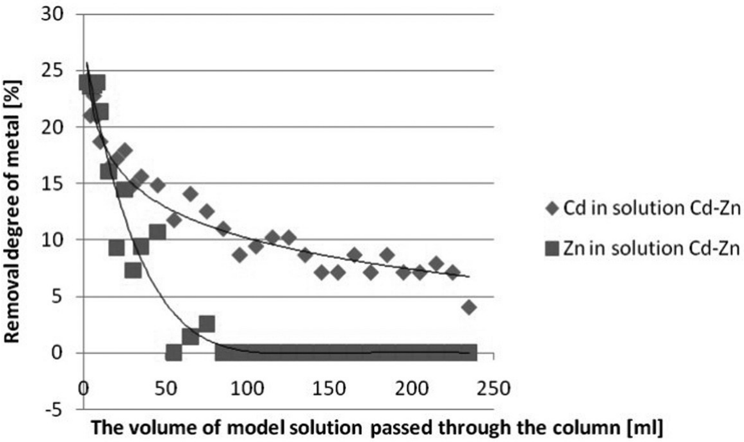

Fig. 5. The relationship between the removal degrees of cadmium and zinc from model solution containing a mixture of these metals with a comparable concentration of about 5000 mg Me/dm^3 and the volume of the model solution , which was passed through a bed

Rys. 5. Zależność stopnia usunięcia jonów cynku i kadmu z roztworu zawierającego mieszaninę jonów o porównywalnym stężeniu 5000 mg Me/dm^3 od objętości roztworu modelowego przepuszczonego przez złoże

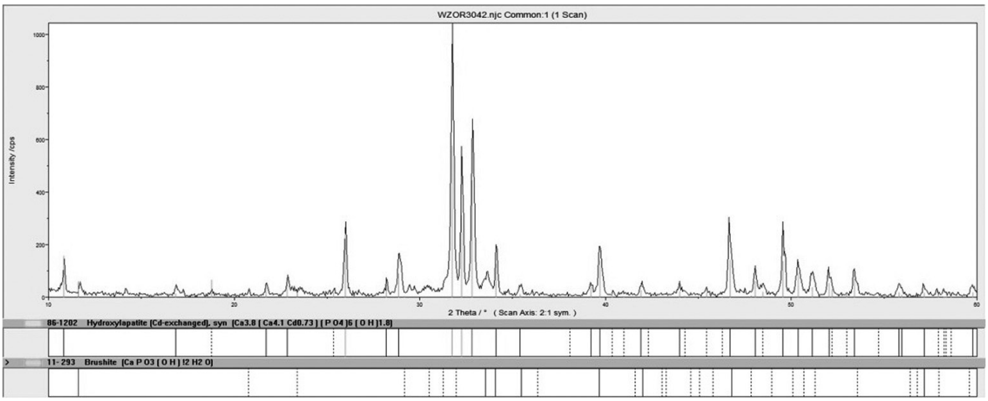

Fig. 6. Diffractogram of ash from burning MBM at 750°C after contact with cadium solution

Rys. 6. Dyfraktogram MBM kalcynowanego w temp. 750°C po adsorpcji jonów kadmu z roztworu

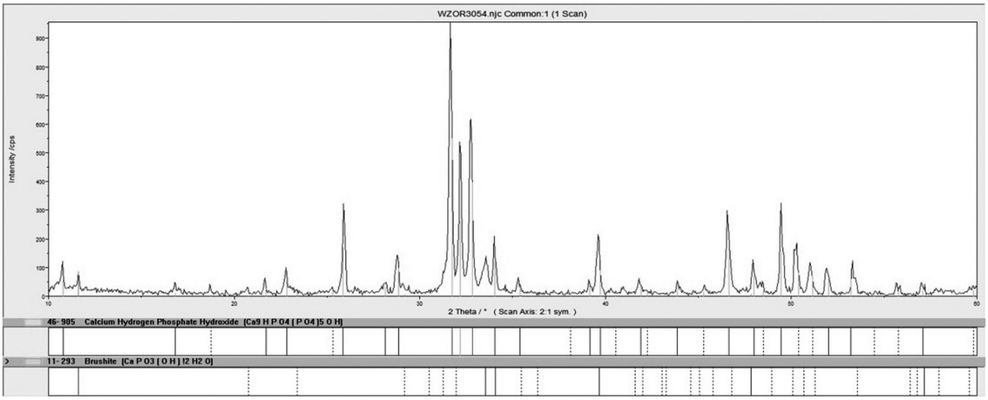

Fig. 7. Diffractogram of ash from burning MBM at 750°C after contact with zinc solution

Rys. 7. Dyfraktogram MBM kalcynowanego w temp. 750°C po adsorpcji jonów cynku z roztworu

3. Conclusions

Ashes obtained after burning of MBM have negligible sorption capacity, as assessed on the basis of experimental studies. It can be assumed that the sorption capacity of ashes is determined by carbon content. Using a static method allows to achieve a greater removal degrees of metal in comparison with the dynamic method but it is related to prolonged time ofcontact ash with the solution. It was found that sorption capacity of ash for cadmium ions is higher than for zinc ions. Adsorbents can displace each other from the surface of the sorbent during the adsorption of multicomponent solutions. The presence of one metal reduces the removal degree of the second metal from the model solution. The presence of cadmium on X-ray spectra suggests that that his removal from the model solution took place through ion exchange with the components of the ash. Removal of the zinc may proceed by another mechanism. The mechanism of binding of these metals should be investigated in future.

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