VELIZAR STANKOVIĆ[1]
MILAN GORGIEVSKI[1]
DRAGANA BOŽIĆ[2]
GROZDANKA D. BOGDANOVIĆ[1]

[1]University of Belgrade
Technical Faculty in Bor, Serbia

[2]Mining and Metallurgy
Institute Bor, Serbia

MINE WATERS PURIFICATION BY BIOSORPTION COUPLED WITH GREEN ENERGY PRODUCTION FROM WOOD AND STRAW BIOMASS

Article Highlights

- A new process for metal ions removal and recovery from mine waters has been proposed
- The process encompasses heavy metal ions biosorption and green energy production
- The biosorption is performed as two-staged, with cross-flowing of the phases
- Energy production comprises a cogenerative way of burning the loaded biosorbent
- The costs and revenues analysis showed the process's economic sustainability

Abstract

A new process for mine water purification has been proposed, based on biosorption followed by burning the loaded biosorbents. Wheat straw and sawdust of trees are convenient as biosorbents in the proposed process. Biosorption was performed in two stages: a cross-flow regime between the mine water and the biosorbent. The achieved copper adsorption degree was > 95%. Based on the mine water volume and its chemical composition, the estimated amount of the biosorbent was 60.000 t/year. The cogenerative mode of the loaded biosorbent combustion was considered for green energy production. For the recovery of metals concentrated in the ash, they must be processed separately. Several possibilities for ash processing were proposed and discussed. For an annual volume of mine water and the copper content in it, the mass and energy balances of the process were estimated, giving some economic data on the process efficiency. The analysis of the revenues and costs, based only on the energy value produced by the combustion of the biosorbent, has shown that the process can economically be viable regardless of the value of the recovered metal.

Keywords: biosorption, biomass combustion, green energy, heavy metal ions, mine water.

Metal or coal mines, active or closed, generate larger or smaller amounts of mining water contaminated with soluble organic or inorganic compounds extracted from ore residues, seriously endangering the local environment. In this sense, the waters from heavy metal mines, known as acid mine drainage (AMD), which contain numerous ionic species, are particularly harmful to surface waters, soil, and wildlife near mines [1–5], which is a great concern for mining owners, and communities near the mining area. Therefore, it is imperative to purify AMDs, which may be the cost for both parties.

The process of mine water generation is complex, involving simultaneous chemical, biochemical, and electrochemical reactions, occurring spontaneously in the presence of sulfide minerals, oxygen, water, and bacteria. The sulfide mineral oxidation processes are well described in the relevant literature [1,6-9] and will not be considered here.

Mine water treatment involves various ion separation and concentration techniques existing on an industrial level for a long time [5,6,8,10–13]. However, each possesses a limited ability of metal ion removal from solutions, as illustrated in Figure 1.
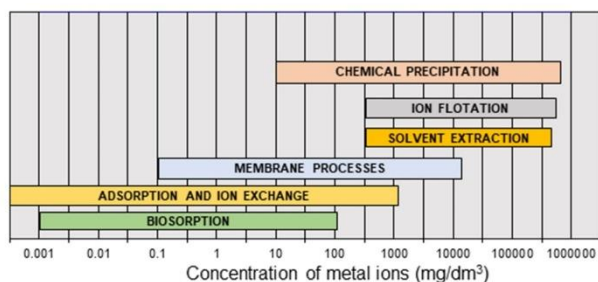
Figure 1. The capability of some methods for metal ions removal from solutions.

Ion adsorption is much more efficient than the other techniques since it can reduce the metal ion concentration well below 1 ppm. On the other hand, biosorption is an emerging version of adsorption that uses natural adsorbents (biosorbents) - a technique not developed on an industrial scale yet, which has shown to be an efficient way of purifying wastewater from metal ions [12,14–17 and literature cited therein]. Various combinations of biosorbents and metal ions were tested through laboratory experiments to determine the adsorption capacity and parameters affecting it; adsorption kinetics and equilibrium. By-products from agriculture and forestry, which show moderate adsorption capacity, have been most frequently tested as biosorbents. Also, their massive production and easy availability make them a good potential for biosorbents. Besides, some of these products are already used as biomass in green energy production [18–22,26,27]. However, despite numerous published papers on biosorption, there is no clear answer to what to do with the loaded biosorbent. Namely, biosorbents change their characteristics after a few adsorption-desorption cycles due to deterioration of their structure, resulting in a reduction of the adsorption capacity, which is a serious drawback of using them on an industrial scale [12,19,22].

Searching for ways to perform metal ions biosorption by omitting desorption, which usually comes after adsorption in conventional processes, led to integrating the two processes – metal ion biosorption from mine waters and green energy production by burning biomass. In this way, three goals would be achieved:

• Mine waters will be purified through adsorption of metal ions from it;

• The charged biosorbent will be burned for energy production without excess CO_2 emission - green energy;

• The adsorbed metals concentrated in the ash will be further processed for metal recovery, thus contributing to a better process economy.

The idea has already been proven on a laboratory scale [12]. The obtained results were encouraging for taking a step towards establishing a process on an industrial scale. That would encompass the following:

• Flowsheet of the copper adsorption process from real mine water;

• Energy and mass balancing;

• Definition of the basic technology units;

• Consideration of the main economic and environmental parameters of the process sustainability.

Mine waters from copper mines, as the aqueous phase, and biomass (either wheat straw or forestry felling), as biosorbent, should serve as a model system in this study.

COPPER IONS BIOSORPTION FOLLOWED BY COMBUSTION OF THE LOADED BIOSORBENT FOR ENERGY PRODUCTION, AND COPPER RECOVERY

Technological aspects of the process

The flow diagram of the newly-proposed process is schematically presented in Figure 2. The process itself consists of four units: the AMDs capturing, collecting, clarifying, and feeding mixture equalizing; preliminary biomass treatment; biosorption and the loaded biomass combustion, the energy production, and the ash treatment; post-treatment of depleted mine water before being discharged into the environment.

Capturing and collecting the AMDs

According to Figure 2, the first operation is to capture all mine water springs and their collection in a collecting pond for equalization. Collecting the AMDs is an engineering issue, which should provide constant initial parameters of the mine water mixture in the collecting pond (chemical composition, flow rate, clarity, and others) entering, as a feeding stream, into the biosorption operation unit. It comprises the design, equipment choice, and provisional costs estimation for capturing the AMD sources, pumping stations, and pipelines for mine water transport to the collecting pond. Eq. (1) can estimate copper concentration in the mixture:

$$C = \frac{1}{Q}\sum_{i=1}^{n}Q_iC_i \tag{1}$$

where: C, C_i (g/m^3) - metal ion concentration in the mixture and each AMD, respectively, Q and Q_i - total flow rate and flow rate (m^3/h) of each AMD spring, respectively.

Mine waters considered in this study originate from

four AMDs of the two copper mines located close to each other [1]. An approximative chemical composition, annual volume V_m (m³/year), and copper quantity of the mine waters mixture, G_{Cu}, (t/year), are evaluated from the individual characteristics of the AMDs, by using Eq. (1) and presented in Table 1. The main expected constituents in the feeding mixture are Cu^{2+}, Fe^{2+}/Fe^{3+} ions and H_2SO_4 (pH = 3 to 5). The

concentration of other metal ions is much lower and will not affect the biosorption of copper ions. Since an optimal pH value for copper biosorption is about 4.5 to 5 [14,16], adjusting the pH to the required value, if it is necessary, can be done with a solution of lime or caustic soda.

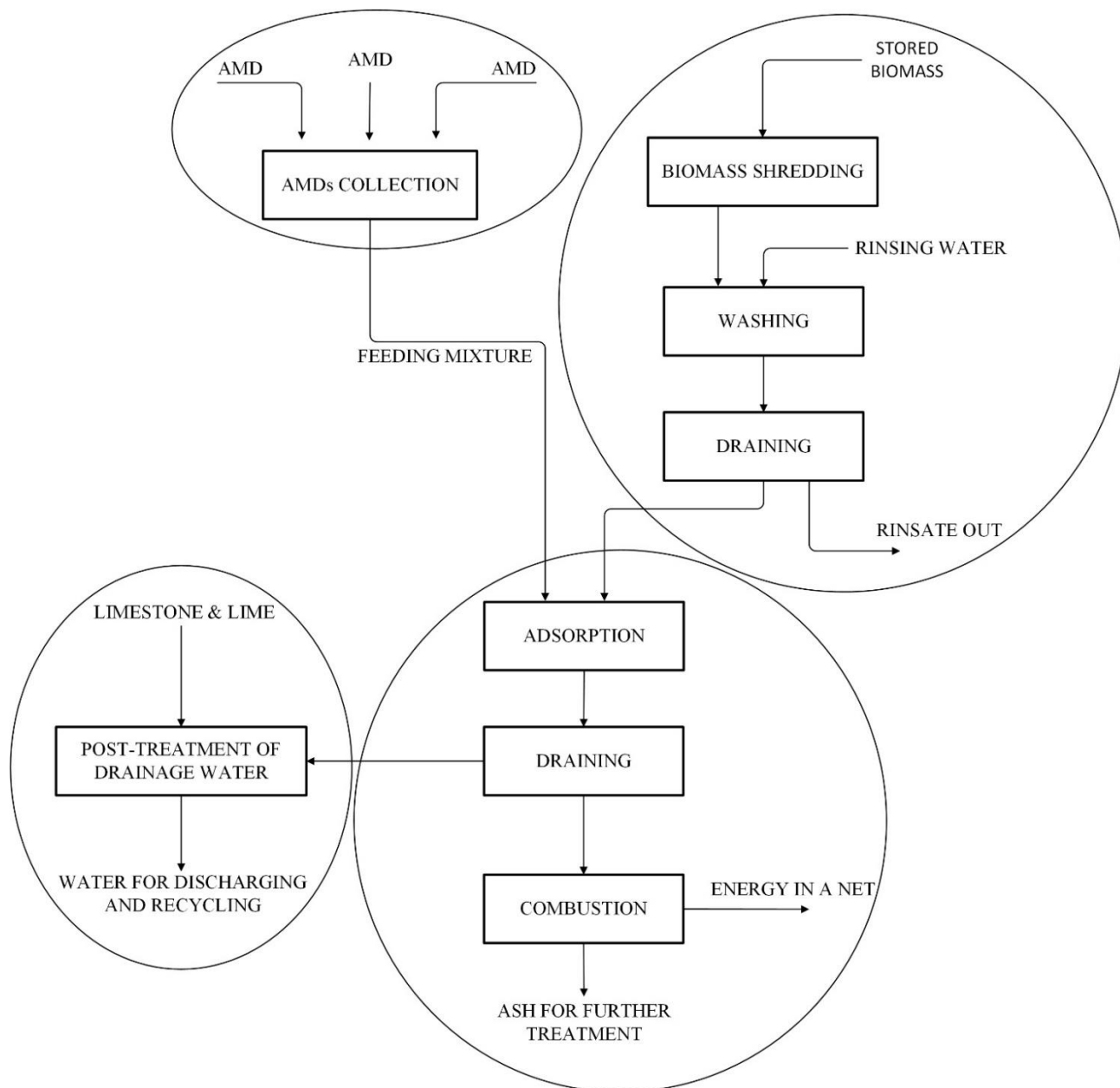Due to the neutralization reaction, fine solid parti-

Figure 2. Flowsheet of the process for copper recovery from mine waters by biosorption.

Table 1. Mean values of ion concentration, volume, and copper quantity in the mine water

C_{Cu}, mg/dm³	C_{Fe}, mg/dm³	C_{Zn}, mg/dm³	C_{Mn}, mg/dm³	V_m, m³/year	G_{Cu}, t/year	pH
93	150	7	<10	2,460.000	222	3 to 5

cles of $Fe(OH)_3$ and $CaSO_4 \cdot 2H_2O$ will be formed in the feeding mixture. Its efficient clarification in the collecting pond is crucial to get a minimum concentration of particles entering the biosorption unit in the mixture. The clarified feeding mixture from the collecting pond enters the biosorption column to contact the biosorbent. Mean residence time between phases must be long enough to achieve an outlet concentration of Cu^{2+} close to equilibrium. Water, depleted in metal ions, leaves the adsorption unit and enters the post-treatment unit, consisting of a pond and a reactive limestone barrier, to neutralize the acid and the remaining metal ions (passive treatment). The purified mine water must fulfill a required quality for being discharged into the nearest watercourse, while the pond size, settling surface, and water hold-up must meet these requests.

Biomass movement through the process

Whether the biosorption will be performed either in a batch stirring tank or a fixed bed adsorption column, stored biomass must be shredded and sieved, obtaining an optimal sieve fraction of 5 to 10 mm. The uniform size of biomass particles contributes to a better carrying out of the biosorption process [12,22]. It was proven that the particles size of straw or sawdust does not affect the biosorption kinetics or the adsorption capacity [14,16,24].

The preparation of the biosorbent comprises washing to remove small particles of dirtiness and leach partly out alkali and alkaline earth metals from it. After drainage and drying, it enters the adsorption unit. The leaching of alkalies refers mainly to straw containing a significantly higher concentration of alkalies than wood residues [22,23]. Besides, the adsorption capacity will be increased by washing approximately 25 to 30% [16,24,25].

The biosorbent, loaded with the adsorbed metal ions, will be separated from the aqueous phase and dried, reaching a natural humidity of 10 to 15% before combustion. The off-gases pass through the heat exchanger, through the gas dedusting unit, before being discharged into the atmosphere. The combustion unit may operate as a heat generation or as a cogeneration unit, in which case the produced electricity will be delivered to a net. Finally, the ash will be disposed of for cooling, further processing, and metal recovery.

MASS AND HEAT BALANCE OF THE PROCESS

Mass balance of metal ions to be adsorbed

Here, the mass balance will relate only to copper ions as the most represented and most valuable ionic

specie, which is transferred from the aqueous to the biosorbent phase. Since other ions, such as Zn^{2+} and Mn^{2+}, have a much lower concentration in the feeding mixture and a lower selectivity coefficient, they will be co-adsorbed with copper in a negligible amount. The latter especially relates to Mn^{2+}, which has the smallest selectivity coefficient. Therefore, the adsorption of Fe^{2+}/Fe^{3+}, having the smallest affinity to be adsorbed, can also be considered negligible [12,14,16].

Assuming the process, presented schematically in Figure 2, should work 330 days a year, the flow rate Q, based on data from Table 1, will be:

$$Q = V_m / 330 \cdot 24 \cdot 60 \; m^3 / min = 5.18 \; m^3 / min$$
$$Q \approx 5.2 \; m^3 / min \tag{2}$$

According to data from Table 1, the copper mass flow G is:

$$G = Q \cdot C_{in} = 0.483 \; kg / min \tag{3}$$

Assuming that the adsorption efficiency in the adsorption unit, defined as:

$$\eta \% = (1 - C_{out} / C_{in}) \cdot 100 \geq 95\% \tag{4}$$

the outlet copper concentration should be:

$$C_{out} = C_{in}(1 - 0.95) \leq 4.65 \; g / m^3 \tag{5}$$

The outlet concentration of $C_{out} < 4.65$ g/m³ of copper ion is low enough and can be treated with limestone in the passive treatment unit. From the total annual copper content $G_{in} \approx 222$ t (See Table 1):

$$G_{ad} = G_{in} \cdot \eta / 100 = 210.9 \approx 211 \; t / year \tag{6}$$

would be recovered, while an outlet amount, $G_{out} < 11$ t, will be treated in the post-treatment stage.

Mass of the required biosorbent for copper biosorption from the mine water mixture

It was shown that the average adsorption capacity of the washed beech sawdust is 7 to 9 mg/g [12,14 and the references cited therein], and for the wheat straw, 6 to 8 mg/g [16 and the references cited therein].

The definition equation of the adsorption capacity is:

$$q_{av} = \Delta C \cdot Q / m \tag{7}$$

where: $\Delta C = (C_{in} - C_{out})$ - is the difference between inlet and outlet concentration from the adsorption process (g/m³), Q - flow rate of the mine water mixture passing through the adsorption unit (m³/h), and m - the mass of the biosorbent (kg).

An annual amount of biosorbent m required to remove ≥ 95% of copper ions from the feeding mixture can be evaluated from Eq. (7). By solving Eq. (7), ac-

cording to the unit mass of biosorbent m, and assuming that an average adsorption capacity is q_{av}= 8 mg/g, the annual amount of biosorbent needed for the yearly total volume V_m is obtained:

$$m = \Delta C \cdot V_m \, / \, q_{av} = \ 27.060 \ t \, / \, year \qquad (8)$$

The mass of biosorbent m, added in a surplus of 10% and rounded, gives approximately $m \approx$ 30.000 t/year.

Specific biomass consumption per unit of the adsorbed copper will be:

$$m_{sp} = \ m \, / \, G_{ad} = \ 142.2 \ t \, / \, t_{Cu} \qquad (9)$$

Cross-flow mode of biosorption

Adsorption can be performed in a single pass, or with recirculation of the aqueous phase, in a stirred reactor, but most often in a column with a fixed bed of adsorbent - in one stage or as a multi-staged operation with countercurrent or with cross-flow of the contacted phases.

The published papers on the adsorption kinetics in a batch mixing reactor have shown that biosorption follows a pseudo-second-order kinetic model and rapidly occurs in the first 10 min to 30 min of the contact time. By exceeding this rapid initial period, adsorption enters a period where the adsorption capacity changes very slowly, reaching an adsorption degree of about 80% [12,14,16]. Furthermore, numerous researches have shown that the equilibrium state between Cu^{2+}-ions and both here considered biosorbents can be described quite well by the Langmuir adsorption model [12–17,24 and the references cited therein].

The adsorption process should be carried out at least in two steps, schematically presented in Fig. 3, to achieve the adopted copper removal degree > 95%. By performing the biosorption in a single pass of the aqueous phase through the fixed bed column, the biosorbent will be loaded only about 50% with metal ions before the breakthrough point appearance on the S-curve [12, 28–30]. Therefore, the estimated mass of biosorbent should be doubled to 60,000 t/year, regardless of whether a batch mixing reactor or adsorption column is used. For a deeper understanding, it is necessary to optimize the process. The outlet copper concentration can be even less than the one estimated by Eq. (5): < 0.93 mg/dm^3, performing the biosorption in two stages as a cross-flow of the phases.

Heat balance of the burned biosorbents and the energy to be generated

Some physical characteristics of different types of trees and straws, which would serve as biosorbents, are presented in Table 2. For comparison, the corresponding characteristics of heavy oil are shown in the last row.
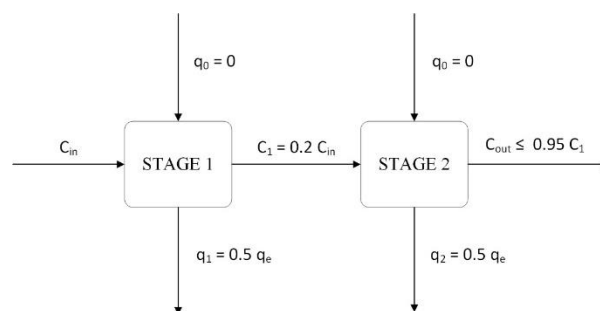

Figure 3. Cross-flow column biosorption of copper ions from mine water mixture.

Table 2. Some physical characteristics of wood and straw biomass

	Moisture, %	Lower heating value, MJ/kg	Ash, %	Remarks
Beech	8 – 22	14.4	0.37	
Oak	13.1	14.1	2	With bark
Poplar	5.5	14.5	< 1	
Felling residue	7–15	15.5	< 1	
Chips	15	15	<1	
Sawdust	5.5–13	17–18.4	<1	
Wheat straw	8.3–14	14	4.5–9	[18, 20]
Barley straw	15	14.2	5–7	
Triticale straw	8–12	15.2	4.6	[31]
Heavy fuel oil	1	min 40	0.2	S < 3 %

Apart from sawdust and triticale straw, the values of lower thermal power (LHV) of other species do not differ significantly and can be considered constant. Oak differs in that it has more than twice the ash content of other deciduous trees. By burning straw, almost 5 to 10 times more ash will be obtained than from the same amount of wood biomass. In this sense, straw biomass seems less suitable as a biosorbent. Based on Table 2, an assumed LHV can be h = 14 to 15 MJ/kg. Combusting the m t/year of the biosorbent, loaded with the adsorbed copper, will generate the energy E:

$$E = h \cdot m = \\ 8.4 \cdot 10^8 \, MJ \, / \, year \ or \ E \approx 23.33 \cdot 10^4 \, MWh \, / \, year \qquad (10)$$

The amount of energy E corresponds to an amount of fuel oil of $\approx 21{,}000$ toe/year. According to the average European price, the worth of energy E will exceed many times the value of copper to be recovered, based on the current price at the London Stock Exchange (LSE). Therefore, the cost-effectiveness of the process is based on the cost of energy produced and sold. Thus, the value of the recovered copper will positively affect the economy of the process.

The total input power N_{in}, assuming working time of $\tau \approx 8000$ h/year, is:

$$N_{in} = E / \tau = 29.2 \; MW \qquad (11)$$

The output power is:

$$N = \eta_{he} \cdot N_{in} = 25.1 \; MW \qquad (12)$$

where: $\eta_{he} = 0.86$ - plant efficiency for cogeneration of heat and electricity [32].

The output power is a sum of the thermal N_h and electricity N_e power, expressed as:

$$N = N_h + N_e \qquad (13)$$

For cogeneration power plants, there is a ratio between thermal and inlet power in a range of $N_h/N_{in} = 0.55$ to 0.7, allowing for the evaluation of the thermal and then electric power [32]. Choosing the ratio value $N_h/N_{in} = 0.62$, it comes out that $N_h = 18.1$ MW. Introducing this value and the value of N in Eq. (13) leads to $N_e = 7$ MW - the power enough for a community of 5 to 8 thousand homes [33]. Therefore, thermal E_h and electrical E_e energy are as follows:

$$E_h = \tau \cdot N_h = 1.45 \cdot 10^5 \; MWh \, / \, year \qquad (14a)$$

$$E_e = \tau \cdot N_e = 5.6 \cdot 10^4 \; MWh \, / \, year \qquad (14b)$$

Produced ash and its processing

Ash amount will depend very much on the burned biomass. Burning 60.000 t/year of felling residue, 220 to 1200 t/year of ash will be produced in extreme cases. By burning wheat straw (see Table 2), the ash mass will be 2 to 24 times greater than that obtained from wood residues. Using blended biomass from wood residues, one can expect < 600 t/year of ash. An amount of copper oxide should be added to this amount, obtained by the oxidation of 211 t/year of the adsorbed copper. It amounts to > 265 t/year or, taking into account oxides of the other adsorbed metals, up to 280 t/year. In total, it amounts to 880—900 t/year of ash. By burning an equal amount of straw, between 2700 and 5400 t/year of ash can be obtained. Adding up the mass of metal oxides, estimated previously, it amounts

to about 3000–5700 t/year of ash. Besides the quantity, a kind of biosorbent affects the produced ash quality. An approximate copper concentration in the wood ash will be about 24%, while in the straw ash, the corresponding one is to be 4 to 7%. The smaller amount of ash implies its cheaper storage, transport, and further processing. One more thing, there are fewer technological problems when burning wood than straw [19,22,23].

The ash processing scheme, shown in Figure 4, suggests several ways to produce copper or commercial products based on copper and other metals less represented in it. Based on the mine water quality and volume, it is possible to predict the ash composition and choose an optimal way of its processing.
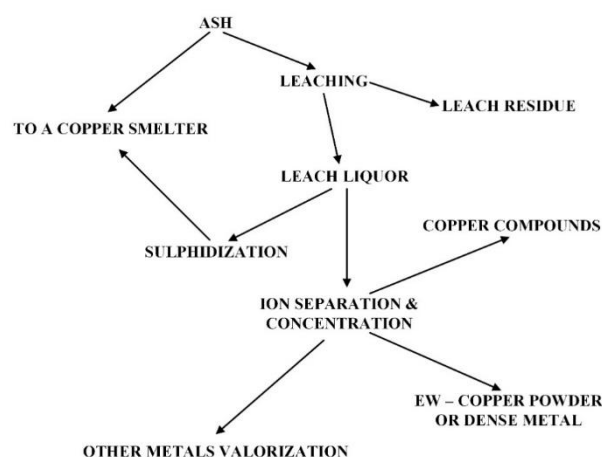

Figure 4. Variants of the ash treatment and metal valorization.

Blending the ash with copper concentrate for charging a copper smelting furnace seems like the shortest and cheapest way for copper recovery as a metal and a way to lose all the other metals in the ash. If there is no copper smelter nearby a copper mine and AMD sources, or if the ash contains other valuable metals in quantities challengeable for recovery, the method of ash processing is leaching and leach liquor processing, as indicated in Figure 4. Such an approach involves a small but complex installation, which could economically be questionable. Because of that, it would be simpler and more cost-effective to sell the ash to a third party that already has a plant for processing similar secondary sources and the market for their products.

ECONOMIC ASPECTS OF THE PROCESS

Biosorbents potential assessment

According to the Ministry of Mining and Energy of Serbia [26], Serbia is a significant producer of various types of biomasses, with a potential of 3.1 Mtoe (expressed as a fuel oil equivalent), having a growing trend. About 1.5 Mtoe is a part of wood biomass from this amount, while 1.6 Mtoe is from agriculture, where

wheat straw and corn stalks make the largest amount. In 2019, for example, wheat straw production was 2.5 Mt. Production of wheat straw in eastern and southeastern Serbia in the same year amounted to 440,000 tons. The price of straw on the market ranges from 30 to 45 €/t. The straw itself participates with less than 30% in that price, while the costs of harvesting, baling, and transport make more than 55%. The rest makes handling and storage. Eastern Serbia has a large forest area, mostly with indigenous deciduous trees. Besides, there are also afforested areas, mainly with acacia and poplar, of which the first one grows well on pyritic substrates near copper mines. Three forest estates from eastern Serbia produce timbers and residues of approximately 124.000 t/year. An approximate price of naturally dried cutting residues (moisture 14%) is c_{bm} = 40 €/t, including transport costs within a radius of 50 km from the place of their production.

To conclude, the annual biomass production from forests and agricultural areas around the copper mines in eastern Serbia is large enough to provide a stable supply of wood or straw in the amount necessary for mine water purification of characteristics as those given in Table 1.

Provisional investment costs and expenditures of the process

Investments in the process, presented in Figure 2, could be provisionally estimated for each unit separately, and the resulting items summed for the whole process. Investments in an ash treatment plant are difficult to estimate due to different possibilities arising from Figure 4 and discussed in subtitle 2.4.

Investment costs

There are different approaches for estimating investment costs for cogenerative power plants burning biomass. The most commonly used method is to apply the coefficient of specific investment costs i_c, defined per installed power unit. According to the literature, the i_c vary in many values – from $0.31 \cdot 10^6$ €/MW to $3.5 \cdot 10^6$ €/MW [19,32–36]. It is worth noting that investments largely depend on the plant size. The larger the plants, the lower the i_c is, and vice versa. The i_c will also vary from country to country, depending on government benefits and credit terms, but very much on the equipment supplier.

Some authors suggest estimating specific investment costs according to a turnkey plant delivery model, including all the preliminary (biomass market research, feasibility studies, ground acquisition, contracting, designing, and others) and post-delivery expenses (training, licensing, etc.) [32].

The chosen i_c = $1.0 \cdot 10^6$ €/MW will be in this study. According to the output power, estimated from Eq. (12), the approximate investment costs i_c will be:

$$I_c = N \cdot i_c = 25.1 \cdot 10^6 € \tag{15}$$

Investments for the two-staged adsorption unit should be added to this value, including all the auxiliary devices, estimated to be $I_a \approx 7 \cdot 10^6$ € [37], including costs for the energy and fluid supply. The biomass preparation system, which includes transport, shredding and dust removal, a rinsing bath, and a drying platform, can be up to I_p =1,500.000 €, so that the total investments will be:

$$I_c = \Sigma I_i = I_h + I_a + I_p = 34.6 \cdot 10^6 € \tag{16}$$

All the construction costs for two ponds and facilities on the micro location should be added to this sum. These costs will strongly depend on the size of the construction area and the surrounding terrain configuration, which cannot be estimated at this stage. The sum in Eq. (16) does not include costs of the land area, building construction works, or the infrastructure construction - local roads, water supply, electricity, taxes, etc.

Since the plant belongs to objects producing green energy, construction of such kinds of plants is being supported by bank credits, EU funds, "carbon credit," local government funds, and finally, the company's investment fund, which usually participates up to 50% in the whole financial construction. Supposing that bank loans make approximately one-third of the total investments, with a repayment period of 10 years and interest of 2.5%, the loan repayment will be $1.18 \cdot 10^6$ €/year.

Major operating costs

Using either wood residue or wheat straw as biomass, at their approximate unit price c_{bm} = 40 €/t, it amounts to:

$$M_{bm} = m \cdot c_{bm} = 2,400.000 € / year \tag{17}$$

The number of workers employed at a cogeneration plant can be estimated based on the following empirical equation:

$$n = 0.3 N_{in} \approx 9 \; workers \tag{18}$$

The number of workers must be doubled for the employees working at the pumping stations, collection ponds, and in the adsorption unit so that the total number of workers is 18. Including the executives, the total number of employees will be 22. An average gross salary in the European countries is set to be: $S_{av} \approx 2000$ €/month. Therefore, the annual sum of the labor costs will be:

261

$$L_c = 12n \cdot S_{av} = 528.000 \; € \, / \, year \qquad (19)$$

The maintenance costs M_c can be set from 4% to 10% of the investment costs. For this calculation, the specific $m_c = 0.009$ €/kWh will check whether the costs are within the relevant range [36]. For the installed power, the M_c will be:

$$M_c = m_c \cdot E = 2,100.000 \; € \, / \, year \qquad (20)$$

Checking gave a figure of 6%, which means the chosen specific price was correct.

The specific depreciation rate d_r depends on the output power, and for such kinds of installations, it is 70.000 €/MW [36]. For an assumed service life of ≥ 25 years, D_r will be:

$$D_r = d_r \cdot N = 1,380.500 \; € \, / \, year \qquad (21)$$

Incomes and expenditures of the proposed mine water treatment process

Energy price varies depending on the country, the type of energy (hydro- or thermal energy), the subsidization by the government, or some other form of support. Green energy production usually enjoys various benefits and promotions over the energy produced from conventional fuels. Based on the published prices from the renewable energy market, the heat energy supplied to local communities, supported due to *feed-in tariff*, is $P_h = 43$ €/MWh. In contrast, the electricity price is $P_e = 82.2$ €/MWh [19]. Based on these unit prices, the heat and electricity energy income will be:

$$IN_h = P_h \cdot E_h = 6,226.400 \; € \, / \, year \qquad (22a)$$

$$IN_e = P_e \cdot E_e = 4,603.000 \; € \, / \, year \qquad (22b)$$

If the current price of copper on the LME is approximately $P_{Cu} = 9000$ $/t (March 2021), the annual income from copper that would be obtained from mine waters, assuming that the ash is processed in a copper smelter, will be:

$$IN_{Cu} = 0.95G_{ad} \cdot P_{Cu} \, / \, 1.19 = 1,515.990 \; € \, / \, year \qquad (23)$$

where: 0.95 is an overall copper removal efficiency, starting from copper concentrate to electrorefining; 1.19 is €/US$ exchange ratio.

The total income is:

$$IN = \Sigma IN_i = 12,345.390 \; € \, / \, year \qquad (24)$$

The considered expenditures include VAT, tax for industrial water discharging (WDT), and ash processing costs (*APC*).

The *APCu* is estimated to be 2000 €/t of copper, or:

$$APC = 2000 \cdot G_{ad} = 440.000 \; € \, / \, year \qquad (25)$$

VAT on the income is assumed to be 10%, so that it will be: VAT ≈ 1.23·10⁶ €/year on an annual level.

The tax for discharging industrial waters into surface waters, according to the local regulations for the unit $WDTu = 4.38$ c€/m³. For an annual volume V_m, it is:

$$WDT = 0.0438 \cdot V_m = 107.700 \; € \, / \, year \qquad (26)$$

In Table 3, the estimated main income and expenditure values of the loaded biosorbent combustion plant are summarized. As expected, the revenue from the delivered energy makes up almost 90% of the total income. Also, the main costs are not so high, making the whole cost analysis positive, with a profit P slightly higher than 2.7·10⁶ €/year. Therefore, an approximate investment repayment period (IRP) can be estimated as:

$$IRP = I_c \, / \, P = 12.6 \; years \qquad (27)$$

This period will be extended, taking into account taxes on the profit.

Indeed, the value of recovered copper is and always will be much smaller than the produced energy. Even if the copper value does not make a significant contribution to the financial balance, the ecological aspect of the process is much more effective, contributing to a cleaner environment in two ways:

- because of metal ions removal from mine water and their eventual reuse;

- because of a contribution to a greenhouse gas reduction.

- Namely, CO_2 from burned biomass has a neutral impact on the environment.

CONCLUSION

A new approach to mine water purification from copper and other metal ions has been proposed, encompassing two processes: metal ions biosorption and energy production by burning the loaded biosorbent. The biosorption would be carried out in two stages, continuously for the aqueous phase, in the cross-flow mode according to the biosorbent. In this way, 99% of copper ions could be adsorbed from the mine waters mixture. Then, the loaded biosorbent would be burnt - producing heat and electricity. Based on the annual volume of mining water and its copper potential, the required amount of biosorbent was determined. In addition, the balance of mass and energy in the process was estimated, enabling the estimate of the plant size and the required investments. The main revenues and costs have shown the process viability and contribution of the recovered copper value to the overall process

Table 3. Basic economic indicators of the cogeneration plant for combustion of the biosorbent loaded with copper

Item	Income·10^6 €/year	Item	Cost·10^6 €/year
Heat	6.2264	Biomass	2.4
Electricity	4.603	Maintenance	2.1
Copper	1.516	Labour	0.528
ΣIN_i	12.3454	Ash processing costs	0.44
		Vat (10 %)	1.23
		Depreciation	1.38
		Loan repayment	1.18
		Financial insurance	0.236
		Water discharge. Tax	0.108
		ΣCO_i	9.602
Total income:	12,345.400	Total costs:	9,602.000

* Average annual profit: $P = \Sigma IN_i - \Sigma CO_i = 2.7434 \cdot 10^6$ €/year.

economy. Therefore, the process will significantly contribute to a cleaner environment in an economically and ecologically sustainable way, producing purified mine waters, which could be either reused or discharged to the nearest water recipients. In addition, due to the natural carbon cycle, combustion of the loaded biosorbent will have almost zero CO_2 emission, giving an additional contribution to a cleaner environment.

Acknowledgment

REFERENCES

[1]	V. Stanković, B. Božić, M. Gorgievski, G. Bogdanović, M. Žikić, J. Min. Metall. A Min. 57 A (1) (2021) 33–42.

[2]	D.B. Johnson, K.B. Hallberg, Sci. Total Environ. 338 (2005) 3–14.

[3]	H. Egerer, P.C. Sandei, O. Simonett, P. Peck, Mining and Environment in the Western Balkans, 1st Edition January 2010, Editor: C. Stuhlberger; Publisher: UNDP, UNEP, OSCE, NATO, UNECE and REC.

[4]	L. Joseph, B.M. Jun, J.R.V. Flora, C.M. Park, Y. Yoon, Chemosphere 229 (2019) 142–159.

[5]	D.K. Nordstrom, R.J. Bowell, K.M. Campbell, C.N. Alpers, Challenges in Recovering Resources from Acid Mine Drainage, in Proceeding of 13th International Mine Water Association Congress - Mine Water & Circular Economy, Lappeenranta, Finland (2017), p.1138–1146.

[6]	M. Gorgievski, D. Božić, V. Stanković, G. Bogdanović, J. Hazard. Mater. 170 (2009) 716–721.

[7]	V. Stanković, V. Milošević, D. Milićević, M. Gorgievski, G. Bogdanović; Chem. Ind. Chem. Eng. Q. 24(4) (2018) 333–344.

[8]	I. Park, C.B. Tabelin, S. Jeon, X. Li, K. Seno, M. Ito, N. Hiroyoshi, Chemosphere, 219 (2019) 588–606.

[9]	F.A. Habashi, Textbook of Hydrometallurgy, 2nd Ed, Laval University, Quebec City, Canada (1999).

[10]	G. Savov, T. Angelov, A. Tsekov, I. Grigorova, I. Nishkov, XXVI IMPC, 2012, New Delhi, India, Ref. number 1026; https://www.academia.edu/5772175 [accessed 22 April 2021].

[11]	D.S. Malik, C.K. Jain, A.K. Yadav; Appl. Water Sci. 7 (2016) 2113–2136.

[12]	V. Stanković, D. Božić, M. Gorgievski, G. Bogdanović, Chem. Ind. Chem. Eng. Q. 15 (2009) 237–249.

[13]	P. M. Biesheuvel, J. E. Dykstra, Physics of Electrochemical Processes, E-Publishing, Part IV, 2020 p.261; http://www.physicsofelectrochemicalprocesses.com [accessed 4 May 2021].

[14]	D. Božić, V. Stanković, M. Gorgievski, G. Bogdanović, R. Kovačević, J. Hazard. Mater. 171 (2009) 684–692.

[15]	A. Beni, A. Esmaeili, Environ. Technol. Innovation 17 (2020) 100503.

[16]	M. Gorgievski, D. Božić, V. Stanković, N. Štrbac, S. Šerbula, Ecol. Eng. 58 (2013) 113–122.

[17]	D. Božić, M. Gorgievski, V. Stanković, N. Štrbac, S. Šerbula, N. Petrović, Ecol. Eng. 58 (2013) 202–206.

[18]	P. Lauri, P. Havlík, G. Kindermann, N. Forselln, H. Böttcher, M. Obersteiner, Energy Policy 66 (2014) 19–31.

[19]	D. M. Urošević, B. D. Gvozdenac-Urošević, Therm. Sci. 16 (2012) 97–106.

[20]	W. Li, B. Mu, Y. Yang, Bioresour. Technol. 277 (2019) 157–170.

[21] N. Hossain, M. A. Bhuiyan, B. K. Pramanik, S. Nizamuddin, G. Griffin, J. Clean. Prod. 255 (2020) 120261.

[22] L. Deng, T. Zhang, D. Che, Fuel Process. Technol. 106 (2013) 712–720.

[23] B. M. Jenkins, R. R. Bakker, J. B. Wey, Biomass Bioenergy, 10 (1996) 177–200.

[24] D. Božić, M. Gorgievski, V. Stanković, M. Cakić, S. Dimitrijević, V. Conić, Chem. Ind. Chem. Eng. Q. 27 (1) (2021) 21–34.

[25] V. Stanković, M. Gorgievski, D. Božić, Biomass Bioenergy, 88 (2016) 17–23.

[26] The Republic of Serbia, Republican Bureau of Statistics, Annual report No. 260, LXIX, 25.09.2019; ISSN 0353-9555; SRB260 PO16 250919.

[27] M. Šupín, V. Kaputa, J. Parobek, Wood biomass as a renewable resources market development in the EU, in Proceeding of 10th International Scientific Conference WoodEMA, Prague, Czech Republic (2017), p. 25–32.

[28] A. Kogej, B. Likozar, A. Pavko, Food Technol. Biotechnol. 48 (2010) 344–351.

[29] P. Kojić, V. Vučurović, N. Lukić, M. Karadžić, S. Popović, APTEFF 48 (2017) 127–139.

[30] V. Stanković, Fenomeni prenosa i operacije u metalurgiji 2 (Prenos toplote i mase) (Translated: Transfer Phenomena and Unit Operation in Metallurgy 2 (Heat and Mass Transfer), University of Belgrade Technical Faculty in Bor, Bor, 1998; CIP 669.021.3/.4(075.8).

[31] I. Jansone, Z. Gaile, Res. Rural Dev. 1 (2015) 40–44.

[32] B. Simović, A. S. Anđelković, M. Kljajić, KGH 4 (2018) 357–364.

[33] G. J. Mayhead, Biomass to Electricity, Woody Biomass Utilization; University of California Berkeley, Oct. 2010.

[34] D. R. McIlveen-Wright, Y. Huang, S. Rezvani, D. Redpath, M. Anderson, A. Dave, N. J. Hewitt, Appl. Energy. 112 (2013) 396–404.

[35] Z. Liu, X. Li, International Conference on Education, Management Science and Economics (ICEMSE-16); Advances in Social Science, Education and Humanities Research (ASSEHR), Volume 65 (2016) 255–258.

[36] P. Odavić, V. Zekić, D. Milić, Economics of Agriculture, 64 (2017) 587–599.

[37] SAMCO, How Much Does an Ion Exchange System Cost? https://www.samcotech.com/how-much-ion-exchange-system-cost/ [accessed on 25 May 2021].

VELIZAR STANKOVIĆ[1]
MILAN GORGIEVSKI[1]
DRAGANA BOŽIĆ[2]
GROZDANKA D. BOGDANOVIĆ[1]

[1]Univerzitet u Beogradu, Tehnički fakultet u Boru, Srbija

[2]Institut rudarstva i metalurgije Bor, Srbija

NAUČNI RAD

BIOSORPCIJA JONA TEŠKIH METALA IZ RUDNIČKIH VODA NA SLAMI I TRINI I DOBIJANJE ZELENE ENERGIJE SAGOREVANJEM TAKO ZASIĆENE BIOMASE

Predložen je novi proces za prečišćavanje voda rudnika bakra, koji bazira na objedinjavanju dva procesa - biosorpciji iza koje sledi proizvodnja energije sagorevanjem zasićenog biosorbenta. Pšenična slama i trina dobijena mlevenjem sečke drveća se već koriste kao biomasa u proizvodnji energije, a pokazali su i dobre adsorpcione osobine prema jonima bakra. Proces obuhvata biosorpciju, koja se izvodi u dva stupnja, u unakrsnom režimu tokova faza, čime se postiže stepen adsorpcije jona bakra > 95 %. Za razmatranu količinu rudničke vode i njen hemijski sastav, bilo bi potrebno oko 60.000 t/god biosorbenta. Analizirano je sagorevanje ove količine zasićenog biosorbenta i kogenerativna proizvodnja zelene energije, pri čemu bakar i ostali adsorbovani teški metali bivaju koncentrisani u pepelu, koji treba da se posebno procesira. Nekoliko mogućnosti prerade pepela, radi dobijanja bakra, su predložene i razmatrane.

Procenjen je takođe bilans mase i energije predloženog procesa, za tretman određene godišnje zapremine rudničke vode i dobijanja bakra koji ona nosi. Uz to, dati su neki ekonomski pokazatelji efikasnosti procesa, bazirani na procenjenim prihodima i troškovima procesa. Ekonomska analiza je pokazala da bi proces bio održiv čak i samo na bazi energije proizvedene sagorevanjem biosorbenta, te da dobijeni metal predstavlja dodatni prihod, pri čemu je emisija CO_2 gotovo jednaka nuli što, pored prečišćene vode, dodatno doprinosi čistijoj okolini.

Ključne reči: biosorpcija, sagorevanje biomase, zelena energija, joni teških metala, rudnička voda.