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Comparative MCDM analysis for AMD treatment method selection

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Abstract

Robule Lake is located in Eastern Serbia, near city of Bor, known for copper production, and it is being influenced by waste materials from mining activities. For the purification of water from Robule Lake, contaminated with various metal ions (Fe, Cu, Zn, Mn, Cd, Ni, etc.), acid

mine drainage (AMD) treatment methods such as: passive treatment method, sequential neutralization, ion exchange, adsorption process based on low cost adsorbents, adsorption process based on natural zeolits, electrodialysis, filtration with nanofiltration membranes, and reverse osmosis, were evaluated by following MCDM methods: TOPSIS, VIKOR, MOOSRA; WASPAS, and CoCoSo. Criteria used for the evaluation were: efficiency in the metal ions removal and the quality of the purified water, necessity of pre-treatment and / or post-treatment of treated water, possibility of using the generated waste, capital costs, operating and maintenance costs, needed area, and sensitivity of the method. The results of the MCDM analysis showed that sequential neutralization was the most appropriate for this wastewater, while passive treatment system and ion exchange were ranked as second and third, respectively.

After the selection of AMD treatment method, neutralization tests with lime were carried out on the water sample from Robule Lake. The results of sequential neutralization testing showed that concentration of Fe ions could be lowered below the maximal allowable concentration prescribed by Serbian legislation at pH value 4. The other metal ions: Cu, Zn, and Ni needed pH value 7, and Mn and Cd needed pH 10 for effective removal.

Key words: Multiple Criteria Decision Making; Acid Mine Drainage; Robule Lake; Wastewater treatment; Metal ions; Neutralization.

1 Introduction

Mining industry is one of the biggest environmental polluters and it is equally affecting air, soil, and water (Chen et al. 2018; Zeng et al. 2018; Mwaanga et al. 2019). Some metals, as

well as other polluting matters such as suspended particles, trough air, soil, and water, are also endangering health of plants, animals, and humans (Nikolic and Nikolic 2012; Yan et al. 2020).

Bor city is located in East Serbia, and it is best known for copper production from several open-pit and underground mines. Mining activities in Bor began in 1903 and are continuing up to date, so a lot of damage to the environment has been made during this period. Air quality in Bor and surrounding area is affected by dust from open pit mines, mining overburden and flotation tailings dumps in dry windy season, but also by exhaust gasses from copper smelter, so suspended particles of metals and other polluting maters are being carried out to the environment, thus polluting soil (Dimitrijevic et al 2009; Milosavljevic et al. 2020). Also, in rainy season dissolution of metals, sulphur and others occurs, so these ions are transferred trough water streams into surface and underground waters (Avramović et al. 2016; Petrovic et al. 2021). Some of surface and underground waters in Bor are polluted by mining activities up to an extent that there are no living organisms in them. One of the examples is Bor River, one of the Europe's most polluted rivers (Milijasevic et al. 2011).

Since clean water is one of the most important resources of 21th century it is crucially important to preserve rivers and water streams and to prevent their further pollution. Therefore, some activities including wastewater treatment must be undertaken. There are many wastewater treatment methods that are being used and their application and efficiency depend on kind of pollutant present in the water.

It is well known that for different types of wastewater different treatment methods can be applied, more or less efficiently. That is the reason why experts in this field can be hesitant when choosing appropriate water treatment method. There are also several factors that can influence the selection, starting from technical possibilities to apply some method, their efficiency,

ecological aspect and also very important, economical factor. All of this additionally burdens the selection of appropriate wastewater treatment method.

Therefore, in recent years numerous Multiple-Criteria Decision Making (MCDM) methods were used to help in the decision making process. These methods can be applied as a support in many areas of life, industry and science. Some of the MCDM methods have considerable variety of applications in different areas, while some have a smaller number of applications for solving some specific problems. The well-known TOPSIS and VIKOR methods have been used for such problems as: ore deposit selection (Popovic et al. 2020), developing model for municipal solid waste management (Mir et al., 2016), flotation machine selection (Stirbanovic et al. 2019), supplier selection (Wu and Liu, 2011), etc. The less-known and less used MOOSRA method was used for solving laptop selection problem (Adali et al. 2017), machine selection (Sarkar et al., 2015), and so on. Finally, the more recently proposed WASPAS and CoCoSO methods have been used for solving a number of different decision-making problems, such as: assessment of achieving goals of the "Agenda 2030" (Stanujkic et al., 2020), cloud service provider selection (Lai et al. 2020), and tourism attraction selection (Luo et al., 2020).

Application of MCDM methods for water management and wastewater treatment was also the subject of some research. Karimi et al. (2011) selected process for wastewater treatment by using AHP and fuzzy AHP methods, while Ilangkumaran et al. (2013) used PROMETHEE and GRA methods for the same purpose. Dursun (2016) applied Fuzzy VIKOR method for evaluating 4 wastewater treatment methods by 9 criteria and the results of the analysis showed that aerated lagoon was the most suitable. Ayyıldız and Özçelik (2018) applied Entropy, SAW, MOORA, and TOPSIS methods to evaluate the performances of wastewater treatment services

in 30 metropolitan municipalities in Turkey. Anaokar et al. (2018) evaluated the performance of six municipal wastewater treatment plants by using the TOPSIS method. Ali et al. (2020) applied fuzzy VIKOR method to select wastewater treatment technology.

The results of the study for selection of wastewater treatment method by five MCDM methods in the case of Robule Lake are presented in this paper. Information about Robule Lake, such as position and chemical composition of the water and also short overview of methods that were considered for the treatment and purification of the water from this lake are provided in the first section. Second section represents applied methodology based on TOPSIS, VIKOR, MOOSRA, WASPAS, and CoCoSo methods. The results and of MCDM analysis for selection of the wastewater treatment method for purification of water from Robule Lake followed by the results of the laboratory testing conducted using the method that was chosen to be the most appropriate are shown in the third section. The final section offers conclusions and final remarks.

1.1 Robule Lake

A permanent lake Robule is located at the southeast perimeter of the mining waste dump zone (Fig. 1), which is fed by surface water drainage and seepage. From seepage of the disposed waste materials and /or from accumulation of leach solution from heap leachings, this water is highly contaminated with the site specific compounds like sulphate, iron and trace metal elements concurrent to low pH-values below 3 (Gardić et al 2017; Markovic et al. 2020). Also, the colour of the water is red (Fig. 2).

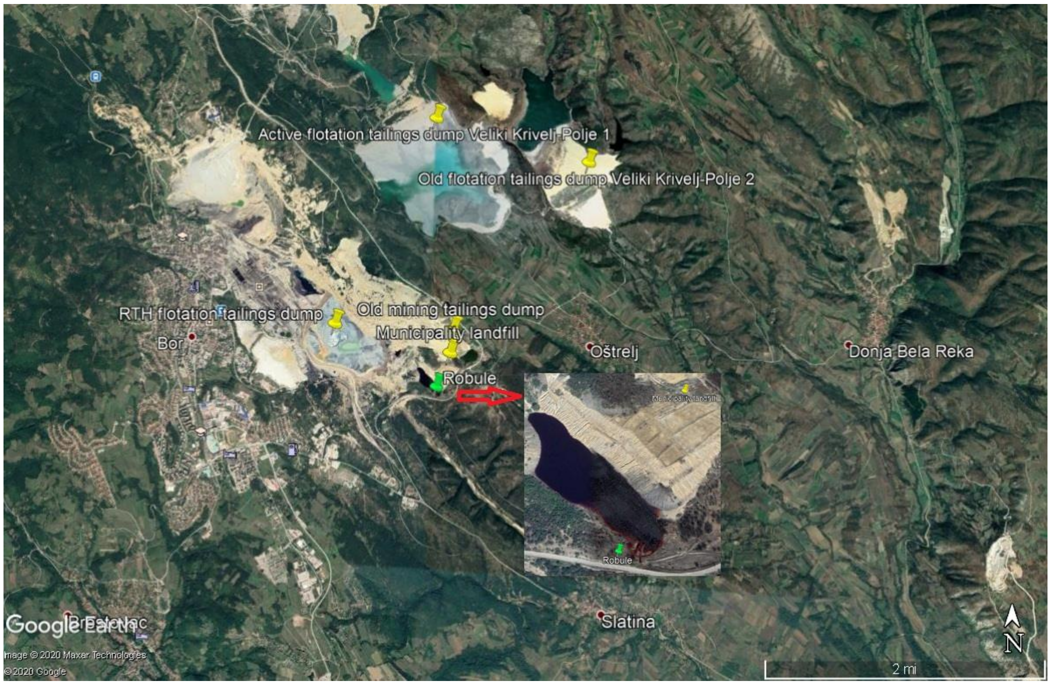

Fig. 1 Location of Robule Lake (Source: Google Earth)

Fig. 2 The appearance of the water from the Robule Lake

Due to its location in the immediate environment and free access to the lake for humans and livestock, Robule Lake represents a high risk of health impairment and as well as an overall environmental risk. At current conditions Robule Lake overflows through a small size pipe conduit and a ditch directly into Bor River. At present Robule Lake still discharges into the Bor River without any treatment.

Water level is mostly constant indicating some water recharge from groundwater or springs. An average flow rate out of the Robule Lake to Bor River is about 500 m³/day [1, 2].

The historical data about Robule Lake water quality is given in Table 1.

Table 1 The historical data about Robule Lake water quality

Characteristic	Unit	Year			Maximum Allowable Concentration (MAC) IV class[4]
		2011[1]	2017[2]	2019[3]	
Colour of water	-	reddish	reddish	reddish	none
Odour of water	-	none	none	none	none
pH	-	2.56-4.20	2.7	2.47	6.5-8.5
Suspended materials on 105 ^{o}C	mg/L	12.0-55.0	-	-	-
SO_4^{2-}	mg/L	4907.5-10570.6	-	7500	300
Fe total	mg/L	526.4-812.0	554.5	287	2
Cu	mg/L	53.0-71.6	64.4	66.39	1
Ni	mg/L	0.6-1.0	0.643	0.6	34
As	mg/L	-	0.0069	<0.007	0.1
Zn	mg/L	24.3-29.1	26.5	17.6	5
Pb	mg/L	-	<0.0021	0.188	14
Cd	mg/L	0.08-0.117	0.0073	0.012	0.9
Mn	mg/L	96.0-133.8	122.6	66	1
Cr	mg/L	-	<0.0017	0.002	0.25

[1]Stevanovic et al. 2013

[2]Gardic et al. 2017

[3]Petronijevic et al. 2019

[4]MAC values for Bor River (Regulation No. 3/1968; Regulation No.50/2012; Regulation No.24/2014)

As it can be seen from Table 1 the water from the Robule Lake is very polluted with various contaminates. The contents of Fe, Cu, and Mn, as well as SO_4^{2-}, are extremely over values proscribed for IV class water (Regulation No. 3/1968). Also, the pH values of the water

are low, i.e. acidic, which can be very dangerous and harmful to the environment. All of these indicators are additionally important bearing in mind that water from Robule Lake is flowing through rivers Bor River and Timok and going to the Danube, which is second largest river in the Europe and also very important habitat for various flora and fauna species.

1.2 Wastewater treatment methods

As it was said earlier, there are numerous wastewater treatment methods that can be equally efficient in terms of quality of obtained water. All of them have some advantages or disadvantages compared to each other (Saha and Sinha 2018), therefore, it is difficult to determine which one is the most appropriate for treatment of particular wastewater.

In this paper following 8 wastewater techniques were analyzed for the treatment of water from Robule Lake:

1. Passive treatment system, i.e. wetland process, is used for treatment of various kinds of wastewaters. Its efficiency in metals removal (Cu, Fe, and Zn) is 70-80%, depending on a metal. Good sides of using this method for treatment of AMD are high daily capacities (up to 3000 m3/day), low operating costs, no need for pre-treatment and post-treatment, while downside is the need for large area.
2. Sequential neutralization process is very efficient for treatment of AMD with high contents of metal ions. Advantages of this method are that pre-treatment is not needed, low operating costs (0.07 $\$/m^3$) and possibilities of income, i.e. sludge valorization.
3. Ion exchange represents a process of purification of aqueous solutions using solid polymeric ion exchange resin. In order to apply this process, it is necessary to perform oxidation, neutralization and precipitation as pre-treatment processes. After that,

efficiency in removal of Cu, Fe, Zn and Cd is 100%. Also, downside of this process is generation of the wastewater and the need for treatment of wastewater from regeneration, which is increasing operating costs, that vary from 0.19-7.3 $\$/m^3$ depending on a source (Sarai Atab et al. 2016).

4. Adsorption process based on low cost adsorbents mainly uses organic or non-organic waste materials for adsorption of metal ions from wastewaters. The efficiency of this process is depending on an adsorbent type and also on a pollutant present in the water. The benefit of this process is low cost of used adsorbents.
5. Adsorption process based on natural zeolites is highly efficient for treatment of wastewaters contaminated with metal ions, but its efficiency depends on ion type. For example, removal efficiency of Fe^{3+}, Mn^{2+}, Zn^{2+}, and Cu^{-} is 80%, 95%, 90%, and 99% respectively. Also, adsorption of elements decreases if initial pH of the AMD solution is lower.
6. Electrodialysis requires pre-treatment such as microfiltration and with this method AMD with higher Fe concentration cannot be treated. On the other side efficiency in metal removal is high, approximately 97%.
7. Filtration with nanofiltration membranes can be used for removal of metal ions (Ni, Cu, Zn, and Pb) from water with over 90% efficiency. Advantage of this method is that no pre/post-treatment of water is needed, and disadvantage is that high water recovery requires high pressure and treatment plant for waste water, i.e. higher operating costs.
8. Reverse Osmosis as a method for treatment of AMD requires no pre/post-treatment, but in order to enhance the water recovery higher pressure is required, which implies higher

treatment costs. Also, treatment plant for wastewater is needed. The efficiency in removal of metal ions (Cu, Fe, Zn, and Mn) is 97-98%.

2 Methodology

In the past few decades, MCDM methods found their applications in solving many problems regarding various selections and making decisions in general, which resulted in proposing numerous new methods. However, only methods that will be used in this study will be mentioned and discussed later: Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) proposed by Hwang and Yoon (1981), Multi-criteria Optimization and Compromise Solution (VIKOR) proposed by Opricovic (1998), Multi-Objective Optimization on the basis of Simple Ratio Analysis (MOOSRA) proposed by Kumar and Ray (2015), Weighted Aggregated Sum Product Assessment (WASPAS) proposed by Zavadskas et al. (2012), and Combined Compromise Solution (CoCoSo) proposed by Yazdani et al. (2018).

2.1 The TOPSIS method

Compared to other MCDM methods, the TOPSIS method is based on the specific idea that an alternative is more appropriate if it is as close as possible to the ideal point and at the same time as far as possible from the anti-ideal point, in Euclidean space. In order to determine the relative distance of alternatives to ideal point d_i^+, i.e. anti-ideal point d_i^-, Eq. (1) and (2) need to be used.

$$d_i^+ = \left\{\sum_{j=1}^{n}\left[w_j\left(r_{ij} - r_j^+\right)^2\right]\right\}^{1/2}, \text{ and} \tag{1}$$

$$d_i^- = \left\{\sum_{j=1}^{n}\left[w_j\left(r_{ij} - r_j^-\right)^2\right]\right\}^{1/2}. \tag{2}$$

In these equations w_j represents the weight of *j*-th criterion, r_{ij} is normalized rating of *i*-th alternative in relation to *j*-th criterion, r_j^+ is *j*-th coordinate of the ideal and r_j^- *j*-th coordinate of the anti-ideal point, while *n* represents a number of criteria.

The relative distance of *i*-th alternative C_i to the ideal and anti-ideal point can be calculated as follows:

$$C_i = \frac{d_i^-}{d_i^- + d_i^+} . \qquad (3)$$

The alternative with the highest C_i is the most appropriate alternative.

2.2 The VIKOR method

The VIKOR method integrates ideas of ideal and compromise solutions. For determining the most appropriate alternative the VIKOR method uses the overall ranking index Q_i, calculated as follows:

$$Q_i = v\frac{(S_i - S^*)}{(S^- - S^*)} + (1 - v)\frac{(R_i - R^*)}{(R^- - R^*)} . \qquad (4)$$

In Eq. (4) S_j represents the average group score of *i*-th alternative and R_j the worst group score of *i*-th alternative, $S^* = min_i S_i$, $S^- = max_i S_i$, $R^* = min_i R_i$, $R^- = max_i R_i$, and ν denotes significance of the strategy (usually is $v = 0.5$).

The average group score of alternatives and the worst group score of alternatives are determined as follows:

$$S_i = \sum_{j=1}^{n} w_j \left(x_j^* - x_{ij}\right) / \left(x_j^* - x_j^-\right) \; ; for\ p = 1, \text{ and} \qquad (5)$$

$$R_i = max_j\left[w_j \left(x_j^* - x_{ij}\right) / \left(x_j^* - x_j^-\right)\right] ; for\ p \rightarrow \infty. \qquad (6)$$

2.3 The MOOSRA method

The MOOSRA method uses ratio between utility of maximization b_i and minimization nb_i criteria, respectively, for determining performance score of alternatives v_i , as follows:

$$v_i = \frac{b_i}{nb_i} = \frac{\sum_{j \in \Omega_{max}} r_{ij} w_j}{\sum_{j \in \Omega_{min}} r_{ij} w_j} . \tag{7}$$

In Eq. (7) Ω_{max} and Ω_{min} denote set of maximization and set of minimization criteria, respectively.

2.4 The WASPAS method

The WASPAS method uses performance score of alternatives Q_i for ranking and selecting the best alternative, where Q_i is usually calculated as follows:

$$Q_i = 0.5 Q_i^{(1)} + 0.5 Q_i^{(2)} = \frac{1}{2} \sum_{j=1}^{n} r_{ij} w_j + \frac{1}{2} \prod_{j=1}^{n} (r_{ij})^{w_j} . \tag{8}$$

In Eq. (8) $Q_i^{(1)}$ and $Q_i^{(2)}$ denote relative importance of *i*-th alternative based on weighted sum and exponentially weighted sum method, respectively.

2.5 The CoCoSo method

The CoCoSo method uses the weighted sum method and the exponentially weighted sum method for calculating performance score of alternatives k_i, where weighted sum and the exponentially weighted sum are calculated, as follows:

$$S_i = \sum_{j=1}^{n} r_{ij} w_j , \tag{9}$$

$$P_i = \prod_{j=1}^{n} (r_{ij})^{w_j} . \tag{10}$$

In Eq. (9) S_i represents utility of *i*-th alternative based on weighted sum method, while in Eq. (10) P_i represents utility of *i*-th alternative based on exponentially weighted sum method.

The performance score of alternatives k_i is calculated as follows:

$$k_i = \frac{1}{3}(k_{ia} + k_{ib} + k_{ic}) + (k_{ia}\, k_{ib}\, k_{ic})^{\frac{1}{3}}. \quad (11)$$

where: k_{ia}, k_{ib} and k_{ic} denote three aggregated appraisal scores which are calculated on the basis of S_i and P_i.

3 Results and discussion

3.1 Criteria for evaluation and selection

For the evaluation of the proposed methods for treatment of waste water from Robule Lake and the selection of the most appropriate one, 7 criteria were used. Criteria for evaluation and selection were chosen by five experts in wastewater treatment and according to their importance in the selection process.

Following criteria for selection of wastewater treatment method are chosen:

1. *Efficiency in the metal ions removal and the quality of the purified water* – is one of the most important characteristics of the water treatment method. Efficiency of a wastewater treatment method is in the function of obtained purified water which is in accordance with increasingly stringent regulations. In this case, the efficiency of metal ions removal from wastewater should be adequate to ensure that the concentration of metal ions in purified water is below the maximum allowed concentration for discharging in surface water or similar according to Serbian legislature,.

2. *Necessity of pre-treatment and / or post-treatment of treated water* – represents one of factors that can influence the economic efficiency of wastewater treatment method. Necessity of pre-treatment and / or post-treatment of treated water in many ways raises the cost of the

treatment: capital costs are higher because of procurement the addition equipment, operation cost is higher because of engagement the additional labour, power, etc.

3. *Possibility of using the generated waste* – could be an added value and have positive effect on applied method. In the case that during the wastewater treatment is generated the waste which can be used in industry, the added value will be given, which will have the positive effect on economic efficiency of wastewater treatment method.

4. *Capital costs* - have direct effect on economic efficiency of wastewater treatment method and include preparatory work costs (construction costs) and equipment procurement as well as all needed licenses for work.

5. *Operating and maintenance costs* – also have direct effect on economic efficiency of wastewater treatment and include: labour, power, normative material, etc.

6. *Needed area* – is the area for wastewater treatment plant. This area may have the effect on the method application in two ways: the availability of the space, as a limiting factor, and the cost of providing it, as an economic factor.

7. *Sensitivity of the method* – has the influence on application of wastewater treatment method in following way:

- if the sensitivity of wastewater treatment method is high, operation costs are higher (the number and the qualifications of the labour must be higher, as well as addition equipment for process control is needed)
- if the sensitivity of wastewater treatment method is low, the method is simpler (the number and the qualifications of the labour is not required to be so high, additional equipment for process control is not needed).

Lower sensitivity of wastewater treatment method has good economic effects.

All the above mentioned criteria are important for evaluation and selection of wastewater treatment method, but still they do not have the same importance. The criteria weights (Table 2) were directly assigned by five experts, based on their experience. The sum of the assigned weights is 1.

Table 2 The criteria weights

Criteria	*Optimization*	*Weight*
Cr_1 *Efficiency in the metal ions removal and the quality of the purified water*	max	**0.30**
Cr_2 *Necessity of pre-treatment and / or post-treatment of water*	max	**0.20**
Cr_3 *Possibility of using the generated waste*	max	**0.10**
Cr_4 *Capital costs*	min	**0.20**
Cr_5 *Operating and maintenance costs*	max	**0.10**
Cr_6 *Needed area*	max	**0.05**
Cr_7 *Sensitivity of the method*	max	**0.05**

3.2 Wastewater treatment methods evaluation and selection

The evaluation of 8 wastewater treatment methods: passive treatment method (A_1), sequential neutralization (A_2), ion exchange (A_3), adsorption process based on low cost adsorbents (A_4), adsorption process based on natural zeolits (A_5), electrodialysis (A_6), filtration with nanofiltration membranes (A_7), and reverse osmosis (A_8), for purification of water from Robule Lake, using 5 above presented MCDM methods (TOPSIS, VIKOR, MOOSRA, WASPAS, and CoCoSo) is discussed in this section. Alternatives were evaluated based on the criteria shown in Table 2.

The starting decision-making matrix, compiled on the basis of opinions of five domain experts, is presented in Table 3.

Table 3 The starting group decision-making matrix

Alternatives	Cr_1	Cr_2	Cr_3	Cr_4	Cr_5	Cr_6	Cr_7
A_1	6	10	5	3	10	2	8
A_2	9	10	10	7	9	9	9
A_3	9	3	1	3	3	8	6
A_4	5	10	1	7	5	8	6
A_5	5	10	1	7	5	3	1
A_6	9	3	1	3	3	3	1
A_7	9	3	1	3	3	3	1
A_8	9	3	1	3	3	3	1

Ranking orders of alternatives, as well as some important calculation details obtained by applying the previously described MCDM methods, are shown in Tables 4 to 8.

Table 4 The TOPSIS method – Calculation details

Alternatives	d_i^-	d_i^+	C_i	Ranking order
A_1	0.11	0.06	0.63	2
A_2	0.13	0.06	0.69	1
A_3	0.08	0.11	0.43	3
A_4	0.07	0.12	0.38	7
A_5	0.07	0.12	0.36	8
A_6	0.08	0.12	0.40	4
A_7	0.08	0.12	0.40	4
A_8	0.08	0.12	0.40	4

Table 5 The VIKOR method – Calculation details

Alternatives	S_i	R_i	Q_i	Ranking order
A_1	0.34	0.23	0.24	3
A_2	0.21	0.20	0.00	1
A_3	0.43	0.20	0.19	2
A_4	0.70	0.30	0.94	7

A_5	0.76	0.30	1.00	8
A_6	0.49	0.20	0.25	4
A_7	0.49	0.20	0.25	4
A_8	0.49	0.20	0.25	4

Table 6 The MOOSRA method – Calculation details

Alternatives	b_i	nb_i	v_i	Ranking order
A_1	0.32	0.16	2.01	4
A_2	0.42	0.10	4.23	1
A_3	0.22	0.16	1.42	5
A_4	0.25	0.10	2.51	2
A_5	0.22	0.10	2.18	3
A_6	0.19	0.16	1.22	6
A_7	0.19	0.16	1.22	6
A_8	0.19	0.16	1.22	6

Table 7 The WASPAS method – Calculation details

Alternatives	$Q_i^{(1)}$	$Q_i^{(2)}$	Q_i	Ranking order
A_1	0.81	0.76	0.78	2
A_2	0.88	0.84	0.86	1
A_3	0.68	0.54	0.61	3
A_4	0.59	0.51	0.55	4
A_5	0.53	0.44	0.49	8
A_6	0.62	0.47	0.55	5
A_7	0.62	0.47	0.55	5
A_8	0.62	0.47	0.55	5

Table 8 The CoCoSo method – Calculation details

Alternatives	S_i	P_i	k_{ia}	k_{ib}	k_{ic}	k_i	Ranking order
A_1	0.66	5.58	0.18	4.81	0.92	2.90	2
A_2	0.79	5.98	0.19	5.48	1.00	3.24	1
A_3	0.57	3.97	0.13	3.86	0.67	2.25	3
A_4	0.30	3.85	0.12	2.66	0.61	1.71	7

A_5	0.24	2.79	0.09	2.00	0.45	1.27	8
A_6	0.51	2.91	0.10	3.19	0.50	1.81	4
A_7	0.51	2.91	0.10	3.19	0.50	1.81	4
A_8	0.51	2.91	0.10	3.19	0.50	1.81	4

The ranking order obtained by applying the five MCDM methods was, for a more precise presentation, again summarized in Table 9 and Fig. 3.

Table 9 Comparisons of ranking orders obtained using five MCDM methods

Alternatives	TOPSIS	VIKOR	MOOSRA	WASPAS	CoCoSo
A_1	2	3	4	2	2
A_2	1	1	1	1	1
A_3	3	2	5	3	3
A_4	7	7	2	4	7
A_5	8	8	3	8	8
A_6	4	4	6	5	4
A_7	4	4	6	5	4
A_8	4	4	6	5	4

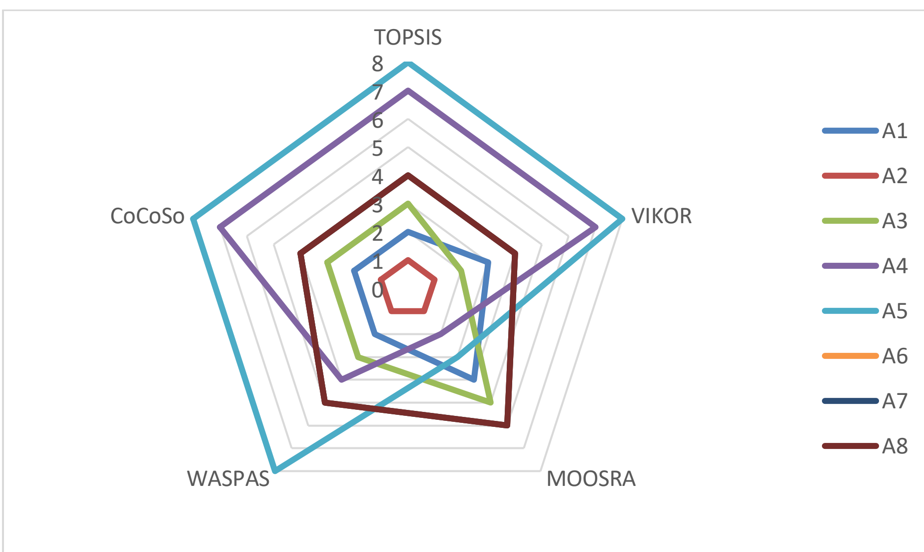

Fig. 3 The ranking orders of alternatives obtained using different MCDM methods

As can be concluded from Table 9, as well as from Fig. 3, the alternative denoted as A_2 was chosen as the most suitable using all the methods used. However, from the above table, it can also be concluded that there was some disagreement regarding the ranking orders of remaining alternatives. As it can be seen, the biggest discrepancy was with MOOSRA method which gave different ranking order, from other methods, for all alternatives except for A_2. Also there were some disagreements in the case of VIKOR method, which gave different ranking orders for A_2 and A_3 alternatives, comparing to other methods. For determining the final rank of remaining alternatives, the following Eq. was used:

$$S_i = \frac{min_i\left(\frac{\sum_{j=1}^{k} R_{ij}}{k}\right)}{\frac{\sum_{j=1}^{k} R_{ij}}{k}}, \tag{12}$$

where: R_{ij} denotes the rank of alternative i obtained using MCDM method j, S_i denotes the total utility of the alternative i obtained based on the usage of five selected MCDM methods, and k denotes number of used MCDM methods.

The results obtained applying Eq. (12) are presented in Table 10.

Table 10 The final rank of alternatives

Alternative	$\frac{\sum_{j=1}^{k} R_{ij}}{k}$	S_i	Rank
A_1	2.60	0.38	2
A_2	1.00	1.00	1
A_3	3.20	0.31	3
A_4	5.40	0.19	7
A_5	7.00	0.14	8
A_6	4.60	0.22	4
A_7	4.60	0.22	4
A_8	4.60	0.22	4

The obtained results confirm that alternative A_2, i.e. sequential neutralization, was the most acceptable, followed by alternatives A_1 (passive treatment system) and A_3 (ion exchange). It can be noticed considerable divergence in performance between mentioned alternatives. It is known that MCDM methods generally give the same ranking order, and that differences are manifested only in certain specific cases (Stanujkic et al. 2013), as a consequence of the applied normalization procedure, the aggregation procedure used, and used criteria weights.

3.3 Neutralization tests

Based on the results of the MCDM analysis, according to which neutralization was found to be the most appropriate method for treatment of wastewater from Robule Lake, laboratory neutralization testing was carried out.

Batch reactor with magnetic stirrer speed of 400 rpm was used for laboratory investigations. Neutralization was carried out with lime milk prepared with $Ca(OH)_2$ in concentration of 2.5 mass %. For the first neutralization step the aim was to reach the pH 4. After reaching the needed pH value, vacuum filtration was used for separation the phases. Liquid phase from the first neutralization step was used as start sample for neutralization to pH 7. Liquid and solid phases were separated in the same way as in the first neutralization step. The next neutralization steps were carried out with the liquid samples from the previous neutralization steps.

Metal ions concentrations were determined by inductively coupled plasma mass spectrometry. All chemical analysis were duplicated and quality control was performed with blank and certified reference materials analysis. Values of concentrations of metal ions obtained by chemical analysis were used for calculations of metal removal degree.

In Table 11 are presented the results of neutralization tests with the wastewater sample from the Robule Lake.

Table 11 Chemical characterization of the Robule Lake wastewater samples treated by neutralization method

pH value	**Concentration, mg/L**					
	Fe	**Mn**	**Cu**	**Zn**	**Cd**	**Ni**
pH 2.79 (start pH)[*]	322.6	90.8	34.7	12.8	0.04	0.41
pH 4[*]	1	62.7	31.5	12	0.041	0.42
pH 7	0.01	42.2	0.04	0.65	0.019	0.21
pH 9	< 0.0070	21.8	0.0051	0.025	0.0035	< 0.0036
pH 10	< 0.0070	0.01	< 0.0033	< 0.0050	0.0001	< 0.0036

[*]Markovic et al. 2020

Results of neutralization tests, presented in Table 11, show that Fe removal degree on pH 4 was 99.7% mass. This value confirmed that Fe conversion into the insoluble hydroxide form was almost finished on pH 4 and it was the good option for separation the Fe ions from the other ions elements that existed in AMD from the Robule Lake. Removal degree for the other elements was as follows: Mn > Cu > Zn > Ni ≈ Cd. Mn removal degree was about 30 mass %. Zn, Cd, and Ni were the originally minor component and the removal degree was very low. This could be explained as the consequence of co-precipitation with the sludge.

On pH 7, removal degree for all elements from Table 11 was as follows: Fe> Cu > Zn > Mn > Cd > Ni.

Results for the neutralization test on pH 9 confirmed that the concentrations of Fe, Cu, Zn, and Ni were under the MAC values. But, the concentration of Mn was more than 20 times higher. Also, the concentration of Cd was higher than MAC value. Based on obtained results, neutralization process was continued up to pH 10.

Concentration of Fe, Cu, Zn, and Ni ions on pH 10 were under the sensitivity limits of the applied method. Mn and Cd ions removal degree was about 99.99 mass %.

As it can be seen from the results of this study, neutralization can be applied successfully for treatment of the wastewater from the Robule Lake, with aim to precipitate metal ions present in this water.

4 Conclusions

Mining activities in Bor have negative influence on the environment, equally polluting air, water, and soil. Water from Robule Lake, which is located near mining waste dump zone and fed by surface water drainage and seepage, is highly contaminated with the site specific compounds like sulphates, iron, and trace metal elements, concurrent to low pH-values below 3.

MCDM model was developed for selection of treatment method for water from Robule Lake. Five experts in the field chose eight wastewater treatment methods such as: passive treatment method, sequential neutralization, ion exchange, adsorption process based on low cost adsorbents, adsorption process based on natural zeolits, electrodialysis, filtration with nanofiltration membranes and reverse osmosis, to be evaluated by five MCDM methods: TOPSIS, VIKOR, MOOSRA, WASPAS, and CoCoSo. Criteria used for the selection of wastewater treatment method were: efficiency in the metal ions removal and the quality of the purified water, necessity of pre-treatment and / or post-treatment of treated water, possibility of using the generated waste, capital costs, operating and maintenance costs, needed area, and sensitivity of the method. Also criteria were assigned weights according to their importance in the selection process. Experts suggested numeric values to every of the eight alternatives for each of the criteria. The results of the MCDM analysis showed that sequential neutralization treatment method was the most appropriate for this wastewater, while passive treatment system and ion exchange were ranked as second and third, respectively. It was noted that some

discrepancies between the ranks of alternatives occurred with some methods. The biggest discrepancy was in the case of MOOSRA method, while the VIKOR method did not coincide with the other three only in terms of second and third rank. Although MCDM methods generally provide the same rank of alternatives, some discrepancies may occur as a consequence of the applied normalization procedure, the aggregation procedure used, and used criteria weights.

After the selection of wastewater treatment method, neutralization tests with lime milk were carried out on water sample from Robule Lake. The results of testing showed that concentration of Fe ions could be lowered below the limit prescribed by Serbian legislation at pH value 4, while other metal ions such as: Cu, Zn and Cd need pH value 7, except for Mn and Cd, for whose effective removal, pH value of the solution needed to be 10.

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Declarations

Ethical Approval

Not applicable.

Consent to Participate

Not applicable.

Consent to Publish

Authors give their permission to publish.

Authors Contributions

Zoran Štirbanović – devised the concept of the paper; participated in writing of the Introduction, Methodology, Results and discussions, and Conclusions sections; participated in MCDM analysis.

Vojka Gardić – participated in devising the concept of the paper by giving suggestions as wastewater treatment expert; participated in writing of the Introduction, Methodology, Results and discussions, and Conclusions sections; participated in MCDM analysis.

Dragiša Stanujkić – participated in writing of the Introduction, Methodology, Results and discussions, and Conclusions sections; did all the calculations for MCDM analysis as an expert in this field.

Radmila Marković – did all the experimental work regarding neutralization tests; participated in writing of the Introduction, Methodology, Results and discussions, and Conclusions sections; participated in MCDM analysis.

Jovica Sokolović – participated by giving suggestions and revising the manuscript; participated in MCDM analysis.

Zoran Stevanović – participated by giving suggestions and revising the manuscript; participated in MCDM analysis.

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Competing interests

The authors declare that they have no conflicts of interest.

Data Availability

The data will be available in article or upon request.

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Figures

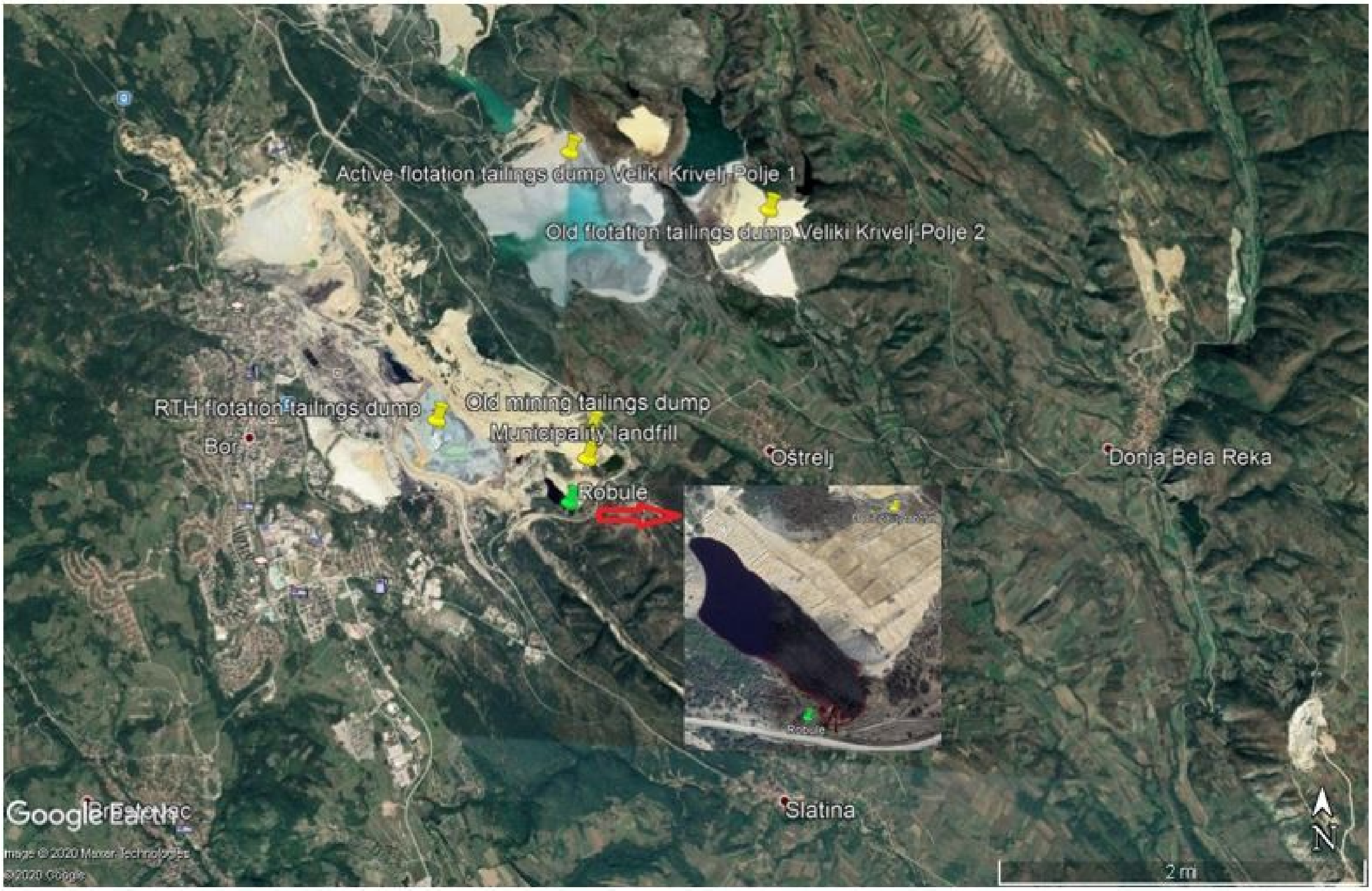

Figure 1

Location of Robule Lake (Source: Google Earth) Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

The appearance of the water from the Robule Lake

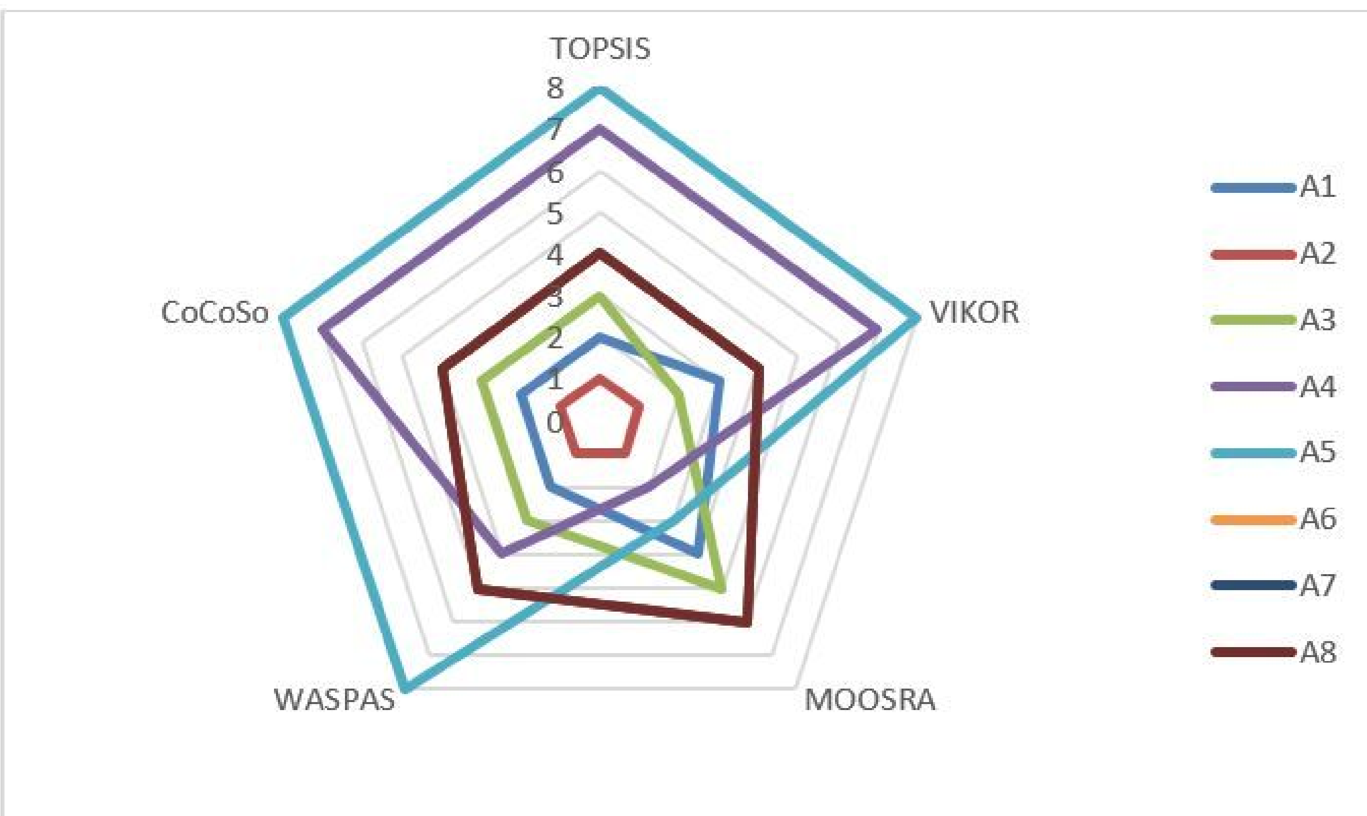

Figure 3

The ranking orders of alternatives obtained using different MCDM methods