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Comparative MCDM Analysis for AMD Treatment Method Selection

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Abstract
Robule Lake, located in Eastern Serbia, near the city of Bor, 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 the 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 method 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 with the water sample from Robule Lake. The results of sequential neutralization testing showed that concentration of Fe ions could be lowered to 1 mg/L at pH 4. The values of Cu, Zn, and Ni ions concentration obtained at pH 7 were 0.04, 0.65, and 0.21 mg/L, respectively, while the values of Mn and Cd ions concentration of 0.01 and 0.0001 mg/L, were obtained at pH 10.

Keywords MCDM · AMD · Robule Lake · Wastewater · 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

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also endangering health of plants, animals, and humans (Nikolic and Nikolic 2012; Yan et al. 2020).

Bor is located in East Serbia, and it is 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 released into the environment, thus polluting soil (Dimitrijevic et al. 2009; Milosavljevic et al. 2020). Also, during the rainy season dissolution of metals, sulphur and others occurs, causing the transfer of these ions trough water streams into surface and underground waters (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 and prevent further pollution of rivers and water streams. Therefore, the activities that include 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 economical factor. All of this additionally burdens the selection of appropriate wastewater treatment method. Thus, before randomly conduct experiments by applying different treatment methods it is much better to select one method that will provide the highest efficiency in pollutants removal with satisfactory ecological impact and the best economical outcomes. Also, opinions of decision makers can be conflicted about some of the methods and to avoid disputes it is for the best to be equipped with some neutral tool that will provide the answer about the best solution based on their opinions.

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: 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), calibration efficiency of hydrological model (Asl-Rousta 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), etc. Finally, the more recently proposed WASPAS and CoCoSO methods have been used for solving a number of different decision-making problems, such as: cloud service provider selection (Lai et al. 2020), and tourism attraction selection (Luo et al. 2021).

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 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 using the TOPSIS method. Mladenović-Ranisavljević et al. (2018) used the PROMETHEE method to determine the water quality of the Danube River. Baghapour et al. (2020) used TOPSIS and AHP methods to optimize big amount of data gathered from a wide range of resources about water quality monitoring, while Pourmand et al. (2020) tried to find the best scenario for acceptable long-term groundwater conservation by applying fuzzy TOPSIS method. TOPSIS method was also used by Yahya et al. (2020) for analyzing the most common wastewater treatment methods. Ali et al. (2020) applied fuzzy VIKOR method to select wastewater treatment technology. Gichamo et al. (2021) did the ranking of natural wastewater treatment techniques by VIKOR method.

The new MCDM model for the selection of the best available wastewater treatment method for particular AMD that can provide significant support to researches in pre-experimental or pre-industrial testing phase was developed. The study was conducted on wastewater from Robule Lake. 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 color of the water is red.

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 an overall environmental risk. At current conditions Robule Lake overflows through a small size pipe conduit and a ditch directly into 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 m^3/day [1, 2].

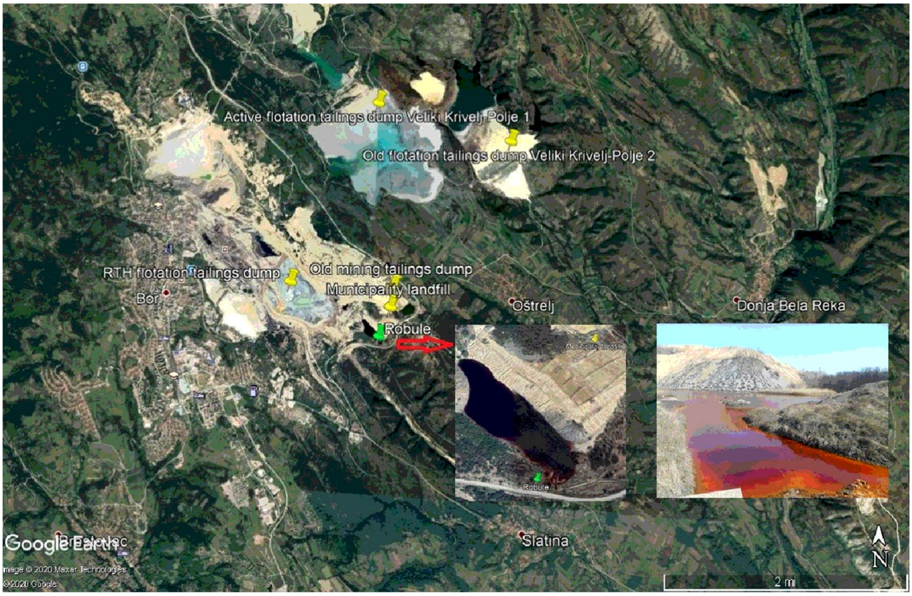
The historical data about Robule Lake water quality is given in Table 1.[1],[2],[3],[4]

[1] Regulations 3/1968; 50/2012; 24/2014.

[2] Stevanović et al. 2013.

[3] Gardic et al. 2017.

[4] Petronijevic et al. 2020.



(Source: Google Earth)

Fig. 1 Location and appearance of Robule Lake

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, Mn, and 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.

Table 1 The historical data about Robule Lake water quality

Characteristic	Unit	Year			Maximum Allowable Concentration (MAC) IV class[1]
		2011[2]	2017[3]	2019[4]	
Color of water	-	reddish	reddish	reddish	none
Odor of water	-	none	none	none	none
pH	-	2.56–4.20	2.7	2.47	6.5–8.5
Suspended materials on 105 °C	mg/L	12.0–55.0	-	-	-
SO_4^{2-}	g/L	4.91–10.57	-	7.50	0.30
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

All of these indicators are important because the water from Robule Lake is flowing through rivers Bor River and Timok and going to the Danube.

1.2 Wastewater Treatment Methods

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 m^3/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%. The downside of this process is generation of the wastewater in regeneration phase and the need for its treatment of wastewater, 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

Proposed methodology is given in Fig. 2. Based on characteristics of wastewater from Robule Lake and Serbian regulations and legislation wastewater treatment methods that could be used for purification of wastewater in question were identified. Selection of the best available wastewater treatment method was performed by applying five MCDM methods based on 7 criteria.

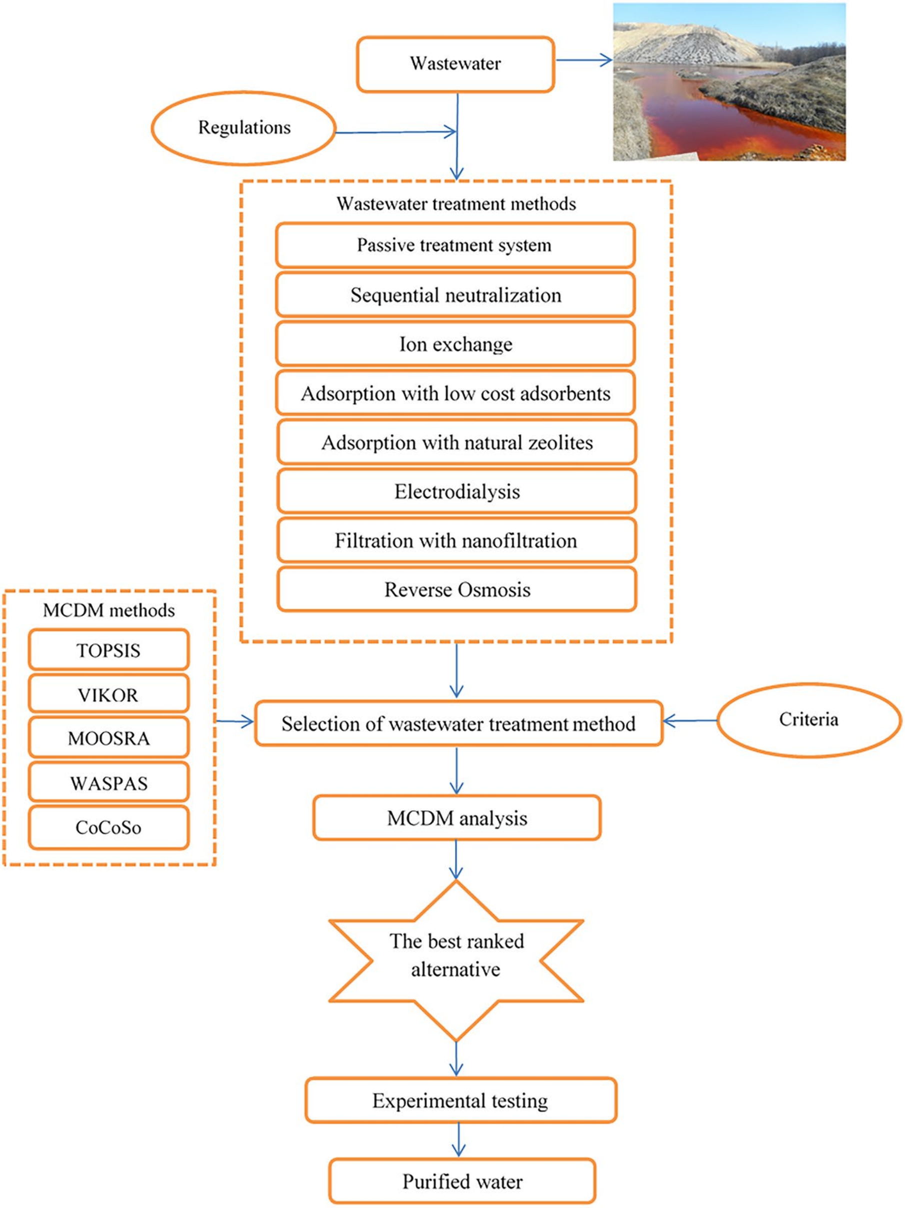


Fig. 2 Methodology flowchart

The MCDM analysis gave the best ranked alternative. Experimental testing was done in order to confirm the results of the MCDM analysis, i.e. to obtain purified water.

2.1 MCDM Methods

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 were used in this study would 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. (2019).

2.1.1 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.

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

and

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

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:

$$C_i = \frac{d_i^-}{d_i^- + d_i^+}. \tag{3}$$

The alternative with the highest C_i is the most appropriate alternative.The TOPSIS method uses the vector normalization procedure to calculate r_{ij} as follows:

$$r_{ij} = \frac{x_{ij}}{\sqrt{\sum_{i=1}^{n} (x_{ij})^2}}. \tag{4}$$

In Eq. (4) x_{ij} denotes set rating of i-th alternative in relation to j-th criterion.

2.1.2 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:

$$Q_i = \frac{\left(S_i - S^*\right)}{\left(S^- - S^*\right)} + (1 - v)\frac{\left(R_i - R^*\right)}{\left(R^- - R^*\right)}. \tag{5}$$

In Eq. (5) 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 v 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:

$$S_i = \sum_{j=1}^{n} w_j \left(x_j^* - x_{ij}\right) / \left(x_j^* - x_j^-\right), \tag{6}$$

and

$$R_i = max_j \left[w_j \left(x_j^* - x_{ij}\right) / \left(x_j^* - x_j^-\right)\right]. \tag{7}$$

In Eq. (6) and Eq. (7) x_j^* and x_j^- are determined as follows:

$$x_j^* = \begin{cases} max_i x_{ij} & x_{ij} \in \Omega_{max} \\ min_i x_{ij} & x_{ij} \in \Omega_{min} \end{cases}, \tag{8}$$

and

$$x_j^- = \begin{cases} min_i x_{ij} & x_{ij} \in \Omega_{max} \\ max_i x_{ij} & x_{ij} \in \Omega_{min} \end{cases}. \tag{9}$$

where: Ω_{max} denotes set of maximization and Ω_{min} denotes set of minimization criteria.

2.1.3 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:

$$v_i = \frac{b_i}{nb_i} = \frac{\sum_{j \in \Omega_{max}} r_{ij} w_j}{\sum_{j \in \Omega_{min}} r_{ij} w_j}. \tag{10}$$

The MOSRA method uses the vector normalization procedure as well as the TOPSIS method.

2.1.4 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:

$$Q_i = 0.5Q_i^{(1)} + 0.5Q_i^{(2)} = \frac{1}{2}\sum_{j=1}^{n} r_{ij}w_j + \frac{1}{2}\prod_{j=1}^{n} \left(r_{ij}\right)^{w_j}. \tag{11}$$

In Eq. (7) $Q_i^{(1)}$ and $Q_i^{(2)}$ denote relative importance of i-th alternative based on weighted sum and exponentially weighted sum method, respectively.

The normalized ratings r_{ij} in Eq. (11) are calculated as follows:

$$r_{ij} = \begin{cases} \frac{x_{ij}}{max_i x_{ij}} & x_{ij} \in \Omega_{max} \\ \frac{min_i x_{ij}}{x_{ij}} & x_{ij} \in \Omega_{min} \end{cases}. \tag{12}$$

2.1.5 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:

$$S_i = \sum_{j=1}^{n} r_{ij}w_j \;, \tag{13}$$

$$P_i = \prod_{j=1}^{n} \left(r_{ij}\right)^{w_j} \;. \tag{14}$$

In Eq. (13) S_i represents utility of i-th alternative based on weighted sum method, while in Eq. (14) 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:

$$k_i = \frac{1}{3}\left(k_{ia} + k_{ib} + k_{ic}\right) + \left(k_{ia}k_{ib}k_{ic}\right)^{\frac{1}{3}}. \tag{15}$$

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.

The normalized ratings r_{ij} in Eq. (13) and Eq. (14) are calculated as follows:

$$r_{ij} = \begin{cases} \frac{x_{ij} - min_i x_{ij}}{max_i x_{ij} - min_i x_{ij}} & x_{ij} \in \Omega_{max} \\ \frac{max_i x_{ij} - x_{ij}}{x_{ij} max_i x_{ij} - min_i x_{ij}} & x_{ij} \in \Omega_{min} \end{cases}. \tag{16}$$

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 the selection of wastewater treatment method were chosen:

1. *Efficiency in the metal ions removal and the quality of the purified water* (Cr_1) – 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 according to Serbian legislature,.
2. *Necessity of pre-treatment and / or post-treatment of treated water* (Cr_2) – 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 of the additional equipment, operation cost is higher because of engagement the additional labor, power, etc.
3. *Possibility of using the generated waste* (Cr_3) – could be an added value and have positive effect on applied method. If the waste which can be used in industry is generated during the wastewater treatment, the provided added value will have the positive effect on economic efficiency of wastewater treatment method.
4. *Capital costs* (Cr_4)—have direct effect on economic efficiency of wastewater treatment method and include preparatory work costs (construction costs), equipment procurement, and all needed licenses for work.
5. *Operating and maintenance costs* (Cr_5) –have direct effect on economic efficiency of wastewater treatment and include: labor, power, normative material, etc.
6. *Needed area* (Cr_6) – is the area for wastewater treatment plant, and it may affect the application of method 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* (Cr_7) – 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 labor 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 labor 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.

Table 2 The starting group decision-making matrix

Criteria	Cr_1	Cr_2	Cr_3	Cr_4	Cr_5	Cr_6	Cr_7
Weight	0.30	0.20	0.10	0.20	0.10	0.05	0.05
Optimization	*max*	*max*	*max*	*min*	*max*	*max*	*max*
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

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 presented MCDM methods (TOPSIS, VIKOR, MOOSRA, WASPAS, and CoCoSo) is discussed in this section. Alternatives were evaluated based on the considered criteria. The criteria weights were directly assigned by five experts, based on their experience. The sum of the assigned weights is 1.

The starting decision-making matrix, compiled based on the opinions of five domain experts, is presented in Table 2.

Ranking orders of alternatives, as well as some important calculation details obtained by applying the previously described MCDM methods, are shown in Table 3.

As can be concluded from Table 3, the alternative denoted as A_2 was chosen as the most suitable by all the methods. However, it can also be concluded that there was some disagreement regarding the ranking orders of remaining alternatives. The biggest discrepancy was obtained with MOOSRA method, which provided different ranking order for all alternatives except for A_2. There were also some disagreements in the case of VIKOR method, which gave different ranking orders for A_2 and A_3 alternatives. For determining the final rank of the remaining alternatives, the following Eq. was used:

$$S_i = \frac{min_i\left(\frac{\sum_{j=1}^{k} R_{ij}}{k}\right)}{\frac{\sum_{j=1}^{k} R_{ij}}{k}}, \tag{17}$$

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. (17) are presented in Table 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

Table 3 Calculation details and ranking orders obtained using five MCDM methods

		A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8
TOPSIS	d_i^-	0.11	0.13	0.08	0.07	0.07	0.08	0.08	0.08
	d_i^+	0.06	0.06	0.11	0.12	0.12	0.12	0.12	0.12
	C_i	0.63	0.69	0.43	0.38	0.36	0.40	0.40	0.40
	Rank	2	1	3	7	8	4	4	4
VIKOR	S_i	0.34	0.21	0.43	0.70	0.76	0.49	0.49	0.49
	R_i	0.23	0.20	0.20	0.30	0.30	0.20	0.20	0.20
	Q_i	0.24	0.00	0.19	0.94	1.00	0.25	0.25	0.25
	Rank	3	1	2	7	8	4	4	4
MOOSRA	b_i	0.32	0.42	0.22	0.25	0.22	0.19	0.19	0.19
	nb_i	0.16	0.10	0.16	0.10	0.10	0.16	0.16	0.16
	v_i	2.01	4.23	1.42	2.51	2.18	1.22	1.22	1.22
	Rank	4	1	5	2	3	6	6	6
WASPAS	$Q_i^{(1)}$	0.81	0.88	0.68	0.59	0.53	0.62	0.62	0.62
	$Q_i^{(2)}$	0.76	0.84	0.54	0.51	0.44	0.47	0.47	0.47
	Q_i	0.78	0.86	0.61	0.55	0.49	0.55	0.55	0.55
	Rank	2	1	3	4	8	5	5	5
CoCoSo	S_i	0.66	0.79	0.57	0.30	0.24	0.51	0.51	0.51
	P_i	5.58	5.98	3.97	3.85	2.79	2.91	2.91	2.91
	k_{ia}	0.18	0.19	0.13	0.12	0.09	0.10	0.10	0.10
	k_{ib}	4.81	5.48	3.86	2.66	2.00	3.19	3.19	3.19
	k_{ic}	0.92	1.00	0.67	0.61	0.45	0.50	0.50	0.50
	k_i	2.90	3.24	2.25	1.71	1.27	1.81	1.81	1.81
	Rank	2	1	3	7	8	4	4	4

(ion exchange). A considerable divergence in performance between mentioned alternatives can be noticed. 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.

Table 4 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

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 pH 4. After reaching the needed pH value, vacuum filtration was used for the separation of phases. Liquid phase from the first neutralization step was used as a starting 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.

Table 5 presents the results of neutralization tests with the wastewater sample from the Robule Lake.

Results of neutralization tests, presented in Table 5, 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 lake. Removal degree for 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 5 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. However, 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 %.

Table 5 Chemical characterization of the Robule Lake wastewater samples treated by neutralization method (*Markovic et al. 2020)

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

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 the 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.

New MCDM model that provides efficient support in selection of treatment method for AMD was developed. Case study for developing the model was Robule Lake. Five experts in the field chose eight wastewater treatment methods: 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. The criteria were also 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 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, and 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 4, while other metal ions such as: Cu, Zn and Cd needed pH 7, except for Mn and Cd, which needed pH 10 for effective removal.

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Data Availability The data will be available in article or upon request.

Declarations

Consent to Publish Authors give their permission to publish.

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