

Article



Application of Electronic Tongue for Detection and Classification of Lead Concentrations in Coal Mining Wastewater

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Abstract: This study evaluates the potential of an electronic tongue (E-tongue) as an innovative and alternative method for detecting and classifying lead concentrations in wastewater generated by coal mining activities in North Santander, Colombia. The Etongue aims to complement traditional environmental monitoring techniques with a more efficient and accurate solution. A total of 110 wastewater samples were collected from two locations at a coal mine in the municipality of Toledo: one inside the mine (Point 2) and another outside the mine (Point 1). This research involved the physicochemical analysis of parameters such as pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), hardness, and alkalinity, conducted at the University of Pamplona's laboratories. The integration of PCA with machine learning algorithms highlighted the E-tongue's capability for the real-time, on-site detection and discrimination of lead concentrations in coal mining wastewater. Achieving a precision and accuracy above 90%, the SVM classifier outperformed alternative models such as the k-NN, Random Forest, Naïve Bayes, and Quadratic Discriminant Analysis. This demonstrates the system's robustness and reliability in environmental monitoring, enabling the accurate classification of lead concentrations within the critical range of 0.05 to 1 ppm, essential for assessing contamination levels and ensuring water safety. These findings highlight the E-tongue system's capability as a rapid, cost-effective tool for monitoring lead contamination in mining wastewater, presenting a viable alternative to conventional methods such as atomic absorption spectroscopy.

Keywords: E-tongue; lead concentrations; coal mining; screen-printed electrodes; metrics; wastewater; PCA; machine learning

1. Introduction

Mineral extraction activities are a fundamental economic pillar in many regions worldwide, as they provide essential resources for industrial and technological development [1]. However, their negative environmental impacts are a growing concern [2], particularly regarding water-source contamination. This issue arises from the excessive use of water in all stages of mining, from land exploration to extraction and leaching processes [2]. Mineral extraction alters natural ecosystems and generates waste that, if not properly managed, can pollute rivers, lakes, and aquifers with high levels of heavy metals, toxic chemicals such as sulfuric acid, cyanide, and polycyclic aromatic hydrocarbons (PAHs), and sediments, which may be discharged into water bodies [3]. However, no exact statistics are available in the literature on the total amount of waste generated by mining, especially coal mining,



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Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/ licenses/by/4.0/). worldwide, as this figure varies depending on factors such as extraction methods, coal quality, and production levels. Nevertheless, the extractive industry generates around 3 billion tons of waste annually. This pollution affects water quality, the health of ecosystems, and the communities that depend on these sources for their livelihood [4]. It is essential to thoroughly examine the impact of mining on water contamination to develop and implement effective measures that mitigate its adverse effects and promote more sustainable practices within the mining industry. Such efforts are vital to achieving the United Nations' Sustainable Development Goal 6 (SDG 6), which seeks to ensure the availability of clean water, sustainable water management, and universal access to sanitation [5]. Throughout history, compound extraction methods have evolved in response to human needs and technological advancements. In ancient times, these processes focused on obtaining minerals and metals to craft tools and objects that facilitated daily activities [6,7].

Over time, extraction techniques have diversified and become more sophisticated, leading to underground and open-pit mining methods, currently the most widely used worldwide. Open-pit mining, accounting for approximately 80% of global mining production, extracts minerals in surface deposits such as coal, copper, iron, bauxite, and phosphates. In contrast, underground mining represents around 20% of global production and extracts minerals at depths greater than 200 m. This method is essential for high-value resources such as gold, platinum, diamonds, nickel, and uranium, enabling access to deposits that are not feasible with surface techniques. Both methods utilize explosives to break apart rock and chemical agents for leaching, efficiently extracting the desired metals [8].

However, the development of these technologies has led to significant environmental impacts, including acid mine drainage, the release of toxic compounds into the atmosphere, and the discharge of heavy metals such as mercury, cyanide, and lead into surface water bodies. When these substances accumulate in high concentrations without proper control, they cause severe ecosystem disruptions [9].

Lead (Pb) is among the most polluting metals in water sources due to its high toxicity and environmental persistence, posing a severe risk to human health and ecosystems [10]. Mining is a significant source of lead contamination, as this metal can be released into water and soil during mineral extraction and processing, affecting the quality of these resources. Lead exposure is associated with numerous health issues, including developmental disorders in children, damage to the nervous and digestive systems, and adverse effects on vital organs. Its low degradability in organisms enables its accumulation, leading to long-term negative impacts on humans and ecosystems [11,12]. Studies have shown elevated lead levels in drinking water and soil near mining operations [13], presenting a significant risk to local communities that lack monitoring and mitigation measures to control exposure. Therefore, it is essential to develop techniques to detect and quantify lead concentrations in water sources to mitigate the adverse effects of this toxic metal. Detection requires advanced methods designed to identify trace metals at both low and high concentrations, thereby ensuring more responsible environmental management [14–16].

Traditional methods for quantifying heavy metals include atomic absorption spectroscopy (AAS), one of the most widely used techniques due to its detection capability across various concentration ranges, particularly at low levels, offering high selectivity and precision. Compared to flame atomic absorption spectrophotometry, which has lower interference, higher precision, and faster results, traditional AAS tends to be more costly and susceptible to interference [17]. Another conventional method is Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES). It combines the ability to analyze multiple elements simultaneously with adequate sensitivity, making it especially useful for studying contaminated water. However, its cost is significantly higher than AAS's [18]. Despite their effectiveness, these methods have considerable limitations, such as high costs, the need for sophisticated equipment and specialized laboratories, and the difficulty of conducting "in situ" analyses. Furthermore, many of these methods are designed to detect a single metal, and their precision can vary depending on the technique employed.

These disadvantages highlight the need for more accessible, portable, and versatile alternatives.

Electrochemical techniques have recently become an efficient alternative for analyzing heavy metals like lead in water samples. These methods are notable for their high sensitivity, speed, and lower cost than traditional approaches [19]. Among these innovative tools are electronic tongue devices designed to simulate the human sense of taste. These technologies can identify and quantify sample components using screen-printed electrodes. Their design allows E-tongues to accurately differentiate metal concentrations and detect multiple contaminants in complex liquid media. This is achieved through advanced electrochemical techniques such as voltammetry and potentiometry, which have been proven to be effective in various studies for analyzing and monitoring contaminants in aquatic environments [20–22].

The use of these devices for detecting heavy metals has been explored in numerous studies. One study reported analyzing wastewater and soils to identify metals and organic and inorganic compounds using polymeric membrane electrodes and voltammetric techniques [22]. Similarly, one work was conducted for the spatial distribution and concentration evaluation of heavy metals in soils [23]. Another study evaluated the use of multi-frequency electrodes in classifying and identifying heavy metal ions in drinking water. This approach yielded promising results using Principal Component Analysis (PCA) to visualize contaminant classification [24]. Additionally, other data analysis methods for E-tongue results, such as partial least squares (PLS) models [25] and colorimetric sensor arrays (CSAs) have contributed to improving metal identification and classification in water samples [26].

This study aims to evaluate the effectiveness of an E-tongue as an innovative and efficient alternative for detecting and classifying lead concentrations in wastewater generated by coal mining activities representing a region's primary mining activity. The device is a promising solution compared to traditional methods for quantifying heavy metals, standing out for its high precision, portability, rapid results, and lower operational costs. Research was conducted in two complementary phases: In the first phase, we performed preliminary tests with synthetic lead solutions at concentrations ranging from 0.5 to 100 ppm and later at lower concentrations from 0.05 to 1 ppm, using PCA and machine learning algorithms to create training models and evaluate the device's performance. In the second phase, real wastewater samples collected from two strategic points at a coal mine in Toledo, Norte de Santander, were analyzed and incorporated into the models. These samples underwent the physicochemical characterization of key parameters such as pH and conductivity, along with a simultaneous comparative analysis between the E-tongue and conventional analytical methods, thus consolidating its feasibility for environmental applications in real-world scenarios.

Figure 1 illustrates the methodology developed during this study for detecting and identifying lead in mining wastewater samples.



Figure 1. Methodology established for lead quantification using electronic tongue.

As mentioned, various machine learning classifiers, including the Support Vector Machine (SVM), k-Nearest Neighbor (k-NN), Random Forest (RF), Naïve Bayes, and Quadratic Discriminant Analysis (QDA), were applied to assess classification accuracy. The confusion matrix demonstrated excellent performance, achieving high accuracy across multiple Pb concentration levels.

2. Materials and Methods

2.1. Collection of Mining Wastewater Samples

In this study, two strategic sampling points were selected to assess the impact of mining activities on nearby water bodies. The first sampling point (Point 1) was located at the mine's outlet, where wastewater used for coal washing and extraction activities is discharged. This location is a direct discharge point into the region's surface water bodies. The second sampling point (Point 2) corresponded to a sedimentation pond within the Toledo mine. This structure allows the settling of solid particles suspended in wastewater generated during mining operations. At this site, the sample was collected from the water surface.

Samples were placed in 1 L polyethylene containers previously washed with distilled water and rinsed with the same sample water to avoid external contamination. Afterward, they were stored at 4 °C and transported to the laboratory within 24 h to ensure their preservation and analytical validity.

It should be noted that standardized protocols were used in this study, which are based on current Colombian regulations to ensure the quality of the collected samples and avoid cross-contamination, among which were Resolution 0631 of 2015 of the Ministry of Environment and Sustainable Development, Decree 3930 of 2010, and the Colombian Technical Standard (NTC) 5667-3, which provide technical guidelines for the collection, conservation, and transportation of water and wastewater samples, guaranteeing the reliability of the analytical results.

2.2. Methods of Analysis of Mining Wastewater Samples

The collected wastewater samples were divided into three volume fractions to perform different types of analysis and characterize their properties.

2.2.1. Physicochemical Characterization

The parameters described in Table 1 were analyzed in the physicochemical characterization of the samples using a combination of instrumental and volumetric methods. To guarantee the precision and reliability of the results, calibrated equipment was used according to international regulations and established protocols, ensuring compliance with quality standards in the analysis.

Parameter	Technique	Standard	Reference
рН	Potentiometric Method	NTC 4113 APHA 4500	[27,28]
Conductivity [µS/cm]	Electrometric Method	NTC 809 APHA 2510-B	[29,30]
Turbidity [NTU]	Nephelometric Method	NTC 4707 APHA 2130-B	[31,32]
Color [UPtCo]	Visual Comparison with Calibrated DisksNTC 5844 APHA 2120-B		[33,34]
Alkalinity [mg/L]	lkalinity [mg/L] Volumetric Method NTC 4903 APHA 2320-B		[35,36]
Hardness [mg/L]	EDTA Titration	NTC 4706 APHA 2340-C	[37,38]
Nitrites [mg/L]	Spectrophotometric Method	NTC 4798 APHA 4500-NO2-B	[39,40]
Sulfates [mg/L]	Turbidimetric NTC 4708 Ilfates [mg/L] Spectrophotometric APHA 4500-SO4 Method		[41,42]
Phosphates [mg/L]	Spectrophotometric Method (Molybdenum Blue)	NTC 5350 APHA 4500-P	[43,44]
SST [mg/L]	ST [mg/L] Gravimetric Method NTC 892 APHA 254		[45,46]
DQO [mg/L]	O[mg/L]Closed RefluxNTC 3Colorimetric MethodAPHA 5		[47,48]
DBO5	Incubation Method	NTC 3963 APHA 5210-B	[49,50]

Table 1. Physicochemical Parameters.

Note: the standards mentioned correspond to those applicable in Colombia (NTC) or internationally recognized standards (APHA—American Public Health Association).

2.2.2. Detection and Quantification of Lead Using Atomic Absorption Spectroscopy (AAS)

The detection and quantification of lead in the wastewater samples were performed following the procedures outlined in standard methods 3030E and 3111B. The samples underwent an acid digestion process using high-purity nitric acid (HNO₃) to decompose organic matter and release the metals present. This process was conducted with an ethos easy microwave digester, which ensured precise control of temperature and pressure conditions during digestion.

Subsequently, the digested samples were analyzed using a Shimadzu AA-7000 Series AAS (Shimadzu Corporation, Kyoto, Japan) with an air-acetylene flame as the energy source. Quantification was carried out using a certified lead standard (CRM) with a concentration of 1000 mg/L, which facilitated the construction of a calibration curve, ensuring high precision and reliability in determining lead concentrations.

During the digestion and analysis process, environmental conditions were carefully controlled, with an average temperature of 23.4 °C and relative humidity of 55.9%. This ensured the chemical stability of the samples and minimized potential interferences in the measurements.

2.2.3. The Implementation of an E-Tongue as an Alternative Technique

An E-tongue was employed as a complementary and innovative approach to detect and quantify lead in the wastewater samples. This analytical device is designed to emulate the sensory function of human taste buds, enabling the detection and analysis of chemical substances in liquid solutions. The system comprises a set of non-selective chemical sensors whose responses partially vary with the diverse compounds in a sample, generating unique patterns or "chemical fingerprints".

To evaluate the capability of the E-tongue in detecting and quantifying lead in wastewater, a two-stage methodology was designed:

- 1. Standard solutions were utilized.
- 2. Real samples collected from the coal mine were analyzed.

This methodology facilitated the system's calibration, the evaluation of its sensitivity and detection limit, and the development of an appropriate discrimination model.

Preparation of lead standard solutions and actual samples

Lead standard solutions were prepared with concentrations ranging from 0 ppm (blank) to 100 ppm. This concentration range was selected based on typical scenarios of mining wastewater contamination reported in previous studies and regulations, simulating real contamination conditions.

In the first test, standard solutions within a concentration range of 0.5 ppm to 100 ppm were used to evaluate the device's ability to classify and discriminate between different lead concentrations. In the second stage, a smaller concentration range, between 0.05 ppm and 1 ppm (see Table 2), was employed, considering the limits established by Colombia's Ministry of Environment and Sustainable Development under Resolution 0631 of 2015. This resolution sets the maximum permissible lead concentration in point-source discharges of non-domestic wastewater (ARnD) into surface water bodies from mining activities at 0.2 ppm. Additionally, distilled water samples were included as blanks, along with real samples collected from the coal mine. This design allowed the evaluation of the E-tongue's ability to classify samples with concentrations near the regulatory value, simulating controlled discharge conditions that comply with the standards.

Subsequently, training algorithms using machine learning techniques were developed alongside mathematical dimensionality reduction models, such as PCA, to describe the data in a reduced space. These models aimed to project the samples collected from Points 1 and 2.

In total, 10 repetitions were performed for each concentration, including the distilled water used as a blank and the real samples. This approach ensured the precision and reproducibility of the results.

Test 1	Test 2
0.5 ppm	Distilled water
1 ppm	0.05 ppm
10 ppm	0.1 ppm
20 ppm	0.3 ppm
40 ppm	0.5 ppm
50 ppm	0.6 ppm
60 ppm	0.8 ppm
70 ppm	0.9 ppm
80 ppm	1 ppm
90 ppm	Sample 1
100 ppm	Sample 2

Table 2. Lead standard solutions and real samples.

• Electrochemical analysis

The samples were analyzed using a µStat8000 potentiostat (Metrohm DropSens, Asturias, Spain) with 8 channels operated through specialized software, DropView 8400 version 3.78, which facilitated the detailed processing and analysis of the electrochemical measurements. Afterward, 50 µL of wastewater was measured using a micropipette and deposited onto C110 screen-printed electrodes (Metrohm DropSens, Asturias, Spain). These electrodes included a carbon working electrode, a carbon auxiliary electrode, and a silver reference electrode, which are widely used in electrochemical analysis for their stability and high reproducibility.

Cyclic voltammetry was employed for the electrochemical analysis, allowing the generation of characteristic current patterns as a function of the applied potential. These patterns were used to identify and quantify the presence of lead. Table 3 outlines the operating parameters used in the electronic tongue, including the potentiostat configurations, potential ranges, and sweep rates applied during cyclic voltammetry.

Z	Assigned Value
Econd [V]	0
Edep [V]	0
Tcond [s]	0
Tdep [s]	0
Tequil [s]	0.3
Ebegin [V]	-1
Evtx1 [V]	-1
Evtx2 [V]	1
Estpe [V]	0.01
Srate [V/s]	0.05
Nscans	10

Table 3. E-tongue operation parameters.

• Data Processing

The initially obtained electrochemical data were preprocessed by extracting two features from the signals generated by the screen-printed electrodes. The parameters were as follows:

$$\Delta C1 = C_{\text{maximum}} - C_{\text{minimum}} \tag{1}$$

$$\Delta C2 = C_{\text{final}} - C_{\text{initial}} \tag{2}$$

where C_{maximum} is the maximum current value obtained from the electrode signals, C_{minimun} is the minimum current value, C_{final} is the final current value reached by the electrode, and C_{inicial} is the initial current value. Additionally, the data were normalized to a range between -1 and 1, providing scaled values within a similar range. After normalization, the unsupervised PCA technique was applied. This statistical method is used to reduce the dimensionality of a dataset while preserving most of its variability despite the complexity of multivariate data, which often includes responses from multiple chemical sensors. In this study, since only carbon electrodes were used and two features (Δ C1 and Δ C2) were extracted from the dataset, PCA primarily served to identify new directions, explaining the most significant data variability. This allowed for dimensionality reduction, as the two extracted PCA features identified two principal components (PC1 and PC2). PC1 captured most of the data variability, while PC2 accounted for the remaining variability.

Therefore, based on the two extracted features, the PCA achieved a projection that maximized the separation between classes, eliminated noise, and reduced dependency between the features, thereby improving the classifiers' performance. The classifiers and learning algorithms used for sample classification are listed below (see Table 4).

Method	Туре	Operation	Applications	Reference
SVM (Support Vector Machine)	Supervised	Finds an optimal hyperplane that maximizes class separation using kernel transformations.	Text Classification, Disease Detection, Image Analysis	[51]
k-NN (k-Nearest Neighbor)	Supervised	Classifies based on the classes of the k-nearest neighbors in the feature space.	Pattern Recognition, Image Classification, Recommendation Systems	[52]
RF (Random Forest)	Supervised	An ensemble of decision trees that uses random sampling and the averaging of predictions to improve accuracy.	Value Prediction, Medical Data Analysis, Fraud Detection	[53]
Naïve Bayes	Supervised	Based on conditional probability and Bayes's theorem; independence between features is assumed.	Text Classification, Spam Detection, Sentiment Analysis	[54]
QDA (Quadratic Discriminant Analysis)	Supervised	Fits quadratic decision boundaries based on class-specific statistics.	Medical Diagnosis, Pattern Recognition, Finance and Marketing	[55]

Table 4. Learning and classification methods used for lead detection in wastewater.

The PCA scores were employed for the classifier methods as they represented the data projected onto PC1 and PC2. This approach eliminated correlations between features and improved class separability. This simplification facilitated the classifiers' performance by focusing on the most relevant features, minimizing noise, and reducing the risk of overfitting. Furthermore, overfitting was mitigated by applying the cross-validation (CV)

method with k = 5 in the machine learning model. This method divided the dataset into five parts or folds where, in each iteration, one fold was used for testing and the other four for training. The process was repeated five times.

Using PCA for preprocessing and as the CV technique, the classifiers were evaluated using transformed, more manageable, and relevant data. As previously mentioned, the 110 measurements for each test were distributed across 11 categories, with 10 measurements per category. At the end of the processing, the predictions made by the classification models were analyzed using confusion matrices and the following metrics: accuracy, precision, sensitivity, specificity, F1-score, negative predictive value (NPV), and area under the ROC curve (AUC).

3. Results

3.1. Physicochemical Analysis

Table 5 summarizes the physicochemical parameters evaluated in the mining wastewater samples compared to the limits established by Resolution 631 of 2015. This Colombian regulation governs the maximum permissible concentrations for discharges into surface water bodies and public sewage systems. As illustrated, the pH levels of the analyzed samples fell within the permissible range (6–9) defined by the regulation, indicating that the water did not exhibit acidic or highly alkaline conditions that could negatively impact the receiving ecosystems. However, the elevated electrical conductivity, reported in μ S/cm, reflected a high concentration of dissolved ions, likely associated with contamination from salts and metals resulting from extractive activities.

Parameter	Sample Point 1 Sample Point 2		Permissible limit	
рН	7.3	8.1	6–9	
Conductivity [µS/cm]	3224	2864	Analysis and Report	
Turbidity [NTU]	424	22.2	Analysis and Report	
Color [UPtCo]	643	181	Analysis and Report	
Alkalinity [mg/L]	340	560	Analysis and Report	
Hardness [mg/L]	2500	966	Analysis and Report	
Nitrites [mg/L]	0.089	0.042	Analysis and Report	
Sulfates [mg/L]	118	115	1200	
Phosphates [mg/L]	2.85	1.3	Analysis and Report	
SST [mg/L]	1370	108	50	
DQO [mg/L]	508	24	150	
DBO5	314	15.1	50	

Table 5. Physicochemical characteristics.

The alkalinity remained within typically reported ranges, essential in buffering pH levels. Hardness was considerably higher at Point 1 than at Point 2 (966 mg/L). This increase was attributed to calcium and magnesium ions in the water.

The turbidity and color values at sampling Point 1 (424 NTU and 643 UPtCo, respectively) were elevated, indicating a high load of suspended particles and dissolved compounds, both organic and inorganic. The total suspended solids (TSS) also reached 1370 mg/L, far exceeding the permissible limit of 50 mg/L. These conditions represent a significant risk to aquatic life and the functionality of receiving ecosystems. In contrast, sulfates, nitrites, and phosphates remained within permissible limits. Nevertheless, their accumulation permits monitoring, as elevated concentrations can lead to cumulative negative impacts on ecosystems. Lastly, the high values of chemical oxygen demand (COD, 508 mg/L) and biochemical oxygen demand (BOD₅, 314 mg/L) at Point 1 indicated a significant organic load. The COD reflected the presence of oxidizable organic and inorganic matter, while the BOD₅ measured the oxygen required for the biological degradation of organic matter, highlighting a direct impact on aquatic ecosystems. Overall, the wastewater from coal mining showed characteristics that significantly exceeded regulatory limits in several critical parameters, particularly at Point 1. This underscores the urgent need to implement effective treatment and mitigation strategies to reduce its environmental impact.

3.2. Detection and Quantification of Lead Using AAS

The analysis of lead concentrations in the mining wastewater samples was conducted using AAS, revealing significant findings in the context of mining activities in the municipality of Toledo. The determined concentrations were 0.4 ppm for Sample 1 and 0.5 ppm for Sample 2. Both values exceeded the maximum permissible limit of 0.2 ppm established by Resolution 631 of 2015. Thus, the elevated lead concentrations can be attributed to several factors related to mining activities, where the geological composition of the area may include lead-bearing minerals that are released and transported by wastewater during coal extraction and processing. Additionally, heavy machinery and auxiliary materials, such as fuels, lubricants, and chemical reagents, may contain traces of heavy metals. Furthermore, the location of Sample 1, collected outside the mine, indicates that water flows in contact with mining waste and leaching zones might contribute to lead runoff into surrounding water bodies. Following standard Methods 3030E and 3111B, the detection procedure ensures high precision in determining lead concentrations. However, the results highlight the urgent need to implement corrective measures at the mine to reduce lead concentrations in effluents, ensuring compliance with current regulations and mitigating environmental impacts.

3.3. E-Tongue

In the cyclic voltammetry graph (see Figure 2), two of the studied concentrations clearly differ in current responses.

The solution containing 1 ppm of lead exhibited a significantly lower current, ranging from $-40 \ \mu\text{A}$ to $-30 \ \mu\text{A}$, compared to the 0.05 ppm solution, which displayed substantially higher current values, approximately $-1 \ \mu\text{A}$. This observation indicates that electrochemical interactions become more pronounced with increasing lead concentration, signifying a proportional relationship between the current magnitude and the concentration of metal ions in the samples.

Additionally, variations in potential behavior along the X-axis are observed, with no clearly defined peaks visible in Figure 2. This absence of distinct peaks is likely due to the weak redox processes of lead or their masking by the system's capacitive current. In the 0.05 ppm curve (blue), the low lead concentration results in an almost linear signal, lacking sufficient intensity to produce noticeable redox peaks. Likewise, in the 1 ppm curve (orange), while the current magnitude is higher, no distinct peaks are observed, likely due to diffusion limitations, slow electrochemical kinetics, or the predominance of capacitive currents. These results indicate that the E-tongue demonstrated high sensitivity and specificity in distinguishing between lead concentrations, even at levels such as 0.05 ppm. This performance is attributed to the design of the E-tongue's non-selective electrodes, which

partially reacted with the analytes present in the samples, generating unique electrical signals that allowed for the characterization of the chemical profile.



Figure 2. The response of the C110 electrode of the E-tongue to lead concentrations of 0.05 ppm and 1 ppm in wastewater.

3.3.1. Concentrations for Evaluating the Performance of the E-Tongue

Figure 3 depicts the response of the PCA based on measurements obtained using the E-tongue based on C110 carbon electrodes. For this experiment, synthetic lead solutions were prepared within a concentration range of 0.5 ppm to 100 ppm, with the primary objective of evaluating the E-tongue's ability to detect and differentiate specific lead concentrations in wastewater samples. The data were preprocessed using the "mean-centering" normalization method to ensure that the variables were centered around their mean before applying the PCA. This step was essential to eliminate biases arising from scale differences between the extracted features, enabling the principal components to reflect the underlying variability in the dataset accurately. PC1 captured 97.31% of the variance, representing the most correlated variability.



Figure 3. PCA plot of lead concentration (0.5 ppm to 100 ppm) categories in wastewater using E-tongue.

Figure 4 depicts the confusion matrix used to evaluate the performance of the SVM classifier applied to the 110 lead concentration measurements acquired with the E-tongue. A five-fold cross-validation method was employed to ensure the approach's robustness.



Figure 4. Confusion matrix obtained from PCA-SVM classification model of lead concentrations in wastewater using E-tongue (C110 electrode).

In the illustration, the rows represent the actual lead concentration classes, and the columns represent the predicted classes, with the diagonal entries indicating correct classifications. The model demonstrated high accuracy for most lead concentrations; however, misclassifications primarily occurred between the 1 ppm, 50 ppm, and 100 ppm levels, likely due to overlapping electrode responses or similarities in chemical composition. The strong diagonal dominance highlights the effectiveness of the SVM in classifying the measurements, achieving an accuracy rate of 97.30%.

Table 6 presents the performance of the classification methods (SVM, k-NN, Random Forest, Naïve Bayes, and QDA) in classifying lead concentrations in wastewater using measurements from the E-tongue system. Among the methods, the SVM model demonstrated the best performance, achieving an accuracy, sensitivity, and specificity of 97.30% and the highest F1-score of 99.73%. The k-NN model also performed well, with an accuracy of 95.10% and an AUC of 97.00%, while the QDA achieved a good balance with a specificity of 99.36%. Similarly, the Random Forest showed moderately good performance with an accuracy of 90.91%, whereas the Naïve Bayes had the lowest accuracy recorded at 86.36%, indicating marked differences in the performance of the models. Overall, the SVM classifier demonstrated superior performance.

Table 6. Metrics of different classification models for classifying lead concentrations in wastewater through E-tongue (C110 electrode).

ML Model	Accuracy (%)	Precision (%)	Sensitivity (%)	Specificity (%)	F1-Score (%)	NPV (%)	AUC ROC Curve (%)
SVM	97.30	97.52	97.30	97.30	99.73	99.73	98.50
k-NN	94.55	95.10	94.55	94.45	94.57	99.46	97.00
RF	90.91	91.70	90.91	99.09	90.90	99.10	95.00
Naïve Bayes	86.36	86.75	86.36	98.64	86.01	98.65	92.50
QDA	93.64	93.88	93.64	99.36	93.63	99.37	96.50

3.3.2. Concentrations at Points 1 and 2

The PCA plot in Figure 5 demonstrates the distribution of the analyzed samples, which include lead concentrations ranging from 0.05 ppm to 1.0 ppm, distilled water as a reference (0 ppm), and real wastewater samples collected from the two specific points outlined in the methodology. This analysis assessed the ability of the PCA model, developed with synthetic solutions, to project and classify real samples based on their lead content. In the plot, the *x*-axis represents PC1, capturing most of the system's variability (99.93%), demonstrating its ability to differentiate between samples. The *y*-axis, corresponding to PC2, accounts for 0.07% of the variance, providing complementary but limited insights. The distribution along PC1 highlights a clear separation between the cluster of distilled water, projected on the left side of the plot, and the samples containing lead, positioned toward the right. These latter samples include both synthetic solutions and real wastewater samples.



Figure 5. PCA analysis: Lead concentration (0.05 ppm to 1.0 ppm) categories in wastewater samples from Point 1 and Point 2, analyzed using E-tongue system.

The real samples, identified as Sample 1 and Sample 2, exhibited similarities at specific concentrations. In the model, Sample 1 was projected around a lead concentration of 0.3 ppm to 0.4 ppm, while Sample 2 was near 0.5 ppm. This reflects consistency in their chemical profiles and confirms the system's capability to provide quantitative approximations based on the PCA model. These results align with findings from the AAS analysis of the same samples, which determined lead concentrations of 0.4 ppm in Sample 1 and 0.5 ppm in Sample 2. This concordance underscores the precision of the electronic tongue in identifying concentrations close to actual values.

These findings demonstrate the sensitivity and accuracy of the E-tongue in detecting low lead concentrations in wastewater, effectively projecting real samples onto a model previously calibrated with standard solutions ranging from 0.05 ppm to 1 ppm. The separation of groups confirms the E-tongue's efficacy in classifying and quantifying heavy metals, establishing it as a reliable and practical tool for environmental monitoring in industrial contexts, with the ability to deliver rapid and precise results.

The confusion matrix in Figure 6 represents the performance of a PCA-RF classification model used to predict lead concentrations in wastewater samples from two points (Point 1 and Point 2).



Figure 6. Confusion matrix obtained from PCA-RF classification model of lead concentrations in wastewater from Points 1 and 2 using E-tongue (C110 electrode).

Table 7 depicts the performance metrics of machine learning models used to classify lower lead concentrations in wastewater. The SVM and RF models showed the best overall performance, achieving a 90.00% accuracy, 90.00% sensitivity, and high AUC values (SVM at 94.50% and RF at 94.00%). The SVM showed a good precision of 91.05% and specificity of 99.00%, while the RF demonstrated a high NPV of 99.00%.

Table 7. Metrics of confusion matrix for PCA and classification models for classifying lower lead concentrations in wastewater from Point 1 and Point 2 through E-tongue (C110 electrode).

Model	Accuracy (%)	Precision (%)	Sensitivity (%)	Specificity (%)	F1-Score (%)	NPV (%)	AUC ROC Curve (%)
SVM	90.00	91.05	90.00	99.00	90.15	99.01	94.50
k-NN	70.23	70.85	70.00	96.80	70.00	96.82	66.07
RF	90.00	90.59	90.00	98.99	99.02	99.00	94.00
Naïve Bayes	86.36	86.64	86.36	98.64	86.43	98.64	92.50
QDA	87.27	89.52	87.27	98.73	87.44	98.74	93.00

On the other hand, the k-NN performed poorly, with a lower AUC of 66.07% and an accuracy of 70.23%. At the same time, the Naïve Bayes and QDA showed balanced performance, with the QDA achieving an AUC of 93.00% and the Naïve Bayes performing well with specificity of 98.64%. Therefore, the SVM and RF were the most reliable classifiers for detecting lower lead concentrations in wastewater.

4. Discussion

E-tongues and electrochemical sensors have been proven to be promising tools in environmental monitoring, particularly for detecting heavy metals in water and soil, addressing one of the most critical global environmental issues. Recent studies have explored various configurations and methodologies to enhance these devices' sensitivity, selectivity, and applicability. Shimizu et al., 2019 [56] provided a comprehensive review of E-tongues monitoring environmental pollutants, particularly for detecting heavy metals in water. These technologies leverage sensors made of diverse materials, such as polymers, carbon nanotubes, and metal oxides, which demonstrate high sensitivity in identifying contaminants like lead, cadmium, and mercury, even at very low concentrations. However, some

challenges persist, especially in high-conductivity media like industrial or mining wastewater, where phenomena like "screening effects" and the Debye length dependence reduce the precision and reproducibility of sensors in complex solutions, limiting their real-world applicability. Other studies, such as those by Kuhlman et al., 2004 [57], have focused on E-tongues based on REDOX cells employing anodic stripping voltammetry (ASV) for detecting heavy metals like zinc, lead, copper, and manganese at concentrations as low as 10 μ M.

Thus, advanced adaptations, such as screen-printed electrodes modified with materials like carbon nanofibers, antimony films, and chemical agents (e.g., glutathione, cysteine), have allowed the simultaneous detection of metals in complex solutions. Using differential pulse anodic stripping voltammetry (DPASV) and regression algorithms like partial least squares (PLS), these devices have achieved detection limits ranging from 2.6 to 16.8 μ g/L depending on the metal and electrode type. Similarly, potentiometric sensor arrays have been employed to detect multiple heavy metals, such as Cu, Zn, Pb, and Cd, even under challenging conditions like in artificial seawater, with detection thresholds meeting environmental standards. These advancements highlight the progress in sensor technology, with a significant focus on modified electrodes for improved sensitivity and selectivity. However, this study emphasizes commercial electrodes, which achieve comparable precision and classification of metals, notably lead, as they present a cost-effective and accessible alternative, addressing the limitations associated with the additional expenses and complexity of preparing modified electrodes.

While much of the existing literature focuses on synthetic and controlled water samples, this study addresses a critical gap by analyzing real coal mining wastewater, presenting a complex mixture of chemical contaminants and suspended solids. This approach increases E-tongues' applicability to real-world scenarios, addressing the need for the real-time monitoring of industrially impacted water bodies. Despite adverse conditions such as high conductivity, turbidity, and biochemical oxygen demand, combining classical data preprocessing techniques with machine learning algorithms like the SVM and Random Forest enabled robust data classification. The confusion matrices (Figures 4 and 6) and performance metrics (Tables 6 and 7) confirmed the high precision, specificity, and sensitivity achieved by the E-tongue, highlighting the potential of these devices for real-time environmental monitoring.

5. Conclusions

The E-tongue demonstrated high sensitivity and precision in detecting lead concentrations ranging from 0.05 ppm to 1 ppm in mining wastewater, surpassing traditional methods in terms of portability and cost-efficiency.

The SVM classifier achieved a remarkable precision and accuracy rate of 91.05%, outperforming other models like the k-NN, Random Forest, and Naïve Bayes, showcasing its robustness for environmental monitoring applications.

Both sampling points showed lead concentrations exceeding permissible limits (0.2 ppm), highlighting the significant environmental impact of mining activities in the region and the need for practical monitoring tools.

As mentioned, despite the challenging conditions of mining wastewater (high turbidity and organic load), the E-tongue maintained robust performance, proving its applicability in real-world environmental scenarios.

Combining PCA with machine learning algorithms underscores the E-tongue's potential for the real-time, on-site monitoring of heavy metal contamination, addressing a critical need for sustainable mining practices. Furthermore, this application opens the possibility of using additional machine learning methods to evaluate the classification capacity of the E-tongue further. Techniques such as Gradient Boosting Machines (e.g., XGBoost or LightGBM), neural networks, and ensemble methods could provide deeper insights into the classification of lead concentrations in coal mining wastewater. Exploring these advanced algorithms may improve performance further and enhance the robustness of the electronic tongue system for environmental monitoring applications.

This study highlights its contribution to advancing detection and classification techniques for heavy metal contamination in environmental contexts. It underscores the importance of research in addressing critical environmental challenges and enhancing monitoring practices for the sustainable management of heavy metal pollutants.

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