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Research Article

Green Chemistry on the Ores Leaching Processes Using Organic Acids: A Qualitative Pedagogical Content Analysis Study

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Abstract.
Ores leaching projects aimed to recover toxic and valuable metals from industrial residues. Organic acids like acetic acid and methanesulfonic acid were chosen as leaching agents because they have high selectivity on low concentrations of metals and low toxicity. This study aimed to obtain scientists' conceptions of ores leaching using organic acids presented in concept maps and Teaching Learning Sequence (TLS). The method used in this study was qualitative content analysis consisting of literature collection, descriptive analysis, category selection, and material evaluation from textbooks, review articles and research articles. The result of this study was in the form of a concept map, and TLS illustrate five sequences of learning materials consisting of mineral products in Indonesia, valorization of industrial process residue with green chemistry-oriented, industrial process residue treatment steps, organic acid properties, and examples of the ores leaching process. The leaching process of ores using organic acids in learning is contextual learning that integrates the concepts of acids and bases, redox reactions, and the principles of solubility learned by high school students. This process also applies the principles of green chemistry, preventing waste in the process and using safe solvents. The results of the concept map and Teaching Learning Sequence (TLS) showed the application of green chemistry in learning, which is expected to be used as a design for teaching materials and didactic designs that can support education for sustainable development.

Keywords: Green Chemistry, Organic Acids, Pedagogical Content Analysis

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1. Introduction

Indonesia is a country with high potential for mineral products, such as coal, nickel, copper, tin, zinc, and lead. Nickel ore mining results in 2020 reached 48,040,003 tons [1]. Consumption of natural resources likes fossil fuels, metals, and minerals in the next 40 years is expected to increase by 70% in 2050 [2]. As much as 62% of nickel metal is commonly used in industry for stainless steels (Figure 1.), 13% as super alloys and ironless alloys because of its corrosion resistance and high temperature [3].

Figure 1: Nickel as a coating material.

Figure 2: Lead-Acid (LA) battery.

Current technology products such as LA batteries (Figure 2.), solar cells, LED lamps, and LCD screens use lead as their constituent components [4]. As well as the use of Zn which is commonly used to coat iron and steel products [5]. 75-80% of the annual world's zinc metal production (8 million tons) is produced via hydrometallurgical processes and produces a jarosite residue that consisting of Pb and Zn metal which is valuable [6]. Therefore, there is a need for a sustainable waste valorization project to increase the residual value of industrial processes to recover toxic and economically valuable metals. The ores recovery process has been carried out through pyrometallurgical, hydrometallurgical, and solvometallurgical processes [7]. The leaching process uses a leachate agent or is called a lixiviant. Lixiviant is a solvent that is used selectively to extract the desired metal from an ore or mineral [8]. Ores leaching processes that have been carried out previously generally use inorganic acids such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and nitric acid (HNO_3) [8]. However, the leachate in the form of inorganic acids tends to be corrosive and has low selectivity [8]. So, organic acids are used as leachate which aims to be more environmentally friendly and can apply the principles of green chemistry [9].

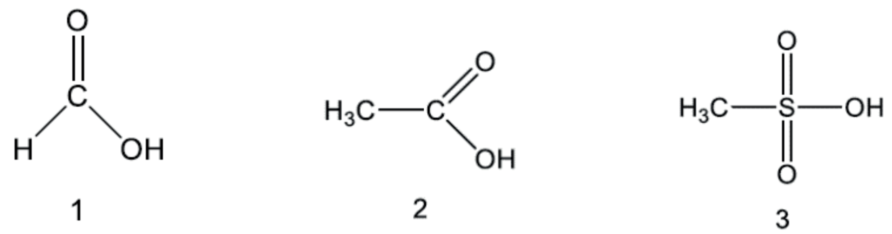

Figure 3: Example of organic acids : 1) formic acid, 2) acetic acid, 3) methanesulfonic acid.

Organic acids such as formic acid, acetic acid, and methanesulfonic acid (MSA) are environmentally friendly organic lixiviants because they are biodegradable and less toxic than mineral acids [10]. Weak acids (formic acid, pKa = 3.82, acetic acid, pKa = 4.76) or strong acids (MSA, pKa = 1.19), can be used as both leaching agents and solvents for metals during leaching [8].

Green Chemistry is a 12 of principles promoting environmentally friendly research in the form of reducing or eliminating the use of hazardous substances in the design, manufacture, and application of chemical products [9]. The principle of green chemistry used in the implementation of this project is expected to be able to include the principle of preventing waste in the process because the leaching of ores aims to recover valuable metals in industrial process residues, so it is hoped that the residues of this industrial process will be safer when disposed of into the environment. Then, another principle is the use safer solvents like organic solvents that are more environmentally friendly.

The leaching process of ores using organic acids topics in learning is contextual learning that integrates the concepts of acids and bases, redox reactions, and the principles of solubility learned by high school students. This process also applies the principles of green chemistry that can support education for sustainable development. So in this article, we will discuss how to integrate the principles of green chemistry into the learning stages in the Teaching Learning Sequence (TLS).

2. Research Method

The method used is the qualitative content analysis in the following stages [11]:

The first stage begins with collecting materials for analysis in the form of textbooks, textbooks, review articles, and research journals. The next stage is to carry out a descriptive analysis of the sources that have been collected, by condensing extensive material into a summary [12]. The third stage is category selection, at this stage incorporating

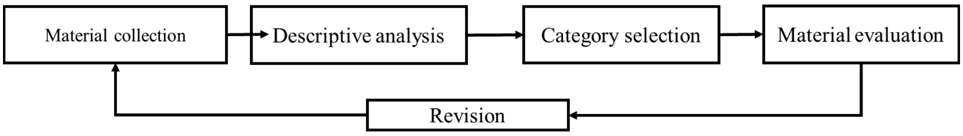

Figure 4: The process of analyzing the qualitative content of literature type.

pedagogic and didactic aspects into the results of the analysis. The last stage is the evaluation of the material, at this stage, the results of the analysis that have been categorized are described in a concept map and TLS. More detailed steps regarding category selection and material evaluation can be seen in Figure 5.

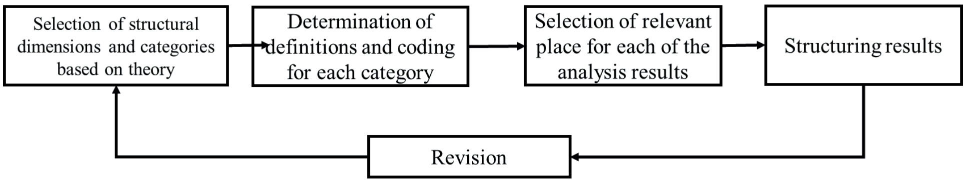

Figure 5: Structure process of content analysis results.

The instrument in this study was the format used at the stage of material collection and descriptive analysis. The instrument format at the material collection stage shows the titles of several sources along with the year of publication and the author is equipped with the code used in the results of the analysis. The format of the instrument can be seen in Table 1. While the instrument used in the descriptive analysis stage is a content analysis format that contains a summary of the results of the analysis as shown in Table 2.

TABLE 1: Material collection instrument format.

Author	**Title**	**Year**	**Code**
…..	……	…..	….

TABLE 2: Descriptive analysis instrument format.

Content	**Analysis Result**
……	……….

3. Results and discussion

3.1. Material Collection

Science content clarification refers to qualitative content analysis from reliable sources. Materials collected for concept analysis include textbooks, review articles, and research journals. Sources of literature as material for analysis are presented in Table 3.

Table 3: The sources of material analyzed.

Author	Title	Year	Code
Palden, T.	Organic lixiviants for metal recovery from industrial process residues.	2021	A
Binnemans, K.; Jones, P. T.	Solvometallurgy: An Emerging Branch of Extractive Metallurgy	2017	B
Dutrizac, J. E.; Jambor, J. L.	Jarosites and Their Application in Hydrometallurgy	2000	C
Asokan, P.; Saxena, M.; Asolekar, S. R.	Recycling Hazardous Jarosite Waste Using Coal Combustion Residues	2010	D
Haldar, S. K.	Mineral Processing in Mineral Exploration	2018	E
Brady,J.E.,Jespersen,N.D.,&Hyslo	Chemistry the Molecular Nature of Matter	2012	F
Pappagiani, et al.	Comprehensive Biotechnology (Second Edition)	2011	G
Speight, J, G. et al.	Chemical and Physical Properties. Reaction Mechanisms in Environmental Engineering	2018	H

3.2. Descriptive Analysis

After collecting library sources, a descriptive analysis is then carried out by condensing the broad material into a summary [12]. The results of the descriptive analysis are presented in Table 4.

3.3. Category Collection

The third stage is categorizing the results of the analysis that has been carried out. From the results of the analysis, it is categorized into 5 parts consisting of of 1) mineral products in Indonesia, 2) valorization of industrial process residue with green chemistry-oriented, 3) industrial process residue treatment steps, 4) organic acid properties, and 5) examples of ores leaching process. Part 1, mineral products in Indonesia, includes their benefits in

Table 4: The results of the descriptive analysis of the leaching of mining minerals with organic acids.

Content	Analysis Results
Industrial process residue treatment	The processing stage of metal residues from industrial processes consists of 3 stages, there are leaching, purification, and metal recovery [7] **[A] Leaching** The process of dissolving a metal from solid material in a lixiviant usually consists of a leaching agent and a solvent [13] **[B].** In hydrometallurgy, the leachate is an acid, a base and a chelating agent (EDTA and citric acid), and a water solvent. Whereas in solvometallurgy the leachate is in the form of organic acids (HCOOH, CH_3COOH, methanesulfonic acid (MSA)), mineral acids (HCl in polar solvents such as acetone, methanol, ethanol), ionic liquids, eutectic solvents [7] **[A]. b. Purification** A purification process to remove unwanted components, and obtain a concentrated solution containing primarily the metal of interest. The various processes used for the concentration and purification of organic PLS include (1) solvent extraction, (2) precipitation/crystallization, and (3) ion exchange [7] **[A]. c. Metal Recovery (Stripping)** Metal recovery is the final unit process in extractive metallurgy where high purity metals or metal salts are produced [6] **[C].** In hydrometallurgy, electrolysis is commonly used to recover metals directly from aqueous PLS or stripped aqueous solutions [14] **[D].** The metal is recovered by precipitation of the desired metal from the electrolyte to the cathode material by electrolytic reduction. This process is also known as electrowinning. Similarly, in solvometallurgical leaching using organic lixiviant, the metal can be recovered directly from organic PLS or stripped of its aqueous solution by electrolysis [15] **[E].**
Organic Acid	Organic acids are organic compounds containing a carboxylic group ($-CO_2H$) or also called carboxylic acids [16] **[F].** The structure of organic acids has an oxygen double bond and one –OH group attached to the C end of the structure [16] **[F].** Organic acids are organic compounds characterized by weak acid properties and do not completely dissociate in water [17] **[G].** Organic acids occur naturally in animals, plants, and microbes. Generally contains one or more carboxylic acid groups such as formic acid, acetic acid, and methanesulfonic acid [18] **[H].**

life and also tell the residues of industrial processes. Then, section 2 describes valorization of industrial process residue with green chemistry-oriented consist of pyrometallurgy, hydrometallurgy, and solvometallurgy, that explains the advantages and disadvantages of each process. Section 3 describes industrial process residue treatment steps residues which will further relate the reasons for choosing organic acids as leachate agents. Section 4 describes organic acids which includes definitions, examples, and characteristics. And the last section describes examples of ores leaching processes using organic acids.

3.4. Material Evaluation

The results clarified chemical concepts are then evaluated based on categories and relationships between concepts. The results of the concept analysis of ores leaching using organic acids are depicted in the form of a concept map and TLS as shown in Figure 6.

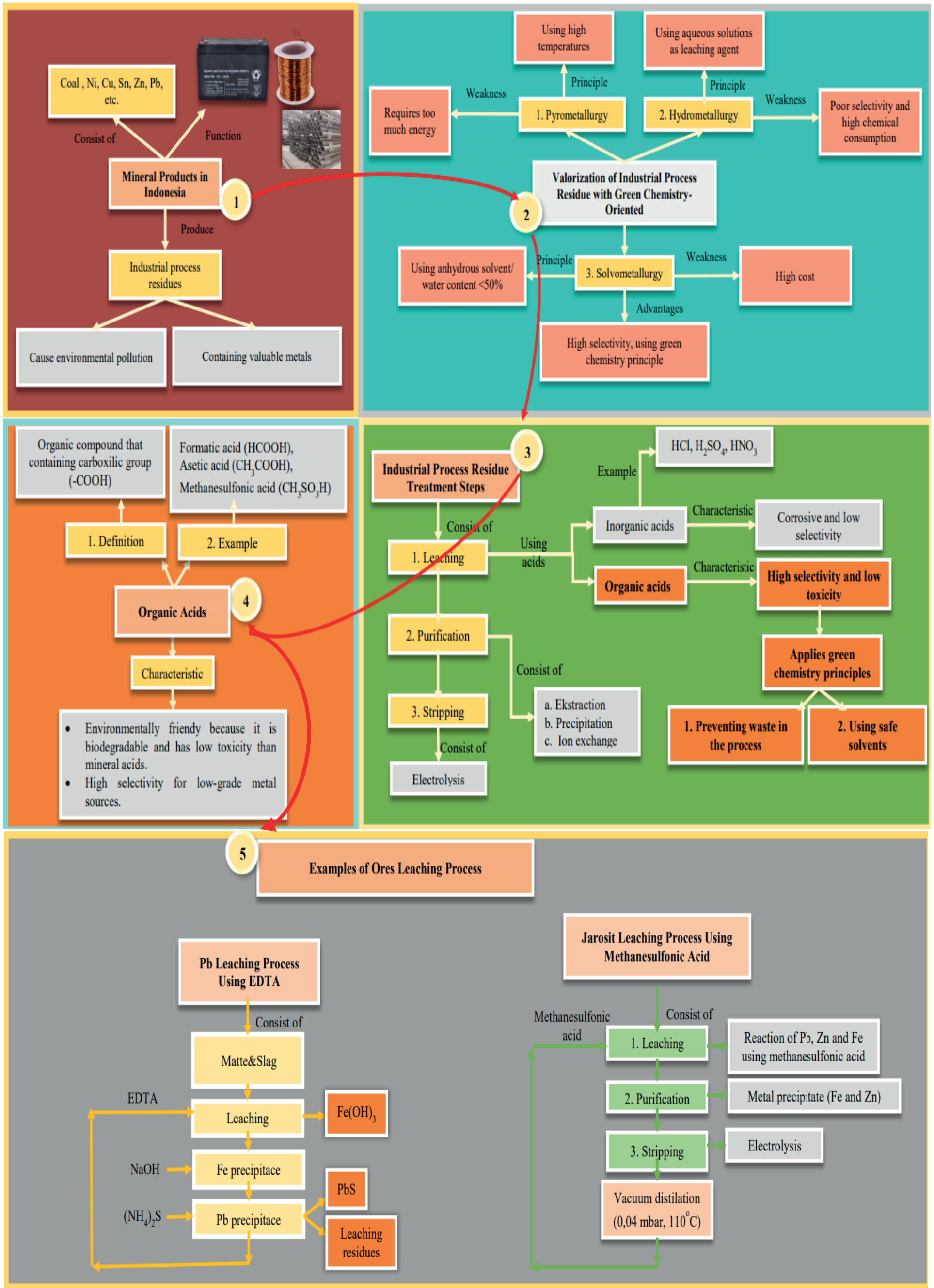

Figure 6: Concept map and TLS regarding concept analysis of ores leaching using organic acids.

Figure 6 is a concept map of the results of the analysis. The concept map shows the interrelationship of each stage which is linked to several questions. Part 1 and part 2 are connected by the questions "What are the mineral products in Indonesia and their benefits in life?", "What are the impacts of industrial process residues?", and

“How to treat industrial process residues?”. Part 1, which describes mineral products in Indonesia, includes their benefits in life as well as the residues of industrial processes. Then part 2 describes a sustainable waste valuation project that is oriented toward green chemistry, consist of pyrometallurgy, hydrometallurgy, and solvometallurgy. The advantages and disadvantages of that processess are explained. Parts 2 and 3 are related to the question “what are the steps of processing industrial process residues?”, which is then explained in 3 stages, consist of leaching, purification, and stripping. In the leaching stage, it was explained that the use of inorganic acids had been carried out but had poor selectivity for low-grade metals and was corrosive. Then an alternative is given using organic acids which have high selectivity for low-grade metals and are also environmentally friendly because its low toxicity. Part 3 and 4 are then linked to the question “What is an organic acid?”. Meanwhile, section 4 and section 5 are related to the question “What is an example of an ores leaching process using organic acids?”.

4. Conclusion

This study aims to obtain scientists’ conceptions of ores leaching using organic acids presented in concept maps and Teaching Learning Sequence (TLS). The method used in this study is qualitative content analysis consisting of literature collection, descriptive analysis, category selection, and material evaluation from textbooks, review articles, and research articles. The result of this study are in the form of a concept map and TLS illustrate 5 sequences of learning materials consisting of 1) mineral products in Indonesia, 2) valorization of industrial process residue with green chemistry-oriented, 3) industrial process residue treatment steps, 4) organic acid properties, and 5) examples of ores leaching process. The leaching process of ores using organic acids in learning is contextual learning that integrates the concepts of acids and bases, redox reactions, and the principles of solubility learned by high school students. This process also applies the principles of green chemistry preventing waste in the process and using safe solvents. The results of the concept map and Teaching Learning Sequence (TLS) show the application of green chemistry in learning which is expected to be used as a design for teaching materials and didactic designs that can support education for sustainable development.

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