Chelation and AOP Approach on Mn-Metal and COD Reduction of Liquid Laboratory Waste

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Abstract: Heavy metal waste and organic material used in flushing laboratory glassware can accumulate and potentially damage the environment. Thus, it needs to be processed before being disposed of to avoid any damage to the aquatic ecosystem. This research aimed to determine the pH wastewater sample and APDC concentration as chelating agents that would be the best for chelation treatment and determine the H\textsubscript{2}O\textsubscript{2} concentration and UV exposure duration to identify the best treatment for the advanced oxidation process. This research was expected to find an alternative in wastewater treatment and provide an overview of the interaction of chelation treatment with organic pollutants as the basis for AOP-treatment management. Laboratory wastewater quality has improved through the extraction treatment of chelate from the pH 4 experiment, ammonium pyrrolidine dithiocarbamate (APDC) concentration at 7.5% with the manganese metal value decreased by 53%, an advanced oxidation process (AOP) treatment of H\textsubscript{2}O\textsubscript{2} concentration at a 5.10-5%, and 31-hour UV exposure, resulting in chemical oxygen demand (COD) decreased by 98.98%. Waste containing both materials was reduced by combining the extraction of chelate formation and AOP, which was detected from the presence of manganese metal and the COD. This treatment can be an appropriate and easy way to degrade laboratory waste in a mini wastewater treatment process. This research succeeded in finding several novelties: first, a suitable pH value to reactivate Mn metal for chelation with APDC; second, the concentration of APDC determined to optimize the Mn metal chelate; third, the concentration of H\textsubscript{2}O\textsubscript{2} to increase the effectiveness of organic matter reduction; fourth, the duration of UV irradiation is effective and efficient as a photocatalyst to reduce organic matter.

Keywords: advanced oxidation process, chelation, chemical oxygen demand, laboratory waste, manganese.

螯合和 AOP 方法减少液态实验室废物的锰金属和鳕鱼

摘要：用于冲洗实验室玻璃器皿的重金属废物和有机材料会积聚并可能破坏环境。因此，在处理之前需要对其进行处理，以避免对水生生态系统造成任何损害。本研究旨在确定废水样品的酸碱度值和亚太发展中心浓度作为螯合剂的最佳螯合剂，并确定过氧化氢浓度和紫外线照射持续时间，以确定高级氧化工艺的最佳处理方法。该研究有望找到废水处理的替代方案，并概述螯合处理与有机污染物的相互作用，作为 AOP 处理管理的基础。通过对酸碱度 4 实验的螯合物进行萃取处理，提高了实验室废水质量，吡咯烷二硫代氨基甲酸铵(亚太发展中心)浓度为 7.5%，锰金属值降低了 53%，高级氧化工艺(AOP)处理过氧化氢浓度为 5.10-5%，以及 31 小时的紫外线照射，导致化学需氧量（鳕鱼）下降 98.98%。通过结合提取螯合物形成和 AOP（从锰金属和鳕鱼的存在中检测到）来减少含有这两种材料的废物。这种处理可以是在小型废水处理过程中降解实验室废物的合适且简单的方法。该研究成功地发现了几个新点：首先，合适的酸碱度值可以重新激活锰金属以与亚太发展中心螯合；其次，确定亚太发展中心的浓度以优化锰金属螯合物；三，提高过氧化氢浓度，减少有机物的效果；第四，紫外线照射的持续时间作为光催化剂有效且高效地减少有机物。

关键词：高级氧化工艺、螯合、化学需氧量、实验室废物、锰。
1. Introduction

Liquid waste resulting from a chemical procedure commonly required in laboratory analysis could be very toxic and dangerous even with a small quantity [1, 2] due to the contents of heavy metals and organic matter [3, 4]. These heavy metals include chrome (Cr), iron (Fe), cadmium (Cd), copper (Cu), cobalt (Co), manganese (Mn), zinc (Zn), lead (Pb), and nickel (Ni) [5]. Heavy metals cannot be easily degraded [6]; they are also easily concentrated, accumulated, and magnified [7], potentially damaging the environment. Organic materials, especially non-degradable organic matter, are always found in laboratory waste; some are synthetic, and some may be toxic [1]. Continuous laboratory activity may accumulate heavy metals and organic materials, thus potentially polluting the environment and disturbing or even decreasing water quality [8].

Chemical treatment of laboratory waste can be done using a chelate extraction method and an advanced oxidation process (AOP). Combining these methods has advantages because they can reduce waste containing heavy metals and organic materials [9, 10] and form a stable complex [11]. They can be applied to laboratory wastewater treatment containing both types of waste.

There are two processes in the extraction of chelate formation: binding and separation of metals by chelating agents [10, 11]. The coating process was carried out using a chelating agent, ammonium pyrrolidine dithiocarbamate (APDC), which worked optimally at acidic pH and concentration [12], while the separation of complex metals from the aqueous phase was carried out using methyl isobutyl ketone (MIBK). APDC chelating agents have the flexibility to extract complexes of more than 30 metals at low pH [12]. However, extraction of the chelate formation also requires methyl isobutyl ketone (MIBK). MIBK is an organic solvent that has non-polar properties and plays a role in separating heavy metals from the aqueous phase in the extraction of chelate formation.

APDC and MIBK are synthetic organic compounds [13, 14] that contribute to the organic matter in the water sample. It has the potential to increase the organic matter contained in the wastewater. Therefore, the use of AOP with a strong oxidizer of H$_2$O$_2$ and UV irradiation was carried out to degrade the toxic complex of organic matters [15-17]. Chemical oxygen demand (COD) will be measured to represent the concentration of organic matter in waste samples treated by the AOP method.

2. Methods

The water sample of 50 L was derived from the waste rinse in the Productivity and Environment Laboratory, Department of Aquatic Resources Management, Faculty of Fisheries and Marine Sciences, IPB University. This waste is colorless with a slightly cloudy and a faintly sweet pungent odor.

This research began by extracting the chelate formation, followed by the advanced oxidation process (AOP). This procedure aimed to determine the acidic pH of the sample, the best concentration of APDC in reducing heavy metals, the concentration of H$_2$O$_2$, and the best UV exposure duration in reducing the content of organic pollutants in the samples.

2.1. Chelation

This treatment was initiated by measuring the COD and AAS manganese concentrations in the wastewater sample and continued by adjusting the pH value and the APDC concentration used as the chelating agent. Following American Public Health Association (APHA) [12] and other references, some modifications were made to the pH and APDC concentrations to run this process.

The pH was adjusted. The pH amount for each container was 2.0, 3.0, 4.0, and 5.0. The use of an acidic pH due to manganese extraction with APDC can only be chelated if manganese dissolves to form Mn$^{2+}$ ions, increasing the efficiency of manganese metal extraction in the pH range 2-4 [12].

The determination of the APDC concentration as a chelating agent was based on three concentration levels: 0.5%, 4.0%, and 7.5% rinsed once with methyl isobutyl ketone (MIBK) using a separating funnel. The lower phase portion is taken as a ready-made APDC solution.

This treatment was set out using a factorial experimental design with a batch system of two factors: the pH and the concentration of the chelation agent. The manganese concentration and COD measurement was based on APHA [12].

2.2. Advanced Oxidation Process (AOP)

This treatment was conducted following the chelation process. The used samples were separated into two parts. The first part was used to determine the H$_2$O$_2$ concentration, and the other part was used to determine the best UV exposure duration to be applied in the main treatment.

H$_2$O$_2$ reagents were made into various concentrations, each treatment with mass fraction (% w/w) of 5.10$^2$%, 5.10$^3$%, 5.10$^4$%, 5.10$^5$%, 5.10$^6$%, 5.10$^7$%, and 5.10$^8$% in the 50 mL experimental sample, exposed under Philips UV-C lamp within 2 meters for 31 hours. The best H$_2$O$_2$ concentration was determined from the greatest change in COD.

A complete randomized research design was used in
this study. The measurement of COD was based on APHA [12].

3. Results and Discussion

Laboratory liquid waste generally contains several pollutants, such as metal and organic matter. These pollutants will become toxic if the levels are too excessive and may be dangerous to humans and the environment [19]. Therefore, waste containing metal and organic matter needs treatment to prevent the spreading of pollutants to the environment.

The first approach used for the treatment of laboratory waste was chelation treatment. In this research, chelation could reduce waste containing heavy metals [10] by observing the manganese (Mn) metal and forming a complex formation or chelate that binds the metal by an organic chelating agent [11, 20]. The stability of the complex formation required the chelating agents and pH of the sample [20]. APDC, which worked at a low pH and was selective on various metals [12], was chosen as the chelating agent.

The difference in pH and APDC concentration treatment resulted in various reduction values of Mn metal. Mn-APDC extraction only occurred with Mn\(^{3+}\) ions in specific acidic conditions (Fig. 6) [21]. The initial pH of laboratory waste was 1.32. The initial pH condition was out of the range, so the treatment was tested in the recommended range of APHA (pH 2-4) [12] and once out of the recommended range (pH 5).

The result of chelation showed a significant reduction in manganese metal (p < 0.05) in all samples of pH treatments and APDC concentrations. Further, the highest significance value of reduction treatment occurred at pH 4 with an APDC concentration of 7.5% (Fig. 1), with a drop difference of 0.1 mg/L. Furthermore, the effectiveness of pH 4 with 7.5% APDC concentration treatment was 53% (Fig. 2) and classified as moderate reduction treatment [18].

Fig. 1 shows the best chelation experiments at pH 4, and Fig. 3 shows a decrease in their effectiveness at pH 5. The 7.5% APDC concentration was the best trial compared to other concentrations; due to the higher level of ligand stability in the APDC condition of 7.5% compared to 0.5% and 4.0% [18].

Many factors could influence stability, such as the central atom and the ligands involved, compromised as thermodynamic stability and kinetic instability factors [2]. The size of the chelating ring could cause the influence of ligands. The five-armed rings and the chelating effects, such as those of APDC, have good stability [22]. In addition, the effect of amphoteric ligand basicity in the acid wastewater atmosphere formed an isoelectric complex [22]. Isoelectric occurred by conditioning the sample's acidity to stabilize the ligand ion charge with metal ions [23]. This caused the pH 4 in this treatment to be assumed as isoelectric, formed by APDC chelate complexes and manganese metal.

The chelation treatment affecting the changes in organic matter (indicated by the chemical oxygen demand or COD value in Fig. 3) was caused by the addition of APDC and MIBK reagents. APDC and MIBK reagents were synthetic organic materials [13, 14] that could increase the COD in the wastewater. The greatest change of COD occurred in chelation waste treatment of pH 5 and APDC 7.5% (Fig. 3), which reached 71% from the initial conditions. Thus, the wastewater still needs to be treated to reduce the COD value by advanced oxidation process (AOP) as the second treatment.

AOP is a further treatment of chelation to reduce organic matters, which involves strong oxidizing reactions (hydrogen peroxide/H\(_2\)O\(_2\)) and photolysis irradiation through exposure to ultraviolet light [9]. In this research, AOP treatment was observed to determine the best concentration of H\(_2\)O\(_2\) and the best UV light exposure time.

In reducing organic matter using AOP, it is necessary to determine the concentration of hydrogen peroxide and UV exposure duration [16]. If the H\(_2\)O\(_2\) concentration is too small, it would be immediately depleted to degrade the organic matter. However, at a higher concentration, the ability of H\(_2\)O\(_2\) to reduce also decreased. In addition, excessive binding of OH\(^-\) by H\(_2\)O\(_2\) caused the amount of OH\(^-\) to decrease, which causes photodegradation of organic compounds to run slowly [26]. Different types of waste might have different specifications before using the AOP treatment.

The result showed that COD was reduced at all levels of their H\(_2\)O\(_2\) concentration (Fig. 4). There was a significant reduction in the values (p < 0.05) at H\(_2\)O\(_2\) concentration of 5.10\(^{-3}\)%, and based on the results of subsequent tests, it appeared that the H\(_2\)O\(_2\) level of
5.10^{-5}\% provided the highest significance from the initial COD, with a reduction effectiveness value of 97.52%.

After obtaining the best \( \text{H}_2\text{O}_2 \) concentration, the best duration of UV light exposure was determined (Fig. 5). The COD decreased along with the increase in exposure duration. The value of the initial COD was significantly different from the COD after application of UV exposure (\( p < 0.05 \)) but only in 1 hour, which means that only 1 hour can be effective for COD reduction.

The ability of AOP to reduce organic matter was because of the production of hydroxyl radicals (•OH) in the AOP process from the stages of initiation, propagation, and termination [17] as follows:

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\begin{align*}
\text{H}_2\text{O}_2 + \text{hv} & \rightarrow 2\text{•OH} \quad \text{(initiation)} \\
\text{•OH} + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{HO}_2\text{•} \quad \text{(propagation)} \\
\text{•OH} + \text{HO}_2\text{•} & \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad \text{(termination)} \\
2\text{•OH} & \rightarrow \text{H}_2\text{O}_2 \quad \text{(termination)}
\end{align*}
\]

The hydroxyl radical is an abstraction reaction to hydrogen bonds [24] by breaking down the bond and producing water. This reaction is described as a hydroxyl reaction between the following compounds of methanol and 1-Propanol [24] (Fig. 7).

Furthermore, hydroxyl radicals break down the organic matter into simple material products such as \( \text{CO}_2 \), \( \text{H}_2\text{O} \), and chlorine ions [25]. This allows organic material in the waste to be continually reduced. In this study, the content of organic matter after the oxidation process reached 357 mg/L (Fig. 5).

The application of various UV exposure durations against waste with the best \( \text{H}_2\text{O}_2 \) concentration (Fig. 5) shows the decomposition of organic matter. The UV exposure will continue to break down \( \text{H}_2\text{O}_2 \) to produce hydroxyl radicals in reducing organic matter until the termination stage of the chemical reaction [17]. The longer the UV exposure duration, the greater hydroxyl radical would be produced. Hence, \( \text{H}_2\text{O}_2 \) decomposition occurs faster to break the organic bound. However, it is necessary to determine the effectiveness of exposure time, which gives a significant reduction. This is the main key to increasing the effectiveness of plant operations [17]. This efficiency factor would subsequently affect the operational costs of the wastewater treatment plant.

### 4. Conclusion

Chelation treatment can be applied to laboratory waste, even though there was an increase in organic matter. However, the increase in the organic matter could be overcome by applying further treatment through AOP. Chelation treatment provided the best effectiveness of manganese metal reduction of 53% were found at pH 4 and 7.5% APDC concentration. Furthermore, the concentration of \( \text{H}_2\text{O}_2 \) at 5.10^{-8}\% and the duration of UV exposure of 1 hour could be considered an efficiency factor of wastewater treatment plant operation that applies AOP.

This research succeeded in finding several
novelties:

1) A suitable pH value to reanimate Mn metal for easy chelation with APDC: The use of pH 4 shows the changes in manganese ions to free Mn$^{2+}$, which can increase the efficiency of manganese metal extraction with APDC;

2) The concentration of APDC that has been determined to optimize the Mn metal chelate: APDC concentration of 7.5% in this study was the best experiment because of ligand properties with manganese atoms which are more stable than other concentrations and suitable for laboratory wastewater treatment;

3) The concentration of $\text{H}_2\text{O}_2$ to increase the effectiveness of organic matter reduction: At the appropriate concentration of $\text{H}_2\text{O}_2$ at 5.10$^{-8}$%, the $\text{•OH}$ formed would not be used up immediately to degrade organic matter and would not produce more $\text{HO}_2$*, which would cause the decrease of $\text{•OH}$ that potentially inhibits the photodegradation;

4) The duration of UV irradiation is effective and efficient as a photocatalyst to reduce organic matter: The irradiation time of 1 hour shows the high effectiveness so that the operation of the waste treatment plant in the future can be projected to work efficiently.

This research can be applied to environmental laboratories located at universities, factories, and other institutions. The design of laboratory wastewater treatment plants might require a small area where the drains are dammed in 2 parallel containers. The first container is a mixer area. The mixer area has an outlet at the bottom so that waste can flow into a second container as the UV exposure area. After the waste is exposed to UV light, it can be discharged into the environment. However, this wastewater treatment method was only proposed at studying manganese metal and COD-containing waste. Further observations on other parameters are needed and might be able to complement this research in the future.

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