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Implementation of electrocatalytic reactor as oxidation unit for residual reagent wastewater of testing laboratory

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ABSTRACT

The remaining reagent from the sample analysis process become a significant source of hazardous waste of laboratory tasting activities. Methylene blue, phenol and oil are pollutants common in the residual reagent waste. The electrocatalytic reactor is effective oxidation units for these organic pollutants. The reactor was made for a 50 L capacity with cylindrical metal oxide as the anode. The three anodes which 6 cm in diameter and 50 cm in length were paired stainless cathode with a distance of 2.5 cm. The reactor was also equipped with a stirrer that is connected to the motor so that the mass transfer and oxidizing agents is more effective. The reactor application was carried out by feeding the residual reagent waste into the electrocatalytic unit and giving DC potential 5 Volt. Each COD content for reagent waste of detergent: 2864 mg/L, phenol: 838 mg/L and oil: 708 mg/L. The reactor has reduced COD to 2157 mg/L (detergent), 399 mg/L (phenol) and 506 mg/L (oil) for 120 minutes. The high COD content in residual is caused by solvent (chloroform or hexane) that used at extraction step in determining the process of a sample. This compound is tough to oxidize into CO_2 by OH radical or hypochlorite acid formed at the anode during the electrolysis process.

1. INTRODUCTION

Besides producing a data for analysis the laboratory testing also release waste in form of water, gas and solid. Based on the nature of the waste, there are also those included in the category of hazardous waste (B3), especially waste derived from the remaining of reagent analysis. Some analysis that has the potential to produce residual reagents must be managed in B3. They are detergent, phenol and oil testing (Benatti et al., 2006)

The BBTPPI Semarang testing laboratory is one of the laboratories with high activity. The great number of samples each month causes the volume of the wastewater from the analysis process to be large. The type of analysis includes physical, chemical and biological parameters. Analysis of chemical parameters such as measurement of detergent, phenol and oil contents always produce waste in the form of residual reagents. Based on the characteristic, this wastewater is classified as B3 waste because of its toxicity (Kementerian Lingkungan Hidup, 2014). While, BBTPPI in the waste management of the residual reagents submit to third parties so that it requires a high cost. In addition, the presence of residual waste reagents requires extensive management in accordance with regulations and temporary storage. Based on this, the wastewater treatment of residual reagents is an alternative solution that will have a positive impact on BBTPPI including: (1) reducing the budget for managing B3 waste to third parties, (2) saving temporary

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storage space (TPS) of B3 waste and (3) eliminating the handling of B3 waste such as packaging and distribution from the laboratory to the TPS.

An advanced oxidation process is one of the appropriate methods to treat recalcitrant and toxic wastewater (Ikehata, K., and El-Din, 2010; Ledakowicz et al., 2001; Oller et al., 2011) as a residual reagent analysis. Mechanism of degradation of pollutants is through the oxidizing promotion activities such as O_3 (Azbar et al., 2004), H_2O_2 (Masoumbeigi & Rezaee, 2015), HClO (Mukimin et al., 2016; Mukimin et al., 2012) and OH^o (Brillas et al., 2009; Mousset et al., 2018). This oxidation method has also made in an electrochemical system know as EAOP (Electrochemical advanced oxidation process). Some EAOP applications include: textile wastewater (Kaur & Kushwaha, 2018; Mukimin et al., 2015), olive processing, pharmaceutical, hospital (Ganzenko et al., 2014) and batik proccessing (Aris Mukimin et al., 2017).

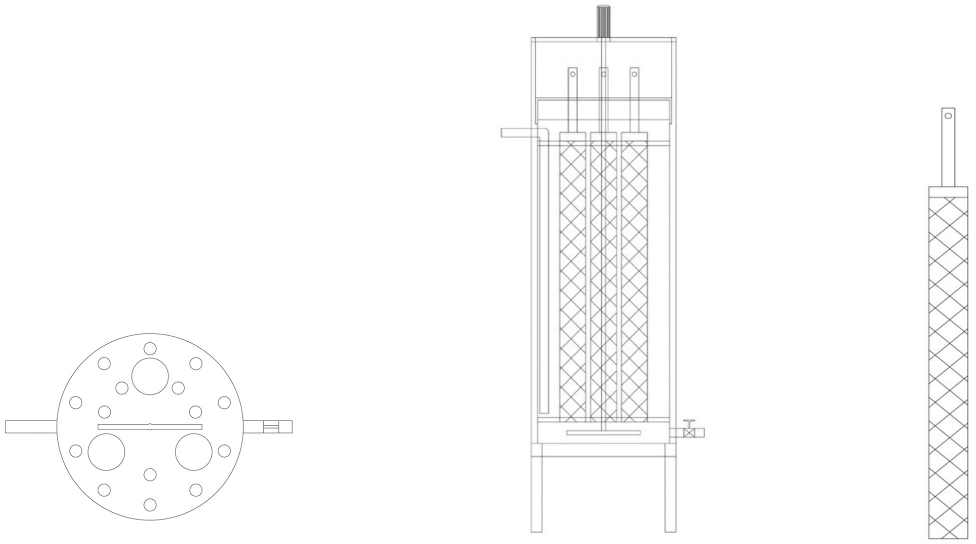
The ability of EAOP method is determined by the type of anode used. Ti/RuO_2 is a potential electrode material that is applied because it is mechanically stable, effectively producing strong oxidizing agents (Cl_2, ClOH, ClO^-), high overpotential oxygen ≈ 2 V (Kaur et al., 2017). The Ti/RuO_2 surface anode also takes H_2O adsorption to be oxidized produce OH^o which also function as a strongest oxidizer against (Kaur & Kushwaha, 2018). The stability of these metal oxide will be further enlarged by doping iridium (A Mukimin & Purwanto, 2018).

The advantages of this technology include: powerful oxidation process, easy operation, can be automated, no producing sludge and electrodegradation process such as on-off switches and can made portable. The propose of this article is to investigate the ability of EAOP reactors to treat hazardous wastewater, especially residual reagent analyzing detergents, oils, and phenols. Electrocatalytic tube reactor is arranged using $Ti/RuIrO_2$ cylindrical anodes and applied to laboratory wastewater from the residual reagent with a batch system.

2. METHODS

2.1. Material and equipment

Electrocatalytic reactor is made from $Ti/RuIrO_2$ metal oxide anodes (ø 6 cm, ℓ 50 cm) and stainless cathodes (ø 2 cm, ℓ 50 cm). The electrode pair is arranged so that have a distance of 2 cm and placed in the PVC tube reactor. The reactor configuration as in **Figure 1**.



(a) (b) (c)

Figure 1. Design of electrocatalytic reactor include: electrode frame (a), main reactor unit (b) and anode (c)

The reactor is also equipped with a supporting unit such as feeding tanks, pumps, pipes, supports, mechanical mixer and DC power supply.

The reactor performance test uses wastewater from the residual reagent of detergent, phenol and oil analysis obtained from the BBTPPI testing laboratory. Determining of COD content using pro analytical chemicals made by Meck without treatment. Testing of the surface image anode and the contents using SEM-EDX from the PHENOM PRO-X DESKTOP type. Measurement of peak absorpt reduction before and after the process is determined by UV-VIS spectrophotometer (SHIMADZU A11454907330).

2.2. Procedure

The reactor application was carried out for residual reagent wastewater from detergents, phenol and oil analysis. The stages of this process were as follows: a 50 L residual reagent of detergent analysis was added with salt to obtain a concentration 2000 mg/L. Feed the wastewater into the reactor using an installed pump, as soon as the reactor was fully charged, the power supply was turned on and the potential is set at 5 V. Turn on the mixer by pressing the switch button on. The reactor performance was is determined by taking samples after 15, 30, 45, 60, 75, 90, 105, and 120 minutes. The COD content was measured using the reflux method with stages according to in APHA-AWWA. The change in absorbance of the sample was measured by UV-Vis scan at a wavelength of 700 – 200 nm. The same procedure was applied to the residual reagent of phenol and oil analysis.

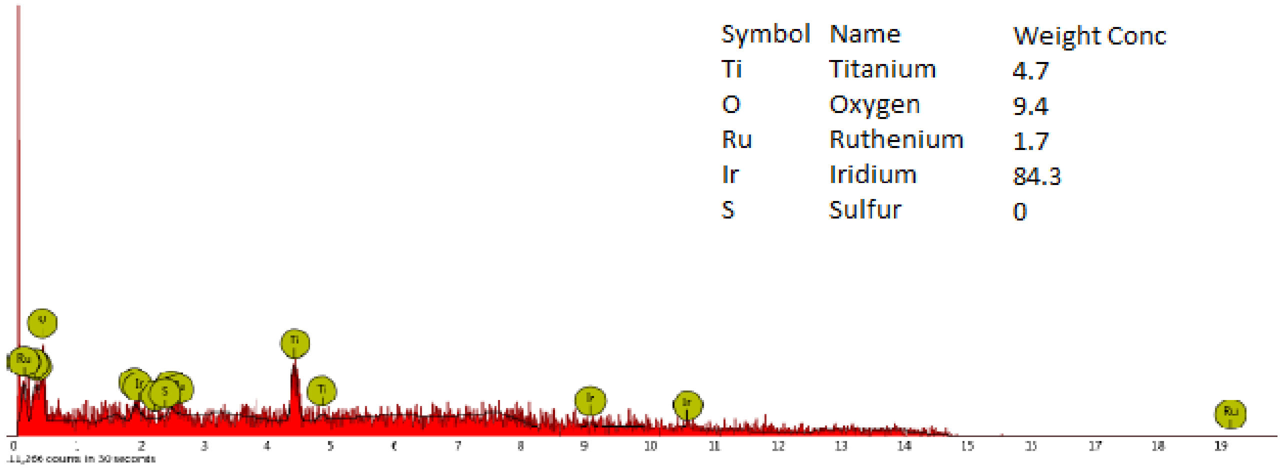
3. RESULT AND DISCUSSION

3.1. Configuration and characterization of electrode

The design of the reactor and the arrangement of electrodes as **Figure 1** have been made and the visuals are as shown in Figure 2.

The anode-cathode pairs have ensured that the two electrodes will not be connected and fix at a distance of 2 cm. The current response which is 5 V indicates that there is no direct connection between the anode and cathode, otherwise, this cell arrangement has produced an electrolyte reaction on the surface of the anode or cathode.

Figure 2. Anode Ti/RuIrO2 pair configuration and stainless cathode installed in an electrocatalytic reactor



Symbol	Name	Weight Conc
Ti	Titanium	4.7
O	Oxygen	9.4
Ru	Ruthenium	1.7
Ir	Iridium	84.3
S	Sulfur	0

Figure 3. EDX spectra of metal oxide material on the surface of the anode

Electrolyte reaction can be indicated by two things, the formation of fine bubbles and the current response that is not too high. On the surface anode, bubbles are formed for a given potential between 4-5 V. The quantity of bubbles increases if the voltage is raised. This fact indicates that there has been an oxidation of water on the $RuIrO_2$ surface with the help of electrical. Bard & Faulkner (2001) and Mukimin et al (2018) have stated the equation of the reaction that is :

$$M + H_2O \rightarrow M(OH^{o}) + H^{+} + e \tag{1}$$

$$M(OH^{o}) \rightarrow M + \tfrac{1}{2}\, O_2 + H^{+} + e \tag{2}$$

The continuity of this reaction can also be proven from the non-extreme current response. The display of power supply shows a normal range value ie 9 A for three pairs of electrodes with an anode surface area of about 2826 cm^2 or a current density value of 3 mA/cm^2.

The oxidation reaction of water identified from the formation of oxygen bubble and also the current response represent the performance of the anode material. $RuIrO_2$ metal oxide has great electroactive properties as stated by several previous studies using this material (Aris Mukimin et al., 2018). The reactivity of this material is determined by the content of ruthenium which composited on the metal oxide material (Kaur et al., 2017; Mukimin & Purwanto, 2018). Characterization of the anode is installed in an electrocatalytic reactor as in **Figure 3**.

EDX analysis has shown Ru content in anode material in addition to other elements such as oxygen and iridium. The titanium is also measured in this material is made possible by the surface morphology of the anode which is not all closed. Surface image using SEM as **Figure 4** has strengthened the detection of Ti.

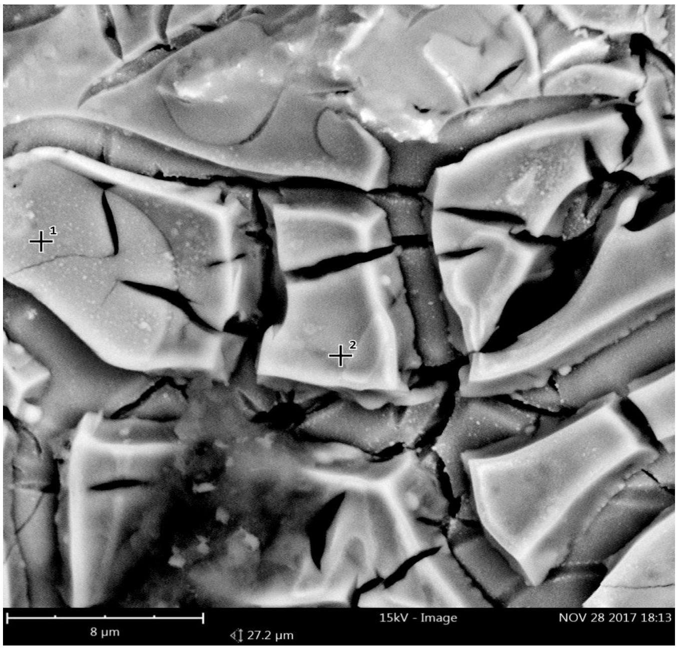


Figure 4. Surface morphology of electrode on magnification 10000x

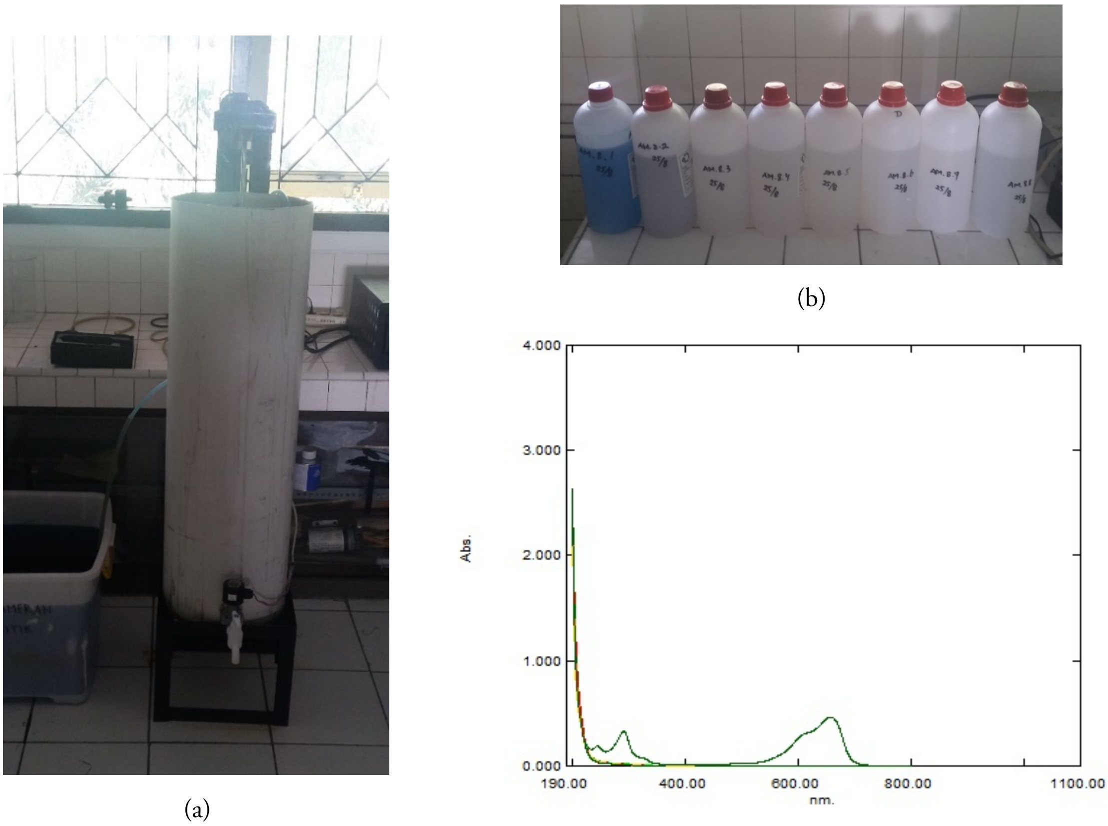
Metal oxide deposited on the titanium plate as buffer or substrate form an uneven layer. These metal oxide composites tend to accumulate in small areas at the size ranging from 4-6 µm with 4 µm long thickly striped slits. The gap formed causes the substrate constituent element to be measured in EDX analysis.

3.2. Performance of reactor in removal pollutant from residual reagent of detergent analysis

Electrocatalytic reactor using an anode as shown in **Figure 2** have been applied to treat a residual reagent wastewater of detergent analysis. Visualization of the processing results as shown in **Figure 5**.

The residual reagent waste of detergent analysis is visually blue, which is caused by the use of methylene blue as a quantitative indicator of surfactant content. The electrochemical degradation of this pollutant is very strongly recognized by a change in the color of the wastewater between before and after the process. Special pollutant from methylene blue has been rapidly degraded because the blue color that appears immediately drops only in during the process of 15 minutes as **Figure 5**b. This decrease caused by the chromophore structure which is easily oxidized by agents which are generated during electrolysis process such as HClO and OH radical (Katheresan et al., 2018; Kaur, et al., 2017; Aris Mukimin et al., 2018). The degradation pollutant also takes place in the basic structure, namely three aromatic rings formed based on the decrease in UV absorption at a wavelength of 300 nm as shown in **Figure 5**c. (Mousset et al., 2016) states that OH radical are strong oxidizing agents which will quickly break the double bond C=C with high reaction constant (108-1010 M-1 s-1)

The degradation process of pollutant in the residual reagent of detergent analysis is strengthened by the measurement of COD content. **Figure 6** shows a decrease in COD during electrolysis ie from 2864 mg/L to 2157 mg/L for a 120-minute process.



(a)

(b)

(c)

Figure 5. Electrocatalytic reactor to treat a residual reagent wastewater of detergent analysis (a), visual of sample is treated (b) and their UV-VIS spectra (c)

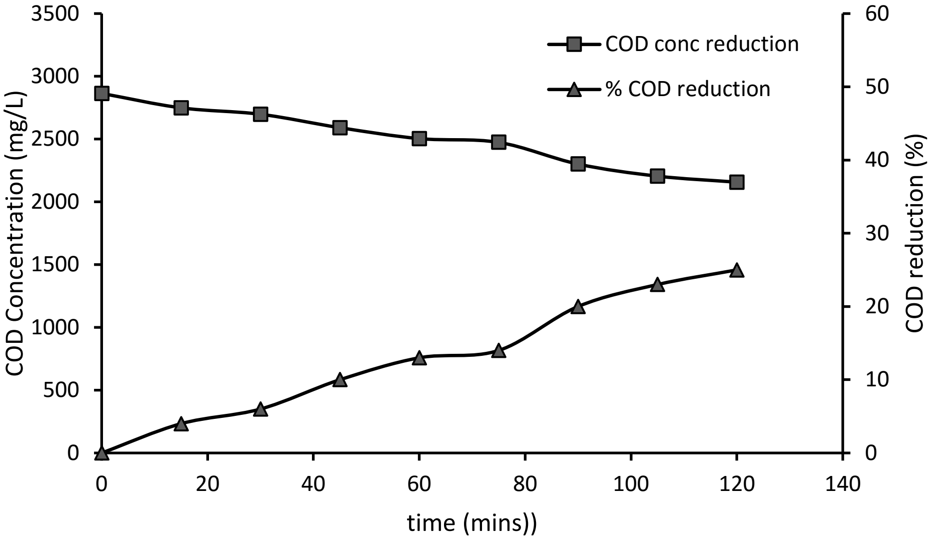


Figure 6. Trend COD reduction during the electrocatalytic process for a residual reagent of detergent analysis at potential 5 V and salt 2000 mg/L

The electrocatalytic reactor has reduced COD ie 707 mg/L in the 2 h duration. This mechanism of degradation through both indirect oxidation and direct at surface anode material. The anode pole which is given a high DC potential will cause the orbital energy level to drop so that the electrons from the pollutant compound will be able to move to the orbital. This direct degradation has also been raised by (Rajeshwar, K. and Ibanez, 1997).

The degradation efficiency of the electrocatalytic reactor in percentage is still low, only about 25% as can be seen from Figure 7. This low value is caused by two things, namely high initial COD concentration (2864 mg/L) and the dominant types of pollutants come from solvents. Electrodegradation process take place on the surface anode, especially by direct mechanism. This phenomenon will limit the amount of pollutant that can be in contact with surface anode. This limitation causes a slowing degradation process. High COD content which is 3000 mg/L requires a long time of degradation with the day order as much biological treatment. The long duration process is not suitable for electrocatalytic technology specification because the cost operating will be high due to electricity consumption. The degradation efficiency is also strongly influenced by the type of pollutant, where the compound that is difficult to be degraded such as solvent will cause processing to not take place.

The residual reagent of detergent analysis has a chloroform which is obtained at extraction stape. This compound is difficult to be degraded because it has a stable structure ($CHCl_3$). (Rossberg et al., 2006) mentions that chloroform will be oxidized by chlorine to form carbon tetrachloride (CCl_4) and chloride acid (HCl). Meanwhile, the electrolysis process in the reactor has produced HClO which can balance with chlorine (Cl_2). This reaction has negative effects on the performance of pollutant degradation, especially solvents which can not be reduced to CO_2 but instead the formation of a new organic compound (CCl_4).

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl \qquad (3)$$

This phenomenon is the main source of high COD content in processed wastewater (2157 mg/L). The presence of chloroform compound in the wastewater is also confirmed from the distillation when it is evaporated. At a temperature of 62 °c this wastewater evaporates to form a distillate up to 10%.

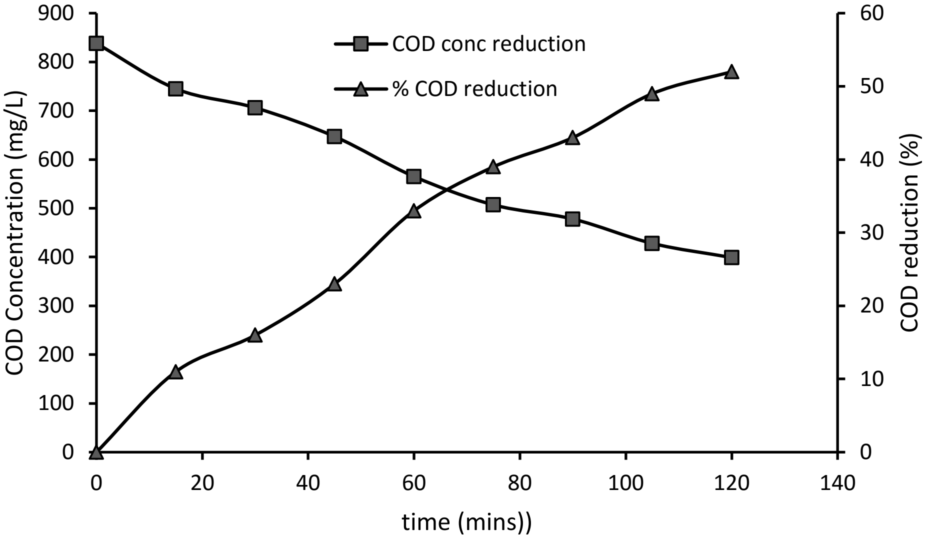


Figure 7.Trend COD reduction during the electrocatalytic process for a phenol analysis reagent waste at potential 5 V and salt 2000 mg/L

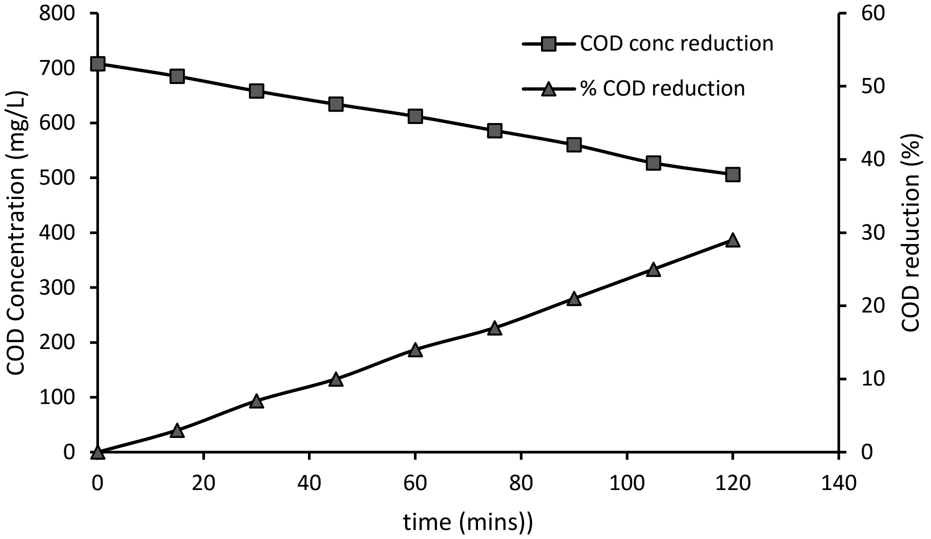


Figure 8. Trend COD reduction during electrocatalytic process for an oil analysis reagent waste at potential 5 V and salt 2000 mg/L

3.3. Performance of reactor in removal pollutant from the residual reagent of phenol analysis

Residual waste from phenol analysis contains several compounds such as phenol, 4-aminoantipirin, $K_4Fe(CN)_6$, NH_4OH, $PO_4^{3-}$and $CHCl_3$. The wastewater is yellowish color formed from the reaction between amino antipyrine and potassium ferricyanide. Degradation of these pollutants by electrolysis has been carried out based on COD content as shown in **Figure** 7.

The efficiency of COD removal was 52 % or reduction from 838 mg/L to 399 mg/L. The remaining of COD is still high due to the solvent pollutants used in this phenol analysis. As with detergent analysis, the method of determining phenol also uses chloroform as solvent extraction. It was previously explained that chloroform is not able to be oxidized to CO_2 but by chlorine, it will form a carbon tetrachloride solvent. The final COD concentration in treated wastewater from the remaining reagent phenol (399 mg/L) is smaller than the detergent (2157 mg/L) which is affected by the volume of chloroform used when extraction.

Pollutant phenol can be degraded through oxidation reaction from OH radical or HClO which are formed during electrolysis. This indirect degradation mechanism will produce chlorophenol as an intermediate compound before it becomes organic acid (Feng & Li, 2003; Aris Mukimin et al., 2015). The mechanism of the direct degradation of phenol pollutant is also possible as mentioned by Marhiyasu et al (Mathiyarasu et al., 2004). Besides phenol, degradation of organic compounds also takes place for aminoantipirene. The double bond in the aromatic ring of this pollutant can be cut off by strong OH oxidizing agent produced on the surface of the Ru anode (Kaur et al., 2017).

The decreasing of potassium ferricyanide takes place through an oxidation by chlorine which is formed during electrolysis. This reaction will produce potassium ferrocyanide with the equation:

$$K4[Fe(CN)] + Cl2 \rightarrow 2\ K3[Fe(CN)6] + KCl \qquad (4)$$

The formed potassium ferrocyanide will come out of the solution to settle. This is in accordance with the facts of the study, where the resulting sediment in wastewater is processed.

3.4. Performance of reactor in removal pollutant from residual reagent of oil analysis

The residual reagent of oil analysis obtained pollutant comes from the substance in the sample that is not extracted. COD content of this wastewater before being treated with a concentration of 708 mg/L indicates chemical pollutants including an organic compound. The electrolysis process has reduced the COD content to 506 mg/L as shown in **Figure 8**. The mechanism degradation of pollutants takes place indirectly and directly as mentioned in the residual reagent of detergent or phenol analysis.

Low efficiency of COD reduction (29%) indicates that wastewater contains compounds that are difficult to be oxidized. Base on the identification of the sample, the use of n-hexane solvent at the time extraction is the causative sources. The structure of a compound that is like a spine with six linear carbon becomes stable so it is difficult to be degraded. However, Koch and Waaf (1973) mention that carbon-hydrogen bonds have the opportunity to reach with some radicals. The slow trend of COD reduction as Figure 9 indicates the n-hexane oxidation process by OH radicals formed in the reactor.

4. CONCLUSION

The electrocatalytic reactor has been able to reduce pollutants found in the residual reagent of detergent, phenol and oil analysis. The performance of COD removal for each wastewater was 25% (2846 mg/L to 2157 mg/L), 52% (838 mg/L to 399 mg/L) and 29% (708 mg/L to 506 mg/L) for 120 minutes processing. The relatively large COD content was caused by solvent chloroform in the detergent and phenol analysis and n-hexane in the oil. This reason is base on analysis procedure used and evaporation result of the waste sample. The stable structure of the solvents makes it difficult to be degraded either by oxidizing agent formed during electrolysis or the direct transfer of electrons to the anode.

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