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THE EFFECT OF USING BIOREMOVAL METHOD *RHIZOPUS Sp* PELLET IN Cr AND COD LEVEL OF BATIK WASTEWATER

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Abstract

This study aimed for treating wastewater batik using *Rhizopussp* pellet and determine the effect of *Rhizopussp*pellet in Cr content and COD. This experimentswere done with a combination of pellet concentration (%w/v) in the wastewaterbatik, whichwere0:10 (% w/v), 5:10 (%w/v), 10:10 (%w/v), 15:10 (%w/v), and 20:10 (%w/v) within a retention time of seven days. Each treatment usedthree replications. The resultsshowed that there wereadecrease in each variation of pellet addition. Obtained optimum decrease in treatment 0:10 (%w/v) and 10:10 (%w/v) with Cr content value are -0.0419 mg/l. COD decreased optimum at 0:10 treatment (%w/v) reached 80.07% with a value is 386.76 mg/l.

Keywords: *bioremoval, COD, Cr content*

INTRODUCTION

A waste if classified as hazardous toxic materials that nature and concentration, either directly or indirectly, damages or pollutes theenvironment or endangers human health. It can be categorized based on the trait that are flammable, explosive, corrosive, oxidizing waste, infectious waste, and toxic waste.One of the hazardous toxic materials is waste of batik industry. The waste generated in the production process which includes waxing, removing starch, bleaching, heating, mercerization, dying, printing and improvingprocess. The wastecontainsheavy metal contaminants belonging to the toxic and hazardous waste, one of which is Cr. The impact of Cr on health, according to Sigit Eddie Wijanto (undated: 8), on the skin causessevere dermatitis and skin ulcers, kidney can lead to renal tubular necrosis, the liver can lead to liver necrosis. Maximum levels of Cr in Central Java Provincial Regulation No. 10 of 2004 on wastewater quality standards and batik textile industry was 1.0 mg/l.

Viera and Volesky (2000)stated basically heavy metals from industrial waste can be separated by means of physics, chemistry, and biology. Heavy metals can notbe converted or degraded so that the separation is biologically an accumulation of heavy metals in the organisms used in the processing. Separationmethod of heavy metals widely used all this time is chemistry method with the addition of certain chemicals to precipitate the formation of a precipitate at high pH as hydroxe. Physics processing is commonly performed using activated carbon adsorption or absorption by using membrane. The use of chemical means and ways to treat industrial wastewater physics require high operational costs. Biosorption can be a part of the solution. Some types of biosorbents, such as seaweeds, molds, yeasts, bacteria or crab shells, are examples of biomass tested for metal biosorption with very encouraging results. According toSuhendrayatna (2001), one of the alternatives that is cheaper and safer for the environmentfor the separation of heavy metals from industrial waste is the use of microorganisms as absorbing heavy metals. Fungal biosorption depends on parameters such as pH, metal ion and biomass concentration, physical and chemical pretreatment of biomass, and presence of various legends in solution (Bisnoi and Garima 2005). Wignyanto (2005) applied bioremoval methods through the use of pellet *Rhizopus stolonifer* waste water textile which is expected to be acheap and easy alternative solution to reduce heavy metal.

Wastewater discharged from various industries such as food processing industry contains hazardous and toxic chemicals, contributes to high levels of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Suspended Solids(Somasiri *et al.* 2008). This study aimed for treating wastewater batik using *Rhizopussp* pellet and determine the effect of *Rhizopussp*pellet in Cr content and COD.

MATERIALS AND METHODS

Waste water used comes from batik home industry in the region Sukoharjo, Central Java. Total of 5 pieces bucket were filled with 10 liters of wastewater batik.

Rhizopus sp Pellet Manufacturing

Inoculation of *Rhizopussp*wasgrown in a liquid medium Peptone Glucose Yeast (PGY) with the composition of glucose (20g/l), yeast extract (5g/l), and peptone (10g/l)whichwere shaken at 150 rpm at 30 °C for 18 hours at room temperature(Suryanti *et al.* 2005). Materials used for the manufacture of pellets weretapioca flour waste with starch as an adhesive (Wignyanto *et al.* 2006). All the ingredients were mixed until homogeneous. Pellet wet chopped dried until its water content 10-20 %.

The experimental design used was a completely randomized design (CRD). This experimentswere done with a combination of pellet

concentration (%/v) in the batik wastewater, which is 0:10 (%w/v) as control group, 5:10 (%w/v), 10:10 (%w/v), 15:10 (%w/v), and 20:10 (%w/v) with a retention time of seven days. Each treatment uses three replications.

Total Chrom testing

The sample will be preserved when the sample can not be analyzed immediately, then the sample ispreserved or storedwith the addition of black to pH less than 2 with a maximum shelf life of 6 months. The working principle of the total chrom testing is in accordance with ISO 06-6989.17: 2004, which aims addition of nitric acid to dissolve metal and eliminate confounding substances contained in the test sample in water and wastewater with the help of electric heaters, then measured by AAS using acetylene gas, C_2H_2.

COD testing

The working principle of COD testingis in accordance with ISO 6989.73: 2009, the organic and inorganic compounds, especially organic in the sample are oxidized by $Cr_2O_7^{2-}$ in closed reflux for 2 hours toproduce Cr^{3+}. Excess potassium dichromate that has not been reduced, will be titrated with Ferro Ammonium Sulfate (FAS) solution using ferroin indicator.Amount of requi redoxi and pressed in equivalent oxygen (O_2 mg /l).

Excess potassium dichromate is not reduced, titrated with a solution of Ammonium Sulfate Ferro (FAS) using indicator ferroin.

RESULTS AND DISCUSSION

*Rhizopus sp*PelletManufacturing

Rhizopus sp wasinoculated in PGY (Peptone Glucose Yeast) media. Itwasusedtoprovide nutrientsformold growth such as nitrogen source (peptone, yeast extract) and carbon sources(glucose, olive oil, and soybean oil) (Ulker *et al.* 2011).

Based on the characteristics of the waste tapioca flour as a wrapper that easily degraded by the environment, the availability of materials are quite abundant, easy handling, speed growth of moldand capableto adjust the height and shape practically feasible to make pellets. Because of those characteristics, waste tapioca flour can be applied as the cheapest alternative solution to reduce heavy metals Cr with adjustable the function of physiology, anatomy and the ability to mold biosorption of heavy metal ions. Pellets were retented in wastewater batik for seven days. Based onWignyanto *et al.* (2006), optimal retention time to reduce heavy metals Cu using *Rhizopus stolonifer* pellet was seven days.Retention time associated with the absorption of wastewater on pellet.

Cr content

Table 1 Cr content and average

Treatment	Replication			Total	Average
	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
Pre treatment	-	-	-	-	0.0048
0:10 (%b/v)	-0.0356	-0.0356	-0.0544	-0.1256	-0.0419
5:10 (%b/v)	-0.0356	-0.0356	-0.0356	-0.1068	-0.0356
10:10 (%b/v)	-0.0356	-0.0544	-0.0356	-0.1256	-0.0419
15:10 (%b/v)	-0.0356	-0.0356	-0.0356	-0.1068	-0.0356
20:10(%b/v)	-0.0356	-0.0356	-0.0356	-0.1068	-0.0356
Total				-0.5716	-0.1906

According to Suhendrayatna (2001), the method bioremoval is accumulated and concentrated pollutants (pollutant) from a liquid by biological material, then through the recovery process this material may be disposed off and friendly to the environment. All metal ions before gaining access to the plasma membrane and cell cytoplasm come across the cell wall. The cell wall consists of a variety of polysaccharides and proteins and hence offers a number of active sites that is capable forbinding metal ions. the potential binding metal groups in this class of microbes are carboxylate, amine, imidazole, phosphate, sulfhydryl, sulfate and hydroxyl.The amino and carboxyl groups, and nitrogen and oxygen of the peptide bonds are also available for coordination bonding with metal ions such as lead (II), copper (II) or chromium (IV). The common filamentous fungi can sorb heavy metal like Cr from aqueos solutions to varying extens (Bishnoi and Garima 2005)

Based on Table 1, Cr content from SSA results (Atomic Absorption Spectro photometer) before bioremoval process amounted to 0.0048 mg/l. After retented with *Rhizopussp* pellets for seven days, each variation of pellet additiontends to decrease. Cr content from SSA results after bioremoval process reaches a negative value or virtually undetectable. Obtained optimum decreases in treatment 0:10 (%w/v) and 10:10 (%w/v) with Cr content value of -0.0419 mg/l.

The decrease of Cr content is caused by, firstly *Rhizopus sp* has saturated by chromium ions due to a longer time of retention, and then binding sites begins slowly releasing back chromium ion. Secondly, owing to a realtively smaller size of biomass cell ofpellet *Rhizopussp,* it causes the surface of the touchpad becomes more widespread. Therefore, metal ions has an effective interaction to active centers on the surface of the cell wall of the biomass becoming more greater. Based onWignyanto*et al.* (2006), long retention time will affect the activity of microorganisms in the fermentation process and allow *Rhizopus sp* to break down the cyanideacid (HCN) that contained in the pellet. The longer retention time, higher the rate of reductionof heavy metals.

According to Saefudin, E. Fitriana, and Kusnadi (undate: 9-10), caused most of the saturated state of the active center of the cell wall has been saturated by chrome metal, so that the contact time/long retention will increase the absorption of chromium metal increased. Reion release due to the bonding between chitin and ion chrome unstable or due to competition with other ions. Retention time affect the absorption of chromium ions from the aspects saturated. When saturation has occurred, additional contact time would be meaningless.

Possibility of optimal retention time *Rhizopussp*to reduce Cr contentin this research was less than seven days. According to Junior *et al.* (2003), cadmium ions can be absorbed by the biomass of *Aspergillusniger* maximum occurs at the contact time of 5 minutes. According to Puranik and Paknikar (2003) more than 90 % zinc and nickel were absorbed by *Rhizopus arrhizus* in a time of 20 minutes. Possibility on the seventh day of microorganisms can not do any more activities for oxygen tha thas been used up. When it does not get the oxygen and active living activities, then the microorganisms will try to survive by producing thickcells. Pellet retended in the long term will have notoxicity of hazardous materials with sufficient oxygen supply. If until beyond the body's defense capabilities, mold will likely die (Suhendrayatna 2001).

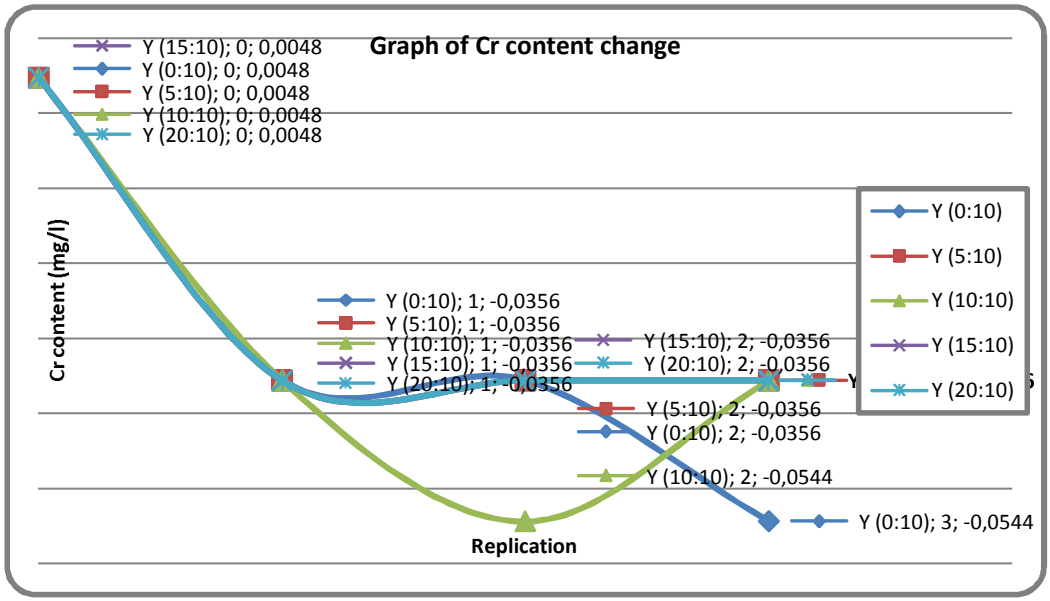

Figure 1. Graph of Cr content change

COD

Table 2. COD, average, and percentagereduction (%)

Treatment	Replication			Total (mg/l)	Average (mg/l)	COD Reduction (%)
	(mg/l)	(mg/l)	(mg/l)			
Pre treatment	-	-	-	-	1,941	-
0:10 (%b/v)	500.1	380.1	280.1	1,160.3	386.76	80.07
5:10 (%b/v)	540.1	480.1	820.1	1,840.3	613.43	68.39
10:10 (%b/v)	680.1	520.1	700.1	1,900.3	633.43	67.36
15:10 (%b/v)	780.1	720.1	740.1	2,240.3	746.76	61.53
20:10(%b/v)	860.1	980.1	780.1	2,620.3	873.43	55.00
Total				9,761.5	3,253.81	

Addition pellet *Rhizopus sp* proven to lower values in the effluent COD different variations on each additional pellets. Result of the adsorption of organic substances by pellets, organic compounds in wastewater batik will be reduced so much oxygen which is needed to oxidize organic substances tobecome fewer. Decrease in COD value indicates that the contaminant load alsodecreases.

Based on Table 2, it can be seen that the effluent COD batik before being subjected to the *Rhizopus sp* pellets has a greatervalue than effluent treatment by *Rhizopus sp* pellets, that is equal to 1.941 mg/l. This is because the content of organic matter in the wastewater is high.The more oxygen required to degrade the organic substances, the more increaseCOD value of the waste. Obtained optimum decreases in treatment 0:10 (%w/v) with a COD reduction reached 80.07 % with a value of 386.76 mg COD/l. This is because the organic matter in the waste is too limitedso that the oxygen required to oxidize organic substances become fewer.On thatcondition, microorganism activity is very low due to limited oxygen. Otherwise, increasing COD occurred at 20:10 (%w/v) becausethe groupswere retended with the highest number of pellets.

COD in this research are still quite large after treatment. It may be caused by less than optimal environments that support process bioremoval therefore contributes to differences in levels of tolerance *Rhizopus sp*.The physical condition of biomass is the most important factor that determines the success of the process bioremoval. In addition, the characteristics of solid waste also determines tapioca. Carbohydrates in tapioca solid waste are also required in the process of biosorption due to covalent bonds with carbon. Carbohydrates that form as ions to form insoluble salts.

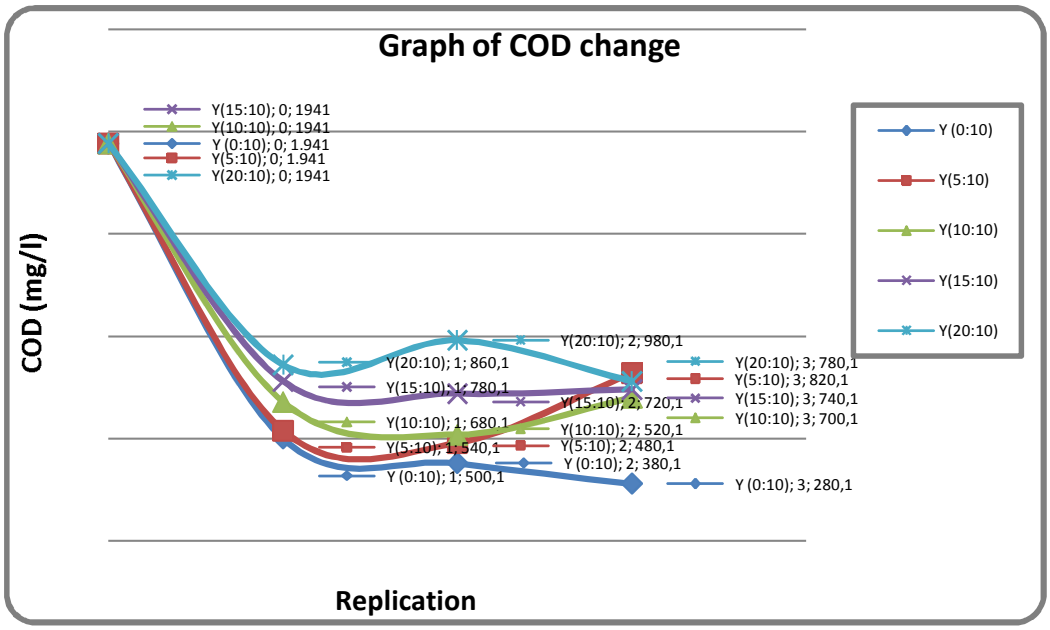

Figure 2. Graphof COD change

Parallel with the research of Musa and Wan Azlima (2010) that conducting research on COD reduction in industrial wastewater using locally isolated bacteria.From this research, the bacterial pellet D, G and I were found to reduce 87%, 77% and 94% respectively of the COD level after exposure to pineapple industry wastewater within 3 days. The wastewater treatment using bacterial pellet showed higher COD reduction as compared to treatment using whole bacterial culture.

CONCLUSION

Decreased levels of Cr in wastewater batik after bioremoval pellet method *Rhizopus sp*. Optimum decline occurred in the treatment 0:10 (%w/v) and 10:10 (% w/v). A decline in the value of COD in wastewater batik after bioremoval pellet method *Rhizopus sp*. Optimum decline occurred in the treatment 0:10 (%w/v).

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