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Editorial Preface

Agro-industry development should be managed and supported by its own agriculture-based industrial society. This sector has been regarded as having significant contribution to country's economic growth such as Indonesia. This sector provides plenty of opportunity for transforming its comparative advantages into competitive ones because of its linkages to both upstream and downstream industries. The abundant availability of raw material constitutes agro-industry's comparative advantages that guarantees sustainability.

Sustainable agro-industry is the development of agro-industry which emphasizes on the application of management, technology, and systems engineering. Such applications can benefit the environment through some breakthrough in green supply chains, life cycle assessments and cleaner production approaches, as well as in other aspects. The development of agro-industry in Indonesia shall be directed to become the backbone of the economy that is capable of creating jobs, hence its presence must be guarded. Issues of climate change impacts on productivity of agricultural raw materials, the application of product quality controls, logistics and distribution, and more defined market segmentation are the challenges to the development of agro-industries in Indonesia.

Trying to enrich the synergy development of agro-industry, the Department of Agro-industrial Technology, Universitas Gadjah Mada, Indonesia is herewith initiating a scientific and practical contribution for the development of agro-industry that is capable of meeting market requirements, both nationally and globally. Supported in fund by Universitas Gadjah Mada and Directorate General of Higher Education of Indonesia, we are proudly to hold the International Conference on Agro-industry (ICoA): *Competitive and Sustainable Agro-industry for Human Welfare*, 24-25 November 2014, Eastparc Hotel, Yogyakarta. This event is well joined by our distinguished colleagues from Ehime University, Japan, Osaka Prefecture University, Japan, Ibaraki University Japan, Kasetsart University, Thailand and Universiti Teknologi Malaysia.

ICoA 2014 had invited scholars, academics and professionals around the world to present, share, and discuss their studies on competitive and sustainable agro-industry from various aspects. Fifty two (52) papers consisting of four (4) review papers and forty eight (48) empirical and practical papers had been selected for publication. Upon the full recommendation from the Association of Agro-industrial Technologist Profession (APTA) and Research and Development of Indonesia Supply Chain (Rispescia), we believe that ICoA 2014 will bring out benefit to the participants in particular and for agro-industry's sake in general.

Finally, we would like to express our sincere gratitude to the editors, guest editors, program chairs, referees and committee members for their valuable contribution upon the publication of this international proceedings.

Yogyakarta, December 20, 2014 General Chair of ICoA

Dr. Adi Djoko Guritno



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The 2014 International Conference on Agro-industry (ICoA) : Competitive and sustainable Agroindustry for Human Welfare

Adsorption Pollution Leather Tanning Industry Wastewater by Chitosan Coated Coconut Shell Active Charcoal

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Abstract

Besides having advantages, Chitosan as biosorbent has also disadvantages. . Chitosan is very soluble in low pH so it cannot adsorb Cr (total) at low pH. It is due to active site (amine group) of chitosan undergo protonation and its adsorption capability is easily influenced by anions in waters. The research studied use of chitosan coating active charcoal of coconut shell to increase adsorption capability of Cr (total), BOD, COD. This research was done to evaluate characteristic of liquid waste quality with IPAL or without IPAL and compare with Regulation of DIY Governor number 7/2010. It studied also effect of pH and Concentration of chitosan coating active charcoal as adsorbent on decrease in Cr (total), BOD, and COD concentration on liquid waste of leather tanning. The results indicate liquid waste of leather tanning industry with IPAL and without IPAL have exceeded quality standard of liquid wast e of leather tanning industry. ANOVA statistical test indicated Cr (total), BOD, COD are significant at 5% (p<0.05), various pH influenced decrease in Cr (total), BOD, COD. The highest removal percentage on effect of chitosan concentration coating active charcoal is obtained in adsorbent C (K3A1), Cr (total) (99.19%); BOD (99.95%); COD (99.825%)

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Keywords:adsorption, chitosan, Cr(total), BOD, COD

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1. Introduction

One of industries having potential to pollute is leather tanning industry. Leather industrial wastewater changes continuously and is different from time to time according to type and amount of raw leather processed, type of finished leather, type and amount of chemical material added and technological level applied. Pollution occurs due to chemical material used in the process that is not absorbed perfectly by processed leather, so wastewater in wet process still contain remnant chemical material in great amount. One of damaging metal is chrome. Chrome in waters environment with certain concentration can cause problem. Cr (VI) in water has high solubility and is toxic, corrosive and carcinogenic that may cause lung cancer when accumulated in human body (Palar, 2008). One of efforts to deal with pollution by leather tanning industry is removal of chrome and organic material from leather tanning industrial wastewater with cheap and natural way by absorption method using natural adsorbent using chitosan and coconut shell active charcoal. According to Griffon et al (2006) chitosan is non-toxic cationic polymer, which is biodegradable and biocompatible. Chitosan is effective pollutant bio-absorbent due to high deacetilization rate and have free amino group, so it is polycationic having capability to bind metal, protein and dye. However, chitosan has also weakness. Use of chitosan as bio-absorbent is soluble in low pH so it cannot absorb Cr (III) at low pH (Onar and Sarisik, 2002). It is due to active site (amine group) of chitosan undergo protonization and its adsorption capability is influenced by anion in waters. In contrary, coconut shell active charcoal or active carbon has wide surface (300-2000 m^2/g) (Suhartana., 2006) and has high absorption rate due to having active site that can absorb organic and inorganic material. According to Rodrigues and Reinoso (1998) active carbon is species with amphoteric characteristic that can have negative or positive content and depend on solution pH to absorb organic and inorganic material. Anionic adsorption will occur in low pH and cationic species will prefer high pH. Due to its usage to absorb heavy metal, it is used as substrate to attach chitosan to absorb heavy metal and organic material from industrial wastewater more effectively.

2. Experimental

2.1 Materials

Chitosan was purchased from Sigma Aldrich Co (USA), Coconut Shell Active Charcoal from Lab Chem-mix Pratama (Indonesia)

2.2. Sample acquisition of leather tanning industrial wastewater

Sample of leather tanning industrial wastewater was taken on discharge flow that is not using wastewater treatment plant and one using wastewater treatment plant. Analysis in laboratory include temperature, pH, BOD, COD, Cr(total), TSS and their comparison to wastewater quality standard according to DIY Governoor Regulation number 7/2010. Wastewater from leather tanning without treatment plant is given with chitosan coating active charcoal to study efficiency in decreasing leather tanning wastewater concentration.

2.3. Making chitosan coated coconut shell active charcoal

Making chitosan coating active charcoal is similar to that done by Nomanbhay and Palanisamy (2005). Fifteen gram active charcoal was entered into 15 ml gel chitosan 1% (1g chitosan in 100 ml oxalate acid 10%) and the mix was shaken with shaker for 24 hours. Ratio of 15 ml gel chitosan 1% and 15 g active charcoal is considered 1:1 that coded with K1A1. The mixture was filtered, washed with distilled water and dried. coating process was repeated three times to obtain thick chitosan on active charcoal. Chitosan-layered active charcoal was separated from solution and soaked in 0.5% NaOH for 3 hours for neutralization and filtered and washed with distilled water to obtain neutral substrate. The active charcoal is dried at 60° C and resulted in constant weight. Similar procedure was done for 15 ml gel chitosan 2%:15 g active charcoal with 2:1 ratio (K2A1) and 15 ml gel chitosan 3%: 15 ml active charcoal with 3:1 ratio (K3A1).

2.4. Test of pH effect and chitosan concentration coated coconut shell active charcoal on Cr(total) absorption, BOD, and COD

The 25 ml sample of leather tanning industry was taken, pipetted and entered into 500 ml Erlenmeyer. Solution pH in each Erlenmeyer was arranged by adding HCl 0.1M and NaOH 0.1 M. pH variation used is 1, 2, 3, 4,5,6 and 7. In each solution, 5 g adsorbent is entered. It is shaken with shaker for 24 hour. Resulted solution is filtered and its filtrate is analyzed with atom absorption Spectrophotometer to identify Cr (total) and to analyze BOD, COD remaining in the solution after interaction with adsorbent.

The removal efficiency (E) of adsorbent on Cr (total), BOD, COD was defined as

$$E(\%) = [(Co - C_1) / C_o] x100$$

where C_o and C₁ are the initial and equilibrium concentration of Cr (total), BOD, COD solution (mg/l), respectively.

3. Results and discussion

3.1. Analysis of leather tanning industry wastewater

Results of analysis of leather tanning industry wastewater with and without wastewater treatment plant for various physical and chemical parameter and comparison with wastewater quality standard in DIY Governor Regulation number 7 of 2010 is presented in Table 1.

Parameters	Unit	Test result without IPAL	Test result with IPAL	Liquid waste quality standard of DIY Province No 7/2010
рН	-	3	7.28	6.0 - 9.0
Suhu	۰C	25.5	30.6	± 3∘C
DHL	μmhos	920.00	550	-
BOD	mg/l	1200.1	128	40
COD	mg/l	3400	1146.08	90
TSS	mg/l	640	105	40
Cr (total)	mg/l	644.850	0.5	0.4

Table 1 Results of analysis of leather tannin liquid waste without and with treatment plant

Based on Table 1 above, following discussion is about physical and chemical parameters:

3.1.1. Temperature

Wastewater temperature measurement is very necessary to observe biological activity, chemical, solvability, oxygen saturation and decomposition. Biological activity and chemical reaction will increase twice each 10° C temperature increase. Oxidation level of organic material is far higher in relatively high temperature than in low temperature. The increase in temperature is accompanied with decrease in dissolved oxygen, so cannot met oxygen requirement for water organism to do metabolism and respiration process (Effendi, 2003). Analysis of wastewater from leather tanning industry without wastewater treatment plant, indicated wastewater temperature of 25.5°C and that with treatment plant is 30.6°C, considered normal for aquatic life with the wastewater with treatment plant is discharged to water body or river. According to wastewater quality standard in DIY Governor Regulation Number 7/2010, the wastewater temperature still according quality standard.

3.1.2. Acidity level (pH)

pH is an important physical parameter in controlling wastewater. Due to many chemical and biological reactions involving microorganism occur in certain pH. Analysis of wastewater from leather tanning industry without wastewater treatment plant, indicated wastewater pH 3 and that with treatment plant is 7.28. When pH of river changes extremely with pH less than 5 as indicated in wastewater without treatment plant directly discharged into water body, there will be change in river water such as disturbed fish life and other water animal, solved damaged mineral or metal, corrosion of iron pipes in water (Fardiaz, 1992). According to Palar (1994) chemical process occurring in water body can cause reduction of Cr (VI) to be Cr (III) when water body in acid condition and for alkali water, Cr (III) ions will be precipitated in water base. According to wastewater quality standard in DIY Governor Regulation Number 7/2010, liquid waste without wastewater treatment plant cannot be discharged directly to water body.

3.1.3. BOD (Biological Oxygen Demand)

BOD does not indicate actual organic material in water used commonly as river pollution indicator that indirectly describes organic material in water (Davis and Masten, 2004). BOD reveal amount of organic content in wastewater. Greater organic material oxidized in wastewater indicates higher BOD. Result of BOD analysis in wastewater without treatment plant and with treatment plant indicate BOD without wastewater treatment plant was 1200.1 mg/l and BOD with wastewater treatment plant was 128 mg/l. related to the wastewater quality standard in DIY Governor Regulation number 7/2010, both values do not meet quality standard, which means the liquid waste with and without wastewater treatment plant do not suit being discharged directly to river, because it will cause pollution in water body.

3.1.4. COD (Chemical Oxygen Demand)

Chemical Oxygen Demand (COD) is amount of oxygen required for discharged organic in water can be oxidized through chemical reaction. COD test only required three hour, while BOD take 5 days. Result of COD analysis in wastewater without treatment plant 3400 mg/l and with wastewater treatment plant are 1146.08 mg/l. compared with wastewater quality standard in DIY Governor Regulation Number 7/2010, the COD value for liquid waste with and without wastewater treatment plant have exceeded threshold and not meet the standard. So it is not appropriate to be discharged directly to water body because it will add pollution in water body.

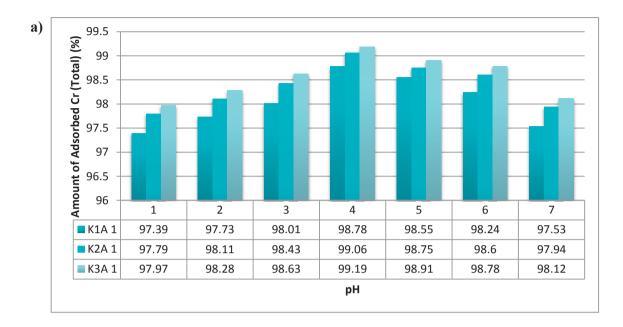
3.1.5. Cr (total)

Chromium (Cr) is heavy metal that is widely used in leather tannin industry. Chrome in wet process still contains remaining chrome in great amount. Result of Cr (total) in liquid waste without and with wastewater treatment plant are 644.8500 mg/l and 0.5 mg/l. the liquid waste with and without treatment plant did not suit wastewater quality standard in DIY Governor Regulation Number 7/2010, so it is not appropriate to discharge directly to water body. The liquid waste should be processed again to reduce Cr (total).

3.2. Test of pH effect and concentration of chitosan coated coconut shell active charcoal on adsorbed Cr (total)

pH variation in Cr (total) adsorption in the solution is factor influencing Cr (total) adsorption by chitosan coated active charcoal. It accords to One-way statistical test. Variable of Cr (total) is significant at 5% (p<0.05), so pH variation affect decrease in Cr (total) of liquid waste from leather tannin industry. Different Cr (total) reduction may be seen in figure 1. Cr (total) adsorption increase in pH 4 through pH 5. It is due to at pH 4 and pH 5, amount of H⁺ ion in the solution decreased so Cr (total) adsorption is easier and there is increase in adsorbed Cr (total). At pH 4, there is increase in Cr (total) adsorption by chitosan coated active charcoal (98.78%, 99.06% and 99.19%) for adsorbent A, adsorbent B, and Adsorbent C, respectively). According to Nomanbhay and Palanisamy research (2005), optimal pH is 4 for Cr (VI) adsorption. At adsorbent A, Cr (total) adsorption is less than adsorbent B and C. it is due to role of coconut shell active charcoal adsorption any material interacting with active charcoal causing heavy metal Cr (total)) pulled by active charcoal and attach on active charcoal surface in combination of complex physical power and chemical reaction. So active group that can bind Cr (total) do not only come from active sites in chitosan but also from coconut shell active charcoal. Result of influence of pH and chitosan

concentration coated active charcoal on adsorbed Cr (total), is presented in figure 1a



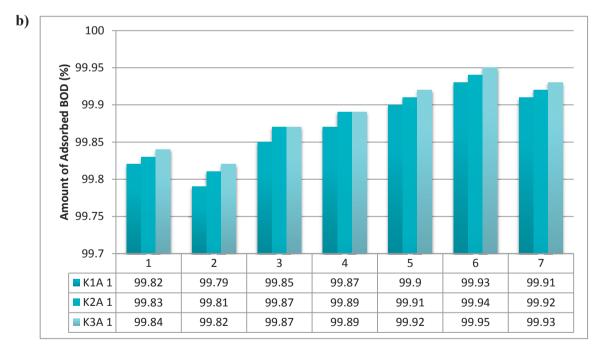


Fig 1.(a) Test of pH effect and concentration active coconut shell charcoal of Cr (total) adsorbed and (b) BOD

3.3. Test of pH effect and concentration of chitosan coated coconut shell active charcoal on adsorbed BOD

pH variety in BOD adsorption in solution is factor influencing BOD adsorption by chitosan coated coconut shell active charcoal. It accords one-way Anova statistical test. BOD variable is significant at 5% (p<0.05) so pH variety affect BOD reduction in liquid waste from leather tannin industry. Result of absorbed BOD analysis is presented in figure 1b. The figure shows that BOD reduction efficiency occur at pH 5 and 6, and at pH 6 its optimal, when absorbed BOD at adsorbent A, B and C are 99.93%, 99.94%, and 99.95%, respectively. According to Marganof (2003) chitosan can be made as coagulant in processing organic and inorganic liquid waste. It is due to coconut shell active charcoal as substrate for attachment of chitosan having high absorption rate and have wide surface (Hadi, 2011). Therefore, BOD adsorption by chitosan coated coconut shell active charcoal is more effective as adsorbent, due to combination of chitosan and coconut shell active charcoal.

3.4. Test of pH effect and concentration of chitosan coated coconut shell active charcoal on adsorbed COD

pH variety in COD adsorption in solution is factor influencing COD adsorption by chitosan coated coconut shell active charcoal. It accords to one-way Anova statistical test. COD variable is significant at 5% (p<0.05) so pH variety affect COD reduction in liquid waste from leather tannin industry. Analytical result in figure 3,the figure shows that at pH 1 there is increase in COD reduction efficiency, where COD absorbed is greater than other pH. It is due to chemical material resistant to biochemical oxidation but not resistant to chemical oxidation. As presented by Fardiaz (1992), COD test in essence resulting in higher oxygen demand than BOD test, due to stable material over biochemical reaction that is oxidized in COD test. At ph 6 and pH 7, there occur increase in reduction efficiency. It is due to at low pH chitosan is not optimal in adsorption organic material due to amine group is protonated to be NH_4^+ so less effective in adsorption organic material in leather tanning liquid waste. Result of COD adsorption analysis on different adsorbent concentration indicated that the different concentration affect efficiency of COD adsorption reduction in adsorbent A, B and C. it may due to adsorbent C contains more chitosan concentration than adsorbent A and adsorbent B that affect COD adsorption, It causes chitosan having amino group and polycationic characteristic can bind remaining protein from leather tannin. According to Marganof (2003), chitosan can be coagulant in handling organic and inorganic liquid waste that influence COD adsorption.

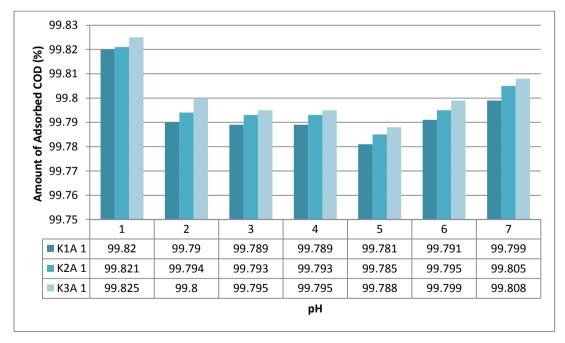


Fig. 2. Test of pH effect and concentration of chitosan coated coconut shell active charcoal on adsorbed COD

4. Conclusions

- 1. Characteristic of liquid waste quality with and without wastewater treatment plant exceed liquid waste quality standard for leather tannin based on DIY governor regulation number 7/2010, so leather tannin industry should improve their wastewater treatment plant to comply with quality standard determined by local government.
- 2. Chitosan coated coconut shell active charcoal is more effective in absorbing heavy metal Cr (total) at pH 4, is more effective in adsorption of BOD at pH 6 and is more effecting adsorption of COD at pH 1.
- 3. Concentration of chitosan coated coconut shell active charcoal at adsorbent C (K3A1) is more effective adsorption of Cr (total), BOD and COD than adsorbent A (K1A1) and adsorbent B (K2A1).

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