Processing of Total Chromium and Organic Compound in Tannery Wastewater Using Eggshell and Zeolite Sand

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Abstract. Tannery industry was generating wastewater from its production activities. This wastewater contains chromium metal ions as a hazardous and toxic compound for human health. In this study, treating of chromium metal ions and organic compounds in the tannery wastewater has been studied. The wastewater processing was used by a combination of precipitation and adsorption methods. Precipitation uses $Ca(OH)_2$ as a natural coagulant that obtained from chicken eggshell after calcined at high temperature. Adsorption process uses zeolite sand that activated with $BaCl_2$. Precipitation performed at pH 11, then followed with adsorption optimized through variation of adsorbent weight and contact time. From the results shows that optimum condition due to the combination of precipitation and adsorption was occurred at pH 11, adsorbent weight 0.5 g and contact time 30 minutes where the methods can reducing total chromium ions and organic compounds up to 99% as elimination level. The content of the wastewater sample after processing reducing total chromium up to 0.043 mg/l, BOD_5 up to 2.56 mg/l, COD up to 4.3504 mg/l and TSS up to 3.00 mg/l. The results explain that the wastewater pollutant referenced the standard quality of tannery industry activities have been fulfilled, so that secure to dispose into the environment.

Keywords: Tannery Wastewater, Chromium Ions, Precipitation, Chicken Eggshell, Natural Zeolite.

1 Introduction

Increased industry development can cause problems because waste produced by the industry can pollute the environment. The leather tanning industry is one of the industries in Indonesia that produces hazardous and toxic substances (B3), i.e, the presence of chromium metal from the tannery industry is toxic. According to Decree of Environment State Minister No. 51/MENLH/10/1995 that concerning wastewater quality standards for industry activities, the maximum limit of total chromium (Cr) allowed to be disposed into the environment is 0.6 mg/l [1].

This study was processing to chromium metal ions from wastewater of leather tanning industry in Sukaregang, Garut. This study was focused on processing the content of

chromium, (Cr^{3+}) and (Cr^{6+}) were mainly found in tannery wastewater [1]. In this study was carried out through a combination process of precipitation and adsorption, so that the processed wastewater is safe to dispose directly into the effluent in the surrounding community.

The batch method is a simple method where it was chosen for this experiment. The batch system is a simple experiment for processing the chromium metal in tannery wastewater using precipitate and adsorbent. While waste sampling carried out through the grab sample method.

Processing of tannery wastewater was carried out through two stages, i.e. precipitation and adsorption. The precipitation of chromium metal ions was carried out by adding strong alkaline into the wastewater sample, thereby changing the physical condition of wastewater from dissolved form to suspended solid [1]. $Ca(OH)_2$ (hydrated CaO) used as an alkaline that prepared by the calcination of chicken eggshell at high temperatures [2]. This $Ca(OH)_2$ has a high alkaline strength where it is environmentally friendly and it can be made from inexpensive sources. The second stage is absorption to process the other pollutants in wastewater where this is done after the precipitation stage. The adsorption process of wastewater uses commercial zeolite sand [3] that activated by $BaCl_2$ to improve its adsorption properties. The adsorption process can use natural zeolite and synthetic zeolite. Almost all types of synthetic zeolite can be used as adsorbents [4]. But the synthetic zeolite is made through methods that are not simple and require pure material [5]–[7]. So that commercial zeolite sand is one of alternative as cheap adsorbents. In addition, measurements of other pollutant were also conducted such as BOD_5, COD, TSS, sulfide and pH.

2 Methodology

Chemicals used in this research are $BaCl_2.2H_2O$ (Merck), H_2SO_4 (Merck), K_2CrO_4 (Merck), commercial zeolite sand from pet shop, chicken eggshell waste and Aqua DM. Wastewater samples were taken at one sampling point from one of leather tanning industries located in Sukaregang Garut.

2.1 Preparation of Eggshell CaO and Activated Zeolite Sand

Chicken eggshell was cleaned, dried, smoothed and sieved that resulted powder with 149 microns size. Then it calcined at a temperature 700 ^oC for 4 hours to get CaO powder. This powder characterized using XRD (X-Ray Diffraction). Zeolite sand was smoothed and sieved become powder with 149 micron size. Then it soaked with a solution of 2 mg/l $BaCl_2.2H_2O$, stirred, let stand for 24 hours. The obtained precipitate is washed with distilled water. The activated zeolite sand was dried and characterized by FTIR (Fourier Transform Infrared).

2.2 Precipitation Process

Each tannery wastewater sample 50 ml was mixed 10% w/v $Ca(OH)_2$ in aqua DM until pH 8, 9, 10, 11 and 12. Then all samples stirred for 30 minutes and let stand for 24 hours thus we determine the optimum pH of precipitation process and then all samples was measured with AAS (Atomic Absorption Spectrometer). Next the filtered supernatant at optimum pH will be used as samples to adsorption process stage.

2.3 Adsorption Process

Resulted wastewater samples of precipitation were added with activated zeolite sand, stirred, and centrifuged then taken the waste water sample. In this adsorption process, variations in weight of adsorbent i.e. 0.5, 1.5 and 2.5 g and variations of contact time i.e. 0.5, 2, 3.5 and 5.5 hours were carried out. Wastewater samples from adsorption at this optimum condition were tested for wastewater quality, i.e. Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Suspended Solid (TSS), sulfide, pH and total chromium ions. AAS (Atomic Absorption Spectrometer) are used to measure the total chromium ions for all samples. Then it compared with the initial wastewater sample that resulted from the same measurement. Calculation of elimination efficiency of pollutant parameter is formulated as E (%) = [(Co-C) / Co] x 100 %, with Co and C are the initial and final (after processing) of concentrations samples, respectively.

3 Results and Discussion

3.1 Precipitation Using Eggshells CaO

Chicken eggshell is a source of $CaCO_3$ which it will decompose become CaO through the calcination process at high temperatures (T > 450 ºC) [8]. CaO is a natural coagulant that it is used to precipitates chromium metal ions in wastewater. Alkaline characteristic of CaO and $Ca(OH)_2$ are more high than $CaCO_3$. Therefore, Eggshell was calcined at temperature 700 ºC intended so $CaCO_3$ can decompose become CaO had better.

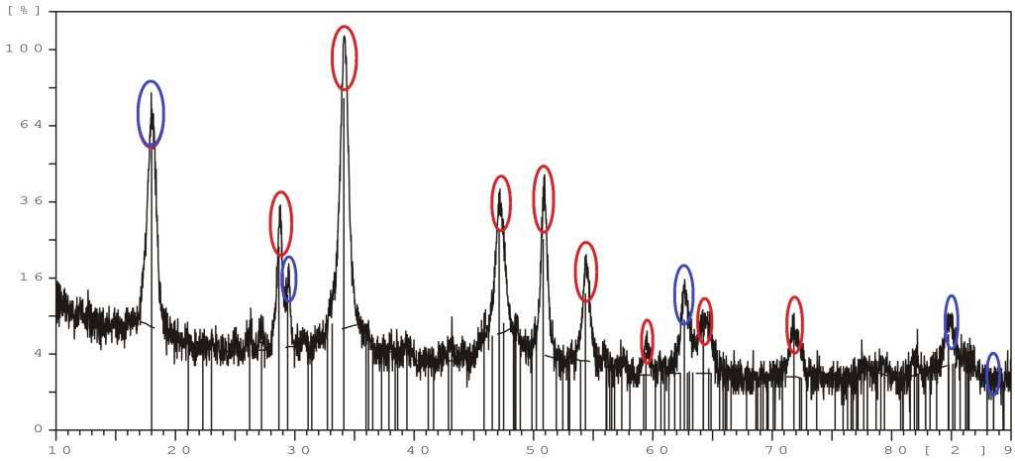

Figure 1. XRD pattern of calcined chicken eggshell at 700°C [red circles ($Ca(OH)_2$, blue circles ($CaCO_3$)].

The results of XRD characterization of calcined chicken egg shells are given in Figure 1, showing the presence of $Ca(OH)_2$ at 2Θ = 28.6º; 34.1º, 47.1º, 50.8º, 54.3º, 59.4º, 64.3º, 71.8º. $CaCO_3$ was found at 2Θ = 18º, 29.4º, 62.5º, 85º, 88.5º [8].

Pollutants in wastewater can precipitated at alkaline conditions, i.e. increasing the initial pH of wastewater from acidic (pH 4.6) to alkaline (pH = 8, 9, 10, 11, and 12) by adding a $Ca(OH)_2$ suspension was slightly. Chromium metal contained in wastewater is 2,646.5 mg/L after 500 times of dilution process, so the chromium content in tannery wastewater is very large. 2.8 ml of $Ca(OH)_2$ suspension was needed to yield pH 8, 3.95 ml to yield pH 9, 8.25 ml to yield pH 10, 9.75 ml to yield pH 11 and 27 ml to yield pH 12. From AAS measurement was resulted that the highest percent of total chromium ions elimination was obtained at pH 11 that shown at Figure 2. Total chromium ions was eliminated from initial concentration 2,646.5 mg/l to final concentration 0.185 mg/l that correlated to activity of OH ions from coagulant. This precipitation process deposits Cr^{3+} ions become $Cr(OH)_3$ through reaction $2Cr^{3+}_{(aq)} + 3Ca(OH)_{2(aq)} \rightarrow 2Cr(OH)_{3(s)} + 3Ca^{2+}_{(aq)}$. Moreover the stirring can increasing the deposition process.

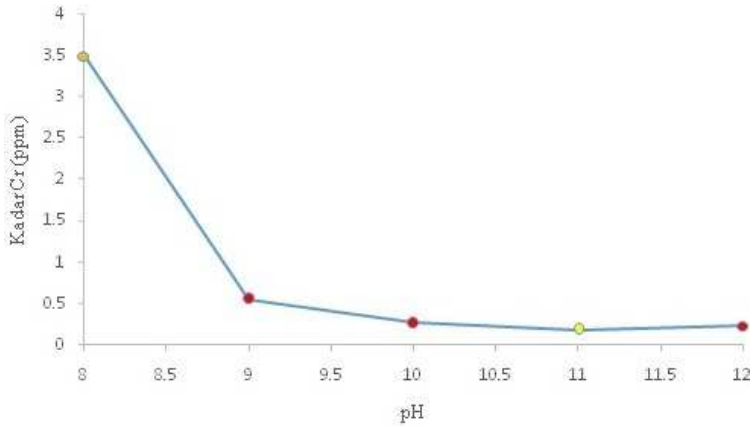

Figure 2. Elimination total chromium ions after the precipitation at various pH.

Beside $Cr(OH)_3$ deposits was formed in wastewater, the precipitation process was change discoloration and odor of wastewater where previously pitch black and bad smell to be clear and odorless. It can be presumed that chromium metal ions, dyes and organic compounds contained in the wastewater almost entirely was settled. Changes of wastewater before and after the precipitation process can be seen in **Figure 3**.

Figure 3. Tannery wastewater from an industry in Sukaregang Garut, after the precipitation (left) and before the precipitation (right).

3.2 Adsorption Using Activated Zeolite Sand

The adsorption process is purposed to optimize the removal of all contaminants in wastewater that has not been lost after the precipitation process. Zeolite sand is a commercial product that easily available. According to improving the adsorption of zeolite sand then it is smoothed as powder of 149 microns size to adding the contact area on surface of the zeolite. After that zeolite powder is immersed in $BaCl_2$ solution to eliminate impurity cations in the zeolite cavity so that the surface of the zeolite becomes active.

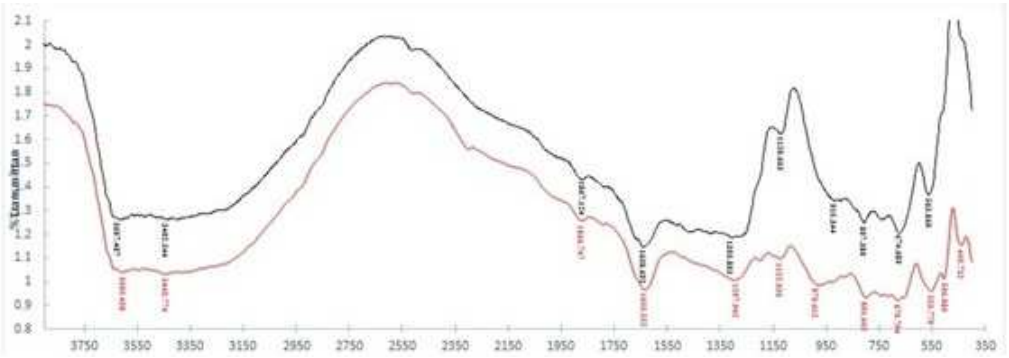

Figure 4. Spectra Infrared of activated zeolite sand (red curve) and zeolite sand (black curve).

The typical absorption of zeolite lies in the wavelength 400-1500 cm^{-1} which characterizes zeolite skeletal structure. In this study, infrared spectra of zeolite sand at Figure 4**.** show absorption at 674.689 cm^{-1} and 679.794 cm^{-1} that characterize the vibrations of Al-O bonds, absorption at 807.380 cm^{-1} and 801.662 cm^{-1} that characterize the vibrations of Si-O-Si bonds, absorption at 915.344 cm^{-1} and 979.612 cm^{-1} that characterize vibrations of Si-O-Al bonds [9], absorption at 1,120.663 cm^{-1} and 1,122.036 cm^{-1} that characterizes the vibrations of Si-O-Al bonds [9], absorption at 1,638.692 cm^{-1} and 1,633.252 cm^{-1} that characterizes vibrations of O-H bonds and absorption at 3,607.407 cm^{-1} and 3,605.458 cm^{-1} that characterize vibrations of O-H bonds [9]. From the infrared spectra, it was predicted that the commercial zeolite sand obtained from pet shop is a natural zeolite but the zeolite type had not been identified. The presence of metal cations in zeolite cavities are characterized as absorption at wavelength smaller than 600 cm^{-1}. This case can predict ion exchange of Ba^{2+} into zeolite cavity is possible been occurred which accordance to presence of vibrations at 569,444 cm^{-1} and strengthening of absorption intensity.

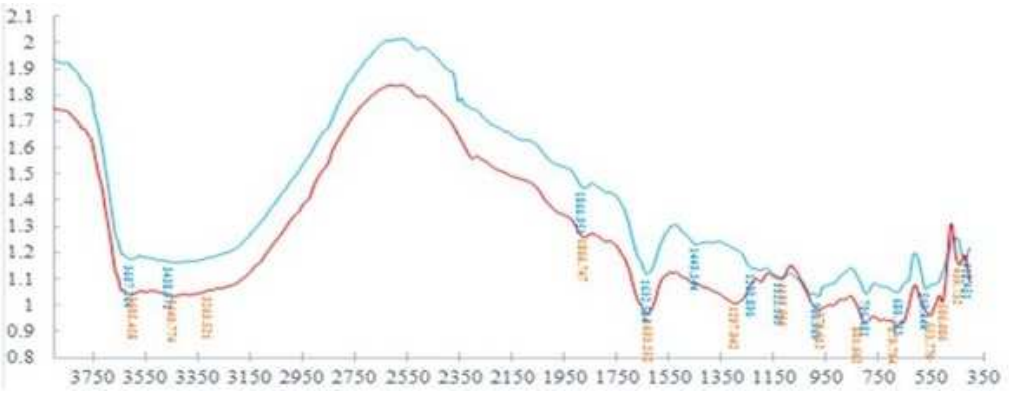

Figure 5. Spectra Infrared of activated zeolite sand before adsorption (blue curve) and after adsorption (red curve).

Figure 5 shows infrared spectra from activated zeolite sand samples after the adsorption process. Some of absorption peaks between total chromium ions and adsorbent appear not too strong because total chromium ions after precipitation process almost entirety has been deposited. The interaction of chromium metal ions with adsorbents occurred at 1600-1700 cm^{-1}.

Table 1. Pollutant content of wastewater before and after processing

No.	Parameter	Max. Concentration* (mg/l)	Concentration** (mg/l)	Concentration*** (mg/l)	Elimination (%)
1.	BOD_5	50	3,920.440	2.56	99.95
2.	COD	110	6,771.062	4.35	99.93
3.	TSS	60	624.000	3.00	99.51
4.	Total Cr	0.6	2,646.500	0.043	99.99
5.	Sulfide (as S)	0.8	0.2050	0.0249	
6.	pH	6.0 - 9.0	4.6	8.6	

*wastewater quality standards from Environment State Minister No. 51/MENLH/10/1995
**initial tannery wastewater content
***final tannery wastewater content after process by precipitation and adsorption

In this study, elimination percent of adsorption was determined to observe the removal of total chromium ions after processed by precipitation with $Ca(OH)_2$. Adsorption test was done by optimize the adsorbent weight i.e. 0.5 g, 1.5 g, and 2.5 g in each 50 ml of wastewater where this adsorption leaving the concentration of 0.098 mg/l, 0.044 mg/l and 0.043 mg/l of total chromium ions, respectively. Whereas by optimize the contact time i.e. 30 minutes, 2 hours, 3.5 hours and 5.5 hours where this adsorption leaving the concentration of 0.048 mg/l, 0.043 mg/l, 0.044 mg/l, and 0.042 mg/l of total chromium ions, respectively. Elimination of total Cr

ions through the adsorption process gives almost the same results towards the variations of adsorbent weight and contact time. So that the optimum adsorption condition along as 30 minutes with an adsorbent weight 0.5 g.

Before processing the initial measurements are taken to determine the level of pollutants in the tannery wastewater. Based on Table 1. it is shown that the parameters that exceed the quality standard are Biological Oxygen Demand (BOD_5) 3,920.44 mg/l, Chemical Oxygen Demand (COD) 6,771.062 mg/l, Total Suspended Solid (TSS) 624 mg/l, total chromium ions 2,646.5 mg/l and pH 4.6. While sulfide that contained in the wastewater does not exceed the quality standard, which is 0.2050 mg/l. BOD_5, COD and TSS are parameters gives the amount of organic compound from the tannery wastewater. While the total chromium ions (Cr) shows heavy metals contained from tannery wastewater as the hazardous and toxic of substances (B3). The measurement results of wastewater sample after treatment showed by reduction of total chromium to yield 0.043 mg/l, BOD_5 to yield 2.56 mg/l, COD to yield 4.3504 mg/l, TSS to yield 3.00 mg/l, sulfide to yield 0.0249 mg/l and pH up to 8.6.

The measurement results in Table 1. show that combination of precipitation and adsorption processes is an effective methods to reduce the pollutant parameters contained in the tannery wastewater. It is shown that all pollutant parameters produce the elimination level up to 99% and according to quality standard for tannery industry activities, so that the wastewater can be disposed directly into the effluent around human settlements.

4 Conclusion

Coagulant from chicken eggshell that calcined at 700°C gives the hydrated CaO that confirmed by XRD analysis, but $CaCO_3$ residues was still present. Activated $BaCl_2$ into zeolite sand that used as adsorbent has been occurred that confirmed by FTIR, which signed by the increase of peaks intensity at typical zeolite absorption area. Pollutant parameters such as total chromium ions, BOD_5, COD, TSS, Sulfide and pH have been decreased which it has been accordance with the quality standards from Decree of Environment State Minister with the efficiency level up to 99%.

Acknowledgment

This publication was supported by Pusat Penelitian dan Penerbitan, Lembaga Penelitian dan Pengabdian Kepada Masyarakat (LP2M) UIN Sunan Gunung Djati Bandung.

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