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Zinc Removal from ZnO Industrial Wastewater by Hydroxide Precipitation and Coagulation Methods: The Role of pH and Coagulant Dose

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ABSTRACT

Liquid waste from the ZnO industry must be treated to meet the quality standards of wastewater into water bodies, according to the Minister of Environment Regulations No.5, 2014. It still contains 79 mg/L of Zn metal, cloudy with turbidity above 500 NTU, and COD value around 222 mg/L. This study aims to determine the effect of pH on reducing Zn metal and the coagulant dose to minimize turbidity and COD in liquid waste produced by the ZnO factory in Depok, West Java. The waste treatment has been carried out by adding alkaline to neutralize the acid conditions in the equalization basin. However, the results have not met the requirements. It is necessary to vary the pH (8.5; 9.0; 9.5; 10.0 and 10.5) to precipitate of Zn optimally, modify the dose of coagulants (50; 100 and 150 mg/L) and reaction times (10; 15 and 20 minutes) to reduce its turbidity and COD concentration. The best results were obtained at a pH of 9.5 with a coagulant dose of 50 mg/L and a reaction time of 10 minutes. This condition can reduce Zn concentration (79 to 3.71 mg/L), turbidity (557 to 1.42 NTU), COD (222 to 68 mg/L) with a removal efficiency of 95.3%; 99.7%; and 69.4% respectively. These values have met the standard requirements according to government regulations.

1. INTRODUCTION

The Industrial wastewater that contains various organic and inorganic pollutants is one source of water pollutions, which at high concentrations can endanger the environment. Inorganic industrial waste such as lead (Pb), zinc (Zn), cadmium (Cd), copper (Cu), chromium (Cr), arsenic (As), nickel (Ni) can be toxic that harmful to human and other lives (Renu et al., 2017a). These metals can damage the liver and nerves. Based on the toxicological point of view, these heavy metals can be divided into two types. The first type is an essential heavy metal in which living organisms need their presence in a certain amount, but in excessive amounts it can cause oxic effects. Examples of these heavy metals are Zn, Cu, Fe, Co, Mn, and others.

At the same time, the second type is non-essential or toxic heavy metals in which its presence in the body is still unknown or can even be toxic such as Hg, Cd, Pb, Cr, and others (Azimi et al., 2017).

Zinc (Zn^{2+}) is a reactive and toxic heavy metal that affects considerably human's body due to its accumulation in the food chain. However, in less quantity, it is essential for human health (Jamshaid et al., 2018). It frequently found in industrials effluent such as battery, mining, metallurgy, electroplating, pigment, paint, smelting, fossil fuel combustion, polymer stabilizers, fertilizer, pesticide, and municipal wastewater treatment plants (Jamshaid et al., 2018; Zhang et al., 2017) According to Environmental Protection Agency (EPA), Zn^{2+} is a dangerous pollutant that causes poisoning cases with symptoms such as dehydration,

stomachache, electrolyte imbalance, skin irritation, vomiting (Renu et al., 2017a), and nausea (Baloch et al., 2019). The reducing of Zn of concentration is very severe or crucial to fulfill the World Health Organization recommendation or Indonesian Minister of Environment Regulation No 5, 2014 that acceptable Zn level is 5.0 mg/L (Zhang et al., 2017). Numerous treatment technologies have been applied to eliminate Zn ions from wastewater include physicochemical methods such as adsorption using activated carbon from agricultural waste (Zhang et al., 2017), biosorption using chemically treated rice husk (Baloch et al., 2019), ion flotation (Hosseinian et al., 2018) membrane filtration, ion exchange, reverse osmosis, chemical coagulation/flocculation (Eggermont et al., 2020), chemical or electrochemical precipitation (John et al., 2016; Zainuddin et al., 2019) and solvent extraction (Jamshaid et al., 2018). The other method is biological methods using various kinds of several microorganisms and microalgae (Jamshaid et al., 2018). Many attempts are also performed to utilize waste materials as adsorbents to reduce the cost of processing heavy metal pollutants. The comparison among wastewater treatment technologies has also been reported by previous researchers (Renu et al., 2017b).

One of the industries that produce zinc oxide (ZnO) treats its zinc-loaded wastewater by making a Waste Water Treatment Plant (WWTP). This waste comes from product analysis in its laboratory that has acid characteristics. Therefore, the waste in the equalization tank is acidic and has only been added alkaline to get the neutral pH. However, the processing results do not meet the quality standards of industrial effluent to the environment because it still has high Zn concentration, turbid with high Chemical Oxygen Demand (COD) as can be seen in the following Table 1. Therefore, it needs improvement in treating the waste.

The commonly used method to treat the zinc removal from wastewater is the precipitation of this heavy metal as hydroxides with the addition of lime, $Ca(OH)_2$ or NaOH (Azimi et al., 2017) in pH variation to get optimum process which is characterized by the most optimum amount of zinc settling (Eggermont et al., 2020; Zainuddin

et al., 2019). This process is an inexpensive and simple method (Azimi et al., 2017; John et al., 2016). A study on zinc removal from the plating industry by chemical precipitation with NaOH was performed by (John et al., 2016), and NaOH and Na_2S were done by Zainuddin et al. (Zainuddin et al., 2019). On the other hand, polyaluminium chloride (PAC) was employed for heavy metal and phosphate removal (Ghorpade et al., 2018;Chen et al., 2019).

Table 1. The characteristic of ZnO industrial wastewater before and after neutralization

	pH	Zn concentration, Ppm	COD, ppm	Turbidity, NTU
Before neutralization	4	79.0	222	557
After neutralization	7	33.2	222	557

In this study, heavy metals removal was performed by the addition of NaOH with pH variation (8.5 - 10.5) to form hydroxide precipitation. Subsequently, the variation of coagulant dose (50 - 150 ppm) was added to the supernatant to reduce the turbidity and COD. The PL-50 coagulant (blends of inorganic and organic coagulants with the composition of Al_2O_3 and cationic polymer) was used. The choice of coagulant dose refers to the previous jar test, and this chemical is relatively cheap. Therefore, the purpose of this study is to determine the effect of pH on Zn removal and Al_2O_3 based coagulant dosage on turbidity and COD reduction from ZnO plant wastewater.

2. METHODS

The ZnO waste sample was taken from the equalization tank of the Waste Water Treatment Plant (WWTP) of the ZnO factory in West Java, Indonesia. The chemicals needed in this study are: $K_2Cr_2O_7$, H_2SO_4, $HgSO_4$ for the making of High Concentrate Digestion Solution, Ag_2SO_4 for reagent solution (Merck), Sulfamic Acid (NH_2SO_3H) (Seidler Chemical), Potassium Hydrogen

Ptalate Solution 425 ppm ($C_8H_5KO_4$) (Merck), Distilled water (electrical transmission <2μS/cm), Coagulant Katfloc PL-50/Al_2O_3-Cationic Polymer (PT Puji Lestari Purnama), Technical NaOH (Asahimas Chemical), Phosphate Buffer Solution (KH_2PO_4, K_2HPO_4, $Na_2HPO_4.7H_2O$, NH_4Cl) (Merck), $CaCl_2$ Solution (PT Mufasa Specialties Indonesia), BOD Seed Solution (Hach InterLab LTD), Standard BOD Solution, Hydrazine Sulfate Solution (($NH_2)_2H_2SO_4$) (Merck), Hexa Methylene Tetramine Solution (($CH_2)_6N_4$) (($NH_2)_2H_2SO_4$) (Merck), 4000 NTU Turbidity Parent Suspension, 40 NTU Turbidity Suspension, Purified Water, Standart Solution of Fe, Pb, Mn, Cu, Co, Cd, Ni, Zn 2000 mg/L, $MgSO_4$ for Magnesium Sulfate Solution (Pudak Scientific), and $FeCl_3$ (Merck).

The equipments used are UV-Vis Spectrophotometer Genesys 10S UV-Vis (Thermo Fisher Scientific USA) with λ from 400 - 700 nm, Digestion Vessel SC150 Environmental Express (Thomas Scientific) with specifications Poly Ethylene 10 - 100 ml, Heating Block SC150 (Environmental Express) with 25 samples, 150 °C, Magnetic Stirrer C-MAG HS-7 (IKA) for 50 - 1500 rpm, Analytical Balance AUY 220 (Shimadzu) for 0.1 mg, Nephelometer/Turbidity Meter ECTN 100 IR (Thermo Scientific) for 0 - 2000 NTU, Atomic Absorption Spectrophotometer A 7099 (GBC Scientific) for λ 185 - 900 nm, pH meter HI 991001 (Hanna) with accuracy ± 0.02, BOD Refrigerated Incubator + RDO/DO Benchtop Meter BOD Kit with Orion Star A213 Model (Thermo Fisher Scientific USA) for Stores over 300 BOD Bottles (300 mL) + AutoStir.

The measurement of heavy metal content is performed by the duplicated method and the measurement results are the average. The removal of zinc metal (Zn) is carried out by precipitation of the sample as hydroxide with the NaOH addition by following a predetermined pH variation, stirring with 80 rpm for 5 minutes and allowed 60 minutes for precipitation to occur. The supernatant of the precipitate results was tested for metals concentration (Zn, Fe, Pb, Mn, Cu, Cd, Co, and Ni) by the AAS.

The supernatant samples were also evaluated for turbidity, COD, and BOD through the addition of coagulant Al_2O_3-based at various loading and reaction times. COD levels were determined using a spectrophotometric closed reflux method according to SNI 6989.2 year 2009 (BSN, 2009). These measurements were carried out by mixing the samples which consist of digestion solution and sulfuric acid, then it heated 150°C and refluxed for 2 hours. After that, the mixed solution was cooled until room temperature and followed by COD measurement. While turbidity was measured with a Nephelometer in accrdance with the SNI 06-6989.25 year 2005 (BSN, 2005).

BOD measurement was carried out by giving seed to a sample that had been diluted, incubated at 20 °C for 5 days. Dissolved Oxygen (DO) was measured before and after the incubation period. BOD was calculated from the difference in the initial DO values (0 days) and after 5 days in accordance with the SNI 6989.72 year 2009 (BSN, 2009). Measurement of the initial conditions is also carried out to determine the process efficiency. All measurements are carried out in duplicate, and the final result is the average.

3. RESULT AND DISCUSSION

The average results of the initial heavy metal concentration of the waste that measured duplicated for 3 days can be depicted in Table 2. From Table 2, it can be stated that the initial Zn concentration is still far above the permitted standard quality. However, for other heavy metals, their concentrations meet the recommended specifications. Figure 1 shows the effect of pH on Zn concentration after the process. All metals, especially Zn, precipitate as hydroxide by the addition of NaOH. The chemical rection mechanism to the formation of the percipitate can be explained as follows:

$$Zn^{2+} + 2\,NaOH \rightarrow Zn(OH)_2 + 2\,Na^+ \qquad (1)$$
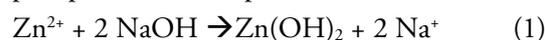
The curve with a minimum point indicates the highest % Zn removal or minimum solubility was achieved, and it occurs at pH 9.5 with the NaOH addition of 5.3 mg for 1 L of wastewater.

Tabel 2. Heavy metal concentration (mg/L) according to standard quality, initial condition and after process at pH variation.

Metal	Zn	Fe	Pb	Mn	Cu	Cd	Co	Ni
St. quality	5	5	0.1	2	2	0.05	0.4	0.2
Initial concentration	79	0.034	0.013	0.140	0.014	0.017	0.033	0.041
pH 8.5	5.701	0.022	0.000	0.031	0.003	0.002	0.002	0
pH 9.0	4.905	0.007	0.000	0.032	0.003	0.002	0.000	0
pH 9.5	3.710	0.009	0.000	0.028	0.003	0.002	0.000	0
pH 10.0	4.530	0.011	0.000	0.031	0.003	0.002	0.000	0
pH 10.5	4.620	0.016	0.000	0.033	0.000	0.002	0.000	0
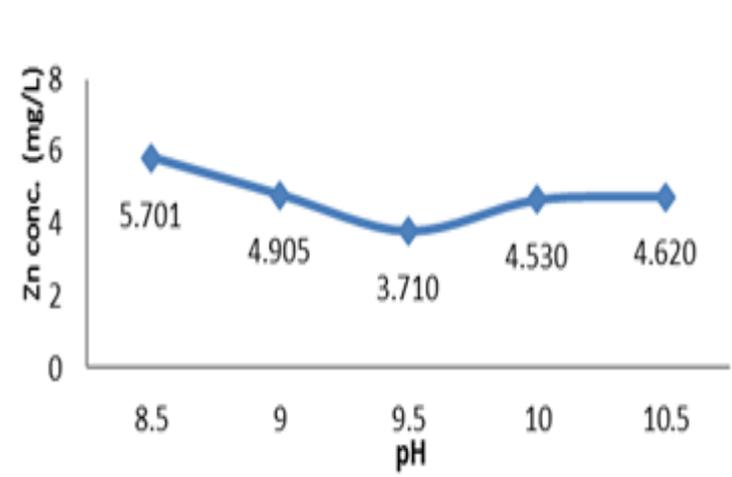
Figure 1. The effect of pH on effluent Zn concentration

Figure 2. The solubility of metals hydroxide at different pH (Zhang et al., 2018)

Figure 1 shows that the best pH for Zn precipitation occurs at pH 9.5 because it generates the lowest effluent Zn concentration of 3.71 mg/L with 95.3% removal. However, the optimum pH is 9.0, with 93.8% removal. At that condition, the effluent of Zn concentration already below 5.0 mg/L (fulfill the acceptable discharge concentration in accordance with the Minister of Environment regulation). Therefore, it utilizes NaOH slightly below compare to at pH 9.5. The results obtained are in accordance with the previous study (Lewis, 2017). Besides, the effluent waste also contains other metals such as Fe, Pb, Mn, Cu, Cd, Co, and Ni. For all metals, the initial conditions of the waste have met the quality standard except Zn. However, after the process at pH ≥ 9.0, all heavy metals comply with the acceptable discharge concentration. When the wastewater containing metal (Zn^{2+}) is added by Na(OH) and followed by mixing, the precipitation of $Zn(OH)_2$ is formed according to reaction presented in the equation (1).

The solubility of metals hydroxide at deferent pH can be seen in Figure 2 in which each type of metal hydroxide is favorable to precipitate at a specific pH range (Zhang et al., 2018). Actually, the temperature differences also affects the solubility of metal hydroxide. According to that figure, the best pH for Zn metal to precipitate take place on the range 9.0 to 9.5. This phenomenon is similar with this study. If the pH condition is not in a suitable range, the metal hydroxide precipitate prefers to resolubilize (Chen et al., 2018).
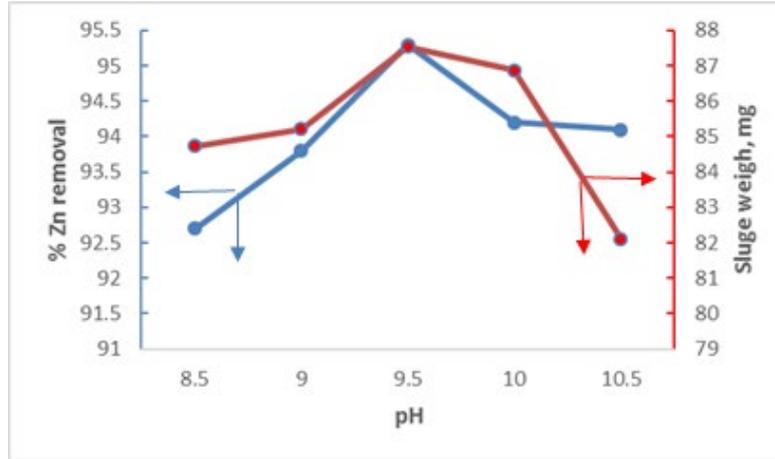
Figure 3. Percentage Zn removal and dry sludge weight at various pH for 1 L wastewater

| a) | b) |
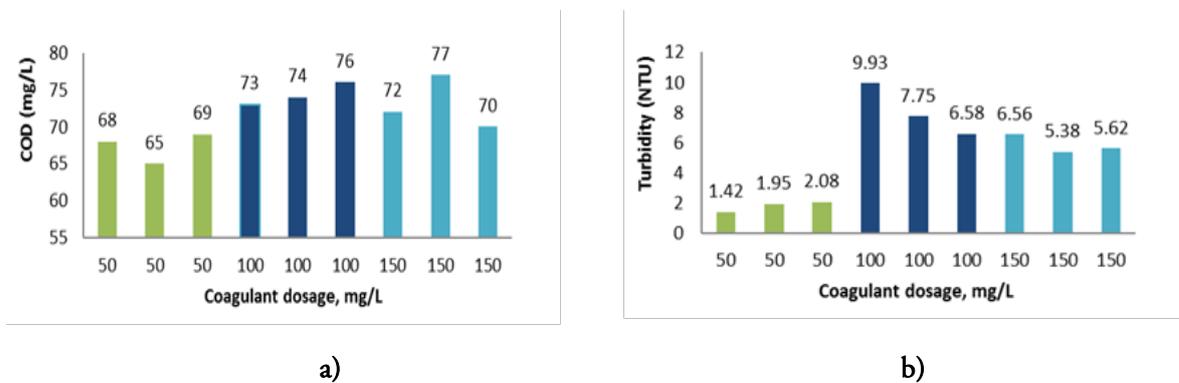
Figure 4. a) COD and b) Turbidity at various coagulant dose and mixing time with 80 rpm (green color for 10 minutes, dark blue for 15 minutes, and light blue for 20 minutes).

Figure 3 shows the % Zn removal and the dry sludge weight obtained at various pH. The maximum point indicates the highest percentage removal efficiency at pH of 9.5 due to the linear correlation between the lowest Zn final concentration, maximum % removal, and maximum dry sludge weight.

After the Zn deposition process at pH 9.5, the supernatant result is still turbid with turbidity 557 NTU and COD 222 mg/L. Therefore, this wastewater still does not meet the industrial waste quality standards. Consequently, this waste must be treated by adding Katfloc PL-50/Al$_2$O$_3$-Cationic Polymer coagulant (Al$_2$O$_3$-based coagulant) with the dosage of 50, 100, and 150 mg/L and stirring time of 10, 15 and 20 minutes. This variation value is based on the jar test results conducted previously. Figure 4 shows the effect of coagulant dosage and reaction time on

COD and turbidity reduction. Based on figure 4, the increasing of the coagulant dose until the optimum value (50 mg/L), results in a higher COD value and turbidity. However, the increasing of mixing time relatively did not affect to the COD and turbidity.

Coagulation-flocculation is a physicochemical method to remove colloids with a negative charge, very fine solid suspension, and some soluble compound present in wastewater (Renu et al., 2017a). The concept is a destabilization of the solution. It is neutralized by mutual collision with opposite ions (coagulant) and followed by the formation of the flock or a process that transforms colloidal particles into flock (Ghafoorisadatieh et al., 2019). Eventually, the flock undergoes sedimentation. This process can also be used for absorbing dissolved organic matter on to the surface of the flock/particulate aggregates

(Bongiovani et al., 2016). Therefore, coagulants' addition will reduce COD since COD illustrates the amount of O_2 needed to oxidize organic substances in the waste. In this case, the decreasing COD occurred due to the formation of the flock and absorption of the organic matter by the flock (Ghafoorisadatieh et al., 2019). Increasing the amount of coagulant until 50 mg/L, the possibility of contact between coagulant and colloidal particles becomes frequent. It results in increasing flock formation until it reaches the maximum point. Hereafter, additional coagulant was not able to create precipitation flock (no flock formation). Therefore, extra coagulant remained in the water until reached saturation, and finally, COD increased doe to the availability coagulant on the aqueous solution. Some coagulants have been used for pollutants and turbidity removal (Ghafoorisadatieh et al., 2019) and pulp/paper wastewater treatment (Irfan et al., 2017).

From a turbidity point of view, it is indicating the amount of suspended solids that proportional to the amount of colloid and suspended solids in wastewater that cannot be precipitated in the usual method (Ghafoorisadatieh et al., 2019). It can scatter the light. Similar to the COD explanation, the excessive amount of coagulant to maximum point caused turbidity in the water and reduction in the turbidity removal percentage (Malik, 2018). In other words, over dozing of coagulant caused charge reversal, and particles start restabilizing.

Figure 4 shows the optimum COD and turbidity removal. It was achieved at coagulant dose of 50 mg/L with 10 minutes reaction time since both the COD and turbidity reduced to 68 mg/L (≤ 100 mg/L) and 1.42 NTU (≤ 2 NTU), respectively. It has met the quality standard with a removal efficiency of 69.4% and 99.7%, respectively. At the optimum condition, the BOD sample was reduced from 7.22 to 3.14. This condition is according to the acceptable discharge concentration. The study was also conducted to evaluate the concentrations of metals after the addition of coagulant on the supernatant. This addition does not reduce Zn concentration marginally (only reduced 1.5% from the initial condition). For other metals, the final concentration

of Fe, Co and Cd can drop to zero. To summarize, the effluent has fulfilled the acceptable discharge concentration.

4. CONCLUSION

In this study, the effects of pH on Zn removal and doses of coagulant on the reduction efficiency of COD and turbidity were performed experimentally. The pH affected the decrease of Zn concentration. The best pH took place at 9.5 due to it increased the quantities of $Zn(OH)_2$ deposition with a reduction in the Zn concentration of 95.3%. Hydroxyte precipitation was directly related to Zn removal and pH. Meanwhile, the addition of coagulant of 50 ppm to the supernatant resulting from the $Zn(OH)_2$ deposition with reaction time of 10 minutes can reduce COD, BOD, and turbidity. However, it only has a slight effect on reducing other metals concentration.

5. ACKNOWLEDGMENT

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