ORIGINAL ARTICLE

Precipitation of heavy metals by lime mud waste of pulp and paper mill

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Abstract

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Precipitation of heavy metals by lime mud waste of pulp and paper mill

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Precipitation of heavy metals in synthetic and actual wastewater with lime mud (solid waste generated from the pulp and paper production process) was experimented using Jar-tests. Separate synthetic wastewater samples were prepared for each of the following heavy metals: lead (1,433.7 mgPb^{2+}/L), chromium (506.7 mgCr^{3+}/L), cadmium (1,095 mgCd^{2+}/L) and mercury (9.37 mgHg^{2+}/L). The actual wastewater was tanning wastewater containing 74.49 mgCr^{3+}/L and COD wastewater containing 683 mgHg^{2+}/L. Adjustments of pH in the acidic range, pH 2-7, were made for each type of synthetic wastewater except for the Hg synthetic wastewater. The optimum conditions obtained from the tests of the synthetic wastewater were used for the actual wastewater samples. Precipitation of heavy metals with lime mud was effective as indicated by the removal efficiency as high as 90% up for Pb, Cd and Hg and 100% for Cr. However, the removal efficiency for the Hg-COD wastewater was only 67%. The precipitating pH was in the range of 10 up, which is the

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common pH range for metal carbonate precipitation. The optimum dosage of lime mud for Pb, Cr, Cd and Hg synthetic wastewater was 0.4-1.0 g/L, 2.0-4.0 g/L, 1.6-2.0g/L and 0.8 g/L, respectively. While the optimum dosage of lime mud for precipitating chromium in tanning wastewater was 3.8 g/L and 3.6 g/L for precipitating mercury in COD wastewater.

Key words : lime mud, pulp and paper, precipitation, heavy metal

บทคัดย่อ

วันเพ็ญ วิโรจนกูฏ เนตรนภิส ตันเต็มทรัพย์ และ พฤกษ์ ตัญตรัยรัตน์

การตกตะกอนโลหะหนักด้วยกากปูนขาวจากอุตสาหกรรมผลิตเยื่อกระดาษ

ว.สงขลานครินทร์ วทท. 2547 26(ฉบับพิเศษ 1) : 45-53

การศึกษาการตกตะกอนทางเคมีของโลหะหนักในน้ำเสียสังเคราะห์ และน้ำเสียจริงด้วยกากปูนขาว (กากของเสียที่เกิดจากอุตสาหกรรมผลิตเยื่อกระดาษ) โดยใช้เครื่องจาร์-เทสต์ น้ำเสียสังเคราะห์ที่ใช้ทดลอง 4 ชนิดคือ น้ำเสียตะกั่ว (1,433.7 มก./ลิตร) ไทรวาเลนท์โครเมียม (506.7 มก./ลิตร) แคดเมียม (1,095 มก./ลิตร) ปรอท (9.37 มก./ลิตร) และน้ำเสียจริง 2 ชนิดได้แก่ น้ำเสียจากโรงงานฟอกหนังซึ่งมีโครเมียม 74.49 มก./ลิตร และ น้ำเสียจากการทดลองซีโอดีซึ่งมีปรอท 683 มก./ลิตร ในการทดลองปรับค่าพีเอชเริ่มต้นของน้ำเสียสังเคราะห์ 4 ค่าในช่วงที่เป็นกรดตามความ เหมาะสมของน้ำเสียชนิดนั้น (พีเอช 2-7) ยกเว้นน้ำเสียปรอทไม่ปรับค่าพีเอชก่อนการตกตะกอน โดยผลการศึกษาประสิทธิภาพการตกตะกอนในน้ำเสียสังเคราะห์ จะนำมาใช้ในการทดลองน้ำเสียจริง จากผลการทดลองพบว่ากากปูนขาว ตกตะกอน ตะกั่ว แคดเมียม และ ปรอท ในน้ำเสียสังเคราะห์ ได้มากกว่า 90% และสามารถตกตะกอนได้ถึง 100% สำหรับน้ำเสียสังเคราะห์โครเมียมและน้ำเสียจากโรงงานฟอกหนัง แต่น้ำเสียจากการวิเคราะห์ซีโอดีสามารถตกตะกอนได้เพียง 67% เท่านั้น ค่าพีเอชที่เกิดการตกตะกอนมีค่าสูงกว่า 10 ขึ้นไป โดยปริมาณกากปูนขาวที่เหมาะสม สำหรับน้ำเสียสังเคราะห์ ตะกั่ว โครเมียม แคดเมียม และปรอท คือ 0.4-1.0 2.0-4.0 1.6-2.0 และ 0.8 กรัม/ลิตร ตามลำดับ ส่วนน้ำเสียจากโรงงานฟอกหนัง และน้ำเสียจากการวิเคราะห์ซีโอดีใช้ปริมาณกากปูนขาวที่เหมาะสมเท่ากับ 3.8 และ 3.6 กรัม/ลิตร ตามลำดับ

ภาควิชาวิศวกรรมสิ่งแวดล้อม คณะวิศวกรรมศาสตร์ /ศูนย์วิจัยแห่งชาติด้านการจัดการสิ่งแวดล้อมและของเสียอันตราย มหาวิทยาลัยขอนแก่น อำเภอเมือง จังหวัดขอนแก่น 40002

Lime mud is solid waste from pulp and paper production. It is generated from the sodium hydroxide recovery unit and is partly reused in the digesting unit of the pulp and paper production process. It is estimated that approximately 0.47 m^3 of lime mud is generated per ton of pulp produced (Consultant of Technology, 2001). The industry can reuse about 30% of the lime mud. The rest has to be disposed of on a landfill. It consumes large landfill area at high disposal costs. If the disposal is not properly operated, the lime mud can also cause environmental impact. Therefore, reuse of lime mud would lower the production costs of pulp and reduce the disposal problems.

The main component of lime mud is calcium carbonate ($CaCO_3$). In the experiment, calcium carbonate was analyzed by X-ray Fluorescence Energy Dispersive Spectrometer Model ED-2000 after the lime mud was sieved through a No. 100 sieve according to the ASTM standard. The analysis showed a calcium carbonate content of about 65.4% by weight and the rest was fine sand and other soil particles. Calcium carbonate can precipitate heavy metals to form metals carbonate (Crear, 2001), and in this way heavy metal contaminants can be removed from wastewater. This research therefore was aimed at investigating the utilization of lime mud to precipitate heavy metals contained in wastewater. The studied heavy metals included lead (Pb^{2+}), trivalent chromium (Cr^{3+}), cadmium (Cd^{2+}) and mercury (Hg^{2+}). This study is therefore concerned about reusing lime mud for wastewater treatment and minimizing waste. That would benefit not only the industry but also the environment

Objectives

The main objective is to reuse lime mud for precipitation of heavy metals in synthetic and actual wastewater. The specific objectives are:

1. To study the precipitation of heavy metals (Pb, Cr, Cd and Hg) of synthetic wastewater in the acidic range.
2. To determine the optimum dosage of lime mud at each pH of each synthetic wastewater.
3. To test for the precipitation of heavy metals in actual wastewater by using the optimum dosage and pH from the synthetic wastewater experiments.

Materials and Method

Synthetic wastewater samples were prepared for each of the studied heavy metals in the following concentrations: Pb about 1,500 mg/L, Cr 500 mg/L, Cd 1,000 mg/L and Hg 10 mg/L. The actual wastewater was chromium contaminated tanning wastewater taken from a tannery, and mercury contaminated wastewater of COD laboratory liquid waste. The precipitation experiments of the heavy metal contaminated wastewater samples (both synthetic and actual) with lime mud taken from a pulp and paper mill were conducted in the laboratory as outlined in the flowcharts in Figures 1 and 2, respectively. Details of the experiments are presented in Tables 1 and 2.

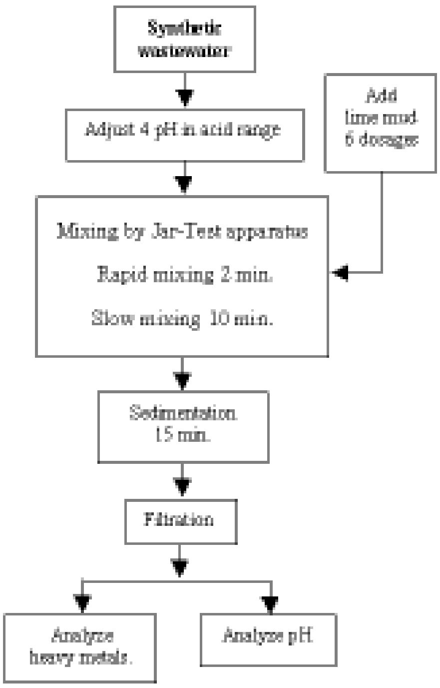

Figure 1. Synthetic wastewater experiment flowchart

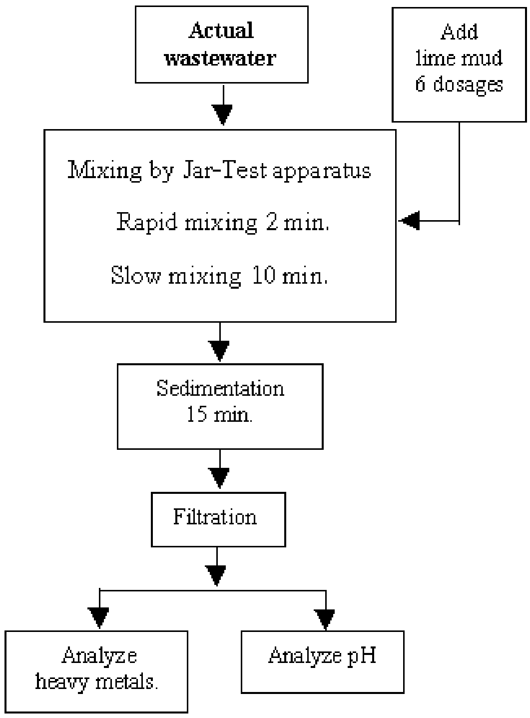

Figure 2. Actual wastewater experiment flowchart

Table 1. Details of the experiments for synthetic wastewater

Synthetic wastewater	Concentration (mg/L)	Adjust pH of wastewater	Dosage of lime mud (g/L)
Lead (Pb^{2+})	1,433.6	4-7	0.1 0.2 0.3 0.4 0.5 and 0.6
Chromium (Cr^{3+})	506.7	2-5	1.0 1.2 1.4 1.6 1.8 and 2.0
Cadmium (Cd^{2+})	1,095.4	3-6	0.4 0.6 0.8 1.0 1.2 and 1.4
Mercury (Hg^{2+})	9.34	-	0.1 0.2 0.3 0.4 0.5 and 0.6

Table 2. Details of the experiments for actual wastewater

Actual wastewater	Concentration (mg/L)	pH of wastewater	Dosage of lime mud (g/L)
Tanning wastewater (Cr^{3+})	74.49	4.61	0.4 0.7 1.0 1.3 1.6 and 1.9
COD laboratory liquid waste (Hg^{2+})	683	-0.32	1.0 1.2 1.4 1.6 1.8 and 2.0

The experiments concerning precipitation of heavy metals in synthetic wastewater were conducted using a Jar-test. The following methodology was applied:

1. Adjusting pH of each synthetic wastewater sample (Pb, Cr and Cd) in the acidic range (Table 1) -except for the Hg synthetic wastewater, for which pH was not adjusted, because Hg is highly toxic and can easily evaporate when heated by acidification.
2. Filling each type of synthetic wastewater of 500 mL to a 600 mL beaker for 6 beakers.
3. Adding lime mud at various dosages for each type of synthetic wastewater (the dosage of lime mud was estimated from the preliminary test).
4. Rapid mixing at 100 rpm for 2 minutes and slow mixing at 30 rpm for 10 minutes, followed by settling for 15 minutes.
5. Filtering the supernatant through a Whatman No.42-filter paper and then analyzing the filtered supernatant for pH and heavy metals.
6. Three replicate experiments were conducted for each pH value of each synthetic wastewater sample.

Precipitation experiments of actual wastewater were conducted for Cr contaminated tanning wastewater and Hg contaminated COD wastewater using a Jar-test and following the same methodology as the synthetic wastewater experiments. The Hg concentration in the COD wastewater sample was very high and the sample was diluted with distilled water (1:100) to lower the Hg concentration to less than 10 mg/L before running the precipitation experiment.

Figure 3 shows the dried lime mud powder that was prepared in accordance with ASTM standard and dried at 103-105 ^{o}C for 24 hours.

Results and Discussion

Lead synthetic wastewater: The results of lead precipitation are shown in Table 3 and Figure 4. The highest precipitation of lead was in the pH range of 10.5 – 11.5 (pH after precipitation) and the optimum lime mud dosages for each initial pH of 4-7 were 1.0, 0.6, 0.8 and 0.4 g/L. The maximum lead removal efficiencies were 94.1%, 94.6%, 92.7% and 79.7%, respectively. The removal efficiencies at pH 4, 5 and 6 were similar while that at pH 7 was lower than at other pH values. This is because the adjusted pH (pH 7) of synthetic wastewater with NaOH before adding lime mud cause very fine precipitate of lead hydroxide that can pass through the filter paper. That made lead remained in the filtered sample.

Figure 3. Lime mud after through a sieve No. 100 according to the ASTM standard

Chromium synthetic wastewater: Table 4 and Figure 5 present the precipitation of chromium in synthetic wastewater. The maximum precipitation of chromium took place at pH 11 up. The optimum dosages for each initial pH (2-5) were 4.0, 2.8, 2.4 and 2.0 g/L, respectively. The removal efficiency was as high as 100% for each initial pH value. Lime mud was highly capable of precipitating chromium. It was noted that the optimum dosage of lime mud decreased as the pH increased.

Cadmium synthetic wastewater: Table 5 and Figure 6 present precipitation of cadmium in synthetic wastewater. The maximum precipitation of cadmium was reached at pH 10 up. The optimum dosages for each initial pH value were in the range of 1.6-2.0 g/L. The removal efficiency was as high as 99% up for each initial pH value.

Mercury synthetic wastewater: Mercury synthetic wastewater contains Hg^{2+} 9.336 mg/L and an initial pH of 5.37. The precipitation of mercury took place at pH 10.5 up. The optimum dosage of lime mud was 0.8 g/L. The highest mercury removal efficiency was 96%, as shown in Figure 7.

Tanning wastewater: The tanning wastewater contained chromium in a concentration of 74.49 mg/L and a pH of 4.6. The optimum dosage of lime mud was 3.8 g/L and the removal efficiency was 100%. The pH after precipitation was 11.78, as shown in Figure 8.

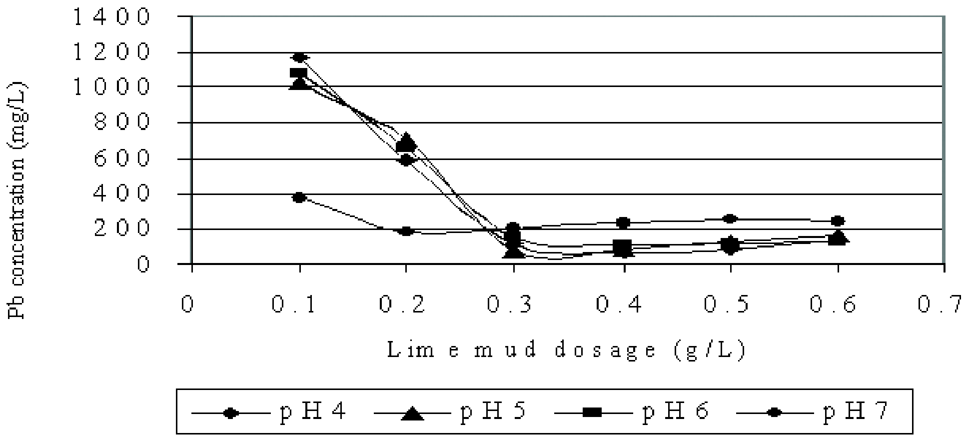

Figure 4. Lead removals at pH 4-7

Table 3. Results of lead synthetic wastewater precipitation (Pb^{2+} 1,433.6 mg/L)

Initial pH	Optimum lime mud dosage (g/L)	pH after precipitation	Conc. after precipitation (mg/L)	Removal efficiency (%)
4	1.0	11.41	87.0	94.1
5	0.6	10.70	76.5	94.6
6	0.8	11.30	103.6	92.7
7	0.4	10.91	183.3	79.7

Table 4. Results of chromium synthetic wastewater precipitation (Cr^{3+} 506.7 mg/L)

Initial pH	Optimum lime mud dosage (g/L)	pH after precipitation	Conc. after precipitation (mg/L)	Removal efficiency (%)
2	4.0	11.11	0.024	99.99
3	2.8	11.40	0.002	100
4	2.4	11.24	0.015	100
5	2.0	11.24	0.011	100

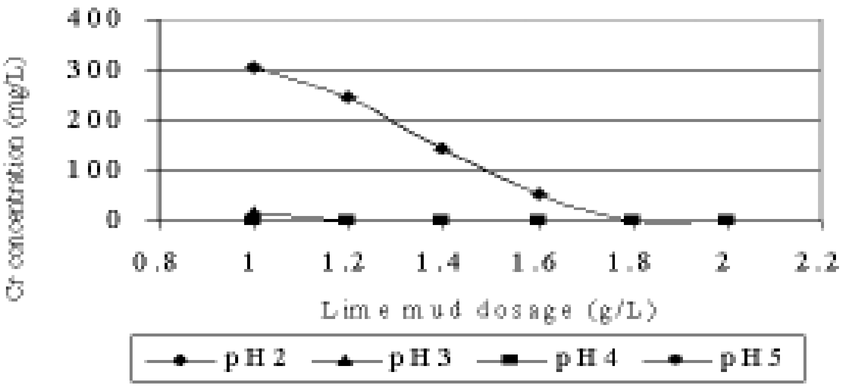

Figure 5. Chromium removal at pH 2-5

COD wastewater: The COD wastewater contained 683 mg/L mercury and pH was too low to be measured. Since the mercury content was very high and pH was extremely low, the wastewater sample was diluted about 100 times with distilled water. The Hg concentration in the diluted wastewater sample was about under 10 mg/L and pH 1.59. The optimum dosage of lime mud for precipitation was 3.6 g/L with a removal efficiency of 66.91% and pH after precipitation was 11.61 (Figure 9). It was noted that the optimum dosage of lime mud for the Hg-COD wastewater was higher than for the Hg synthetic wastewater. Moreover, as the COD wastewater also contained hexavalent

Table 5. Results of cadmium synthetic wastewater precipitation (Cd^{2+} 1,095.4 mg/L)

Initial pH	Optimum lime mud dosage (g/L)	pH after precipitation	Conc. after precipitation (mg/L)	Removal efficiency (%)
3	1.6	10.34	3.33	99.69
4	2.0	11.67	4.62	99.57
5	1.6	11.44	1.78	99.84
6	2.0	11.69	2.39	99.78

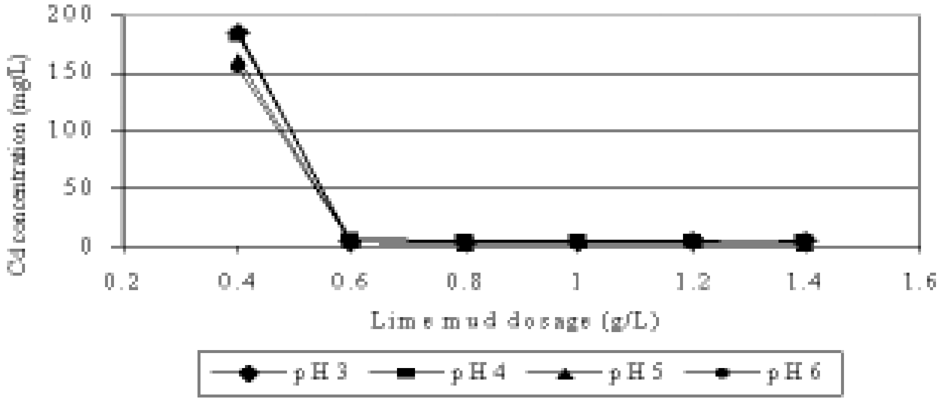

Figure 6. Cadmium removal at pH 3-6

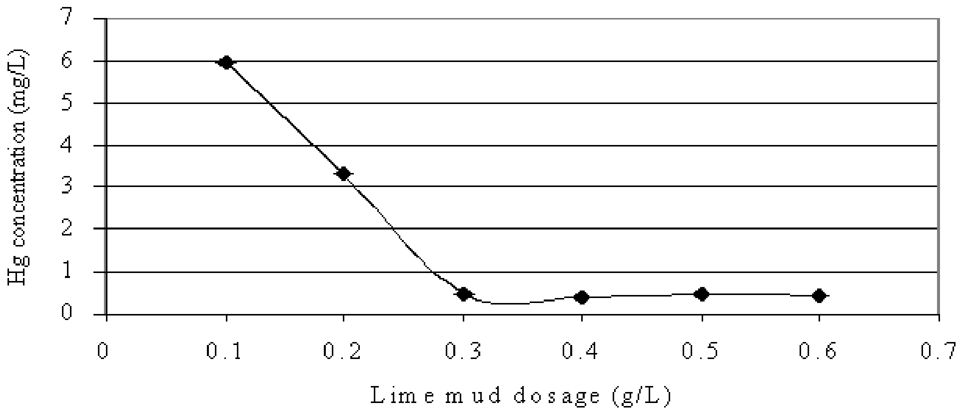

Figure 7. Mercury removal

chromium and ferrous, it required higher lime mud dosage. These metal ions interfere with precipitation of mercury. The removal efficiency of mercury was thus lower than the synthetic wastewater

Conclusion

Utilization of lime mud, which is solid waste generated from pulp and paper mills, and of which

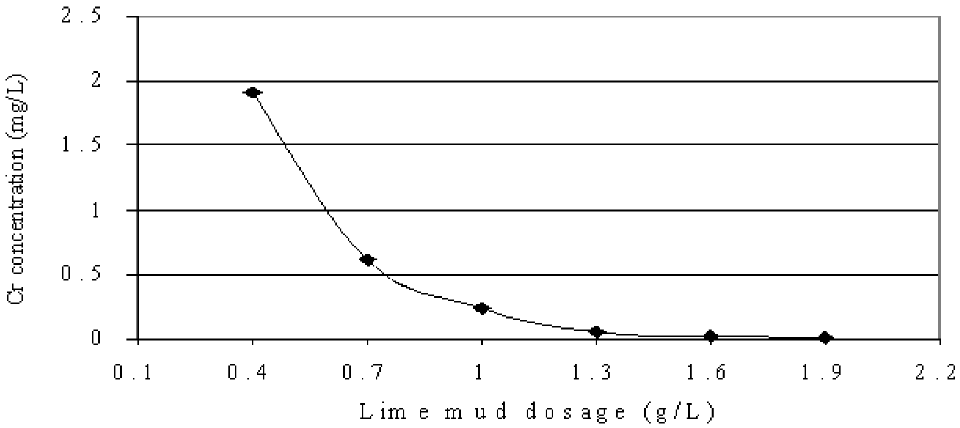

Figure 8. Chromium removal

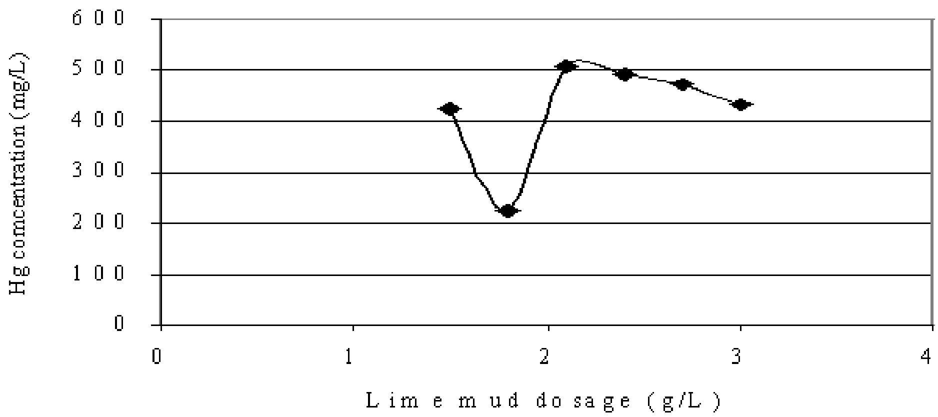

Figure 9. Mercury removal

the main component is calcium carbonate was studied for removal of heavy metals contaminated wastewater by chemical precipitation. The experiments were performed for four different types of synthetic wastewater each containing one of the following heavy metals: lead (1,433.7 mgPb^{2+}/L), trivalent chromium (506.7 mgCr^{3+}/L), cadmium (1,095 mgCd^{2+}/L) and mercury (9.37 mgHg^{2+}/L). In addition, the experiments were carried out on two types of actual wastewater comprising tanning wastewater with chromium content of 74.49 mg/L and COD wastewater with mercury content of 683 mg/L.

Jar-test was used for the precipitation experiments. The synthetic wastewater samples were adjusted in acidic range except for the mercury synthetic wastewater samples. The optimum dosage of lime mud for lead synthetic wastewater with pH 4-6 was in the range of 0.4 to 1.0 g/L with the highest removal efficiency of 93%. The synthetic chromium wastewater with adjusted pH range 2-5, had optimum dosage of lime mud in the range of 2.0-4.0 g/L. Removal efficiencies as high as 100% were recorded for every pH level. The optimum dosages of lime mud for the cadmium wastewater with adjusted pH range 3-6 were similar for all pH values (about 2.0 g/L). The experiments on cadmium wastewater showed removal efficiencies as high as 99% for every pH value. With respect to the synthetic mercury wastewater, which was not pH adjusted, the highest removal efficiency was about 96%. The study of tanning wastewater without pH adjustment indicated up to 100% removal efficiency of chromium while the removal efficiency of mercury from the COD wastewater was not over 65%. However, the remaining concentrations of heavy metals, except chromium, were still higher than the effluent standard. Further treatment of the remaining heavy metals is required.

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