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# Efficiency of Removing Heavy Metals from Chemical Oxygen Demand Test Wastewater by Using Alum Sludge from a Surface Water Supply Treatment Plant

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**Abstract**

Chemical laboratories often use reagents for various determinations containing heavy metals. This is also the case for laboratories controlling the condition of wastewater derived from communities. An indirect way of measuring the content of chemical oxidizing materials in wastewater is the chemical oxygen demand (COD) test. Reagents used for running this test contain heavy metals which contaminate the wastewater of the testing laboratory and should be eliminated before the wastewater of the laboratory is drained out. The aim of this study was to remove heavy metals originated from reagents needed to run the COD test from the laboratory wastewater by using alum sludge filtration. Different pH levels as 3, 4, 5 and 6, and different amounts of alum sludge were tested in order to define an optimal condition for the elimination of heavy metals from the laboratory wastewater. The Kruskal Wallis test was used for statistical analysis. The efficiency of removing silver, chromium and iron depended on the variation of pH. In addition, the increase in amount of alum sludge caused the increase the removal of the heavy metals from the laboratory's wastewater. The optimum pH value was 4 and the optimum volume of alum sludge was 160 g/l and under these conditions 99.9% of the silver, 99.8% of chromium and 99.9% of iron could be eliminated. The residual concentration of chromium within the wastewater fulfilled the requirement for wastewater quality being less than 0.75 mg/l as stipulated by the Ministry of Industry. However, the suspended solid was still too high and did not fulfill the requirement of the standard quality of the Ministry of Industry.

**Keywords**: alum sludge, COD test, removing heavy metals

## 1. Introduction

Heavy metal elimination from waste water is a challenge for surface water supply treatment plants. For instance, laboratories are one source of hazardous wastes generated either from routine determinations or, as true also for universities, from research activities or in instructing students. The chemical oxygen demand (COD) test is one example for a determination, which results in harmful substances within the wastewater of the laboratory ending finally up in water treatment plants. The COD test is used as an indirect method to determine the content of chemical oxidizing agent materials in wastewater. The method makes use of $K_2Cr_2O_7$, Fe $(NH_4)_2(SO_4)_2.6H_2O$, $Ag_2SO_4$ and $HgSO_4$, and finally chromium, silver and iron are dissolved in the wastewater, which once drained will contaminate the environment.

In this study, alum sludge is tested for its ability to eliminate heavy metals from the laboratory wastewater. Alum sludge is usually the result of water treatment processes of sewage plants and is a suspension of colloids. It acts like a large galantine net including anhydrous aluminum hydroxide, inorganic material, carbon, clay, and sand (1) and has a porous surface (2). The heavy metals are removed by sweep coagulation.

The objectives of this investigation is to study the efficiency of alum sludge with adjusting pH at different levels to remove heavy metals from wastewater derived from the COD test, and to study the efficiency of removal heavy metals from the wastewater of the laboratory derived from conducting the COD test using different amounts of alum sludge.

## 2. Materials and Methods

This research was conducted as an experimental study to test the efficiency of heavy metal removal from the wastewater derived from conducting the COD test.

### 2.1 Preparation of alum sludge.

Alum sludge was obtained from the sedimentation process of plain water filtration at the Nong Ko Ta plant of the Khon Kaen Provincial Waterworks Authority. The sludge was allowed to dry for 2 to 3 days, baked at 105 °C for 24 hours and then thoroughly crushed by using a mortar and stone to glide through a No. 100 sieve. The resulting sediment was kept in a cabinet rank prior to use (Figure 1).

**Figure 1.** Alum sludge after grinding through a No. 100 sieve.

### 2.3 Water quality analyses

The wastewater of the laboratory derived from conducting the COD test used, was adjusted pH to 3, 4, 5, and 6, with adding 10 N NaOH and alum sludge at 0 (as a control solution), 120, 140, 160, 180, 200 and 220 g/l (as the test solutions). Each of the samples was mixed according to the Jar test method by an agitating speed of 100 rpm for 1 min and for slow agitation at 30 rpm for 1 min. Then, it was left for sedimentation for 30 minutes. The analyses

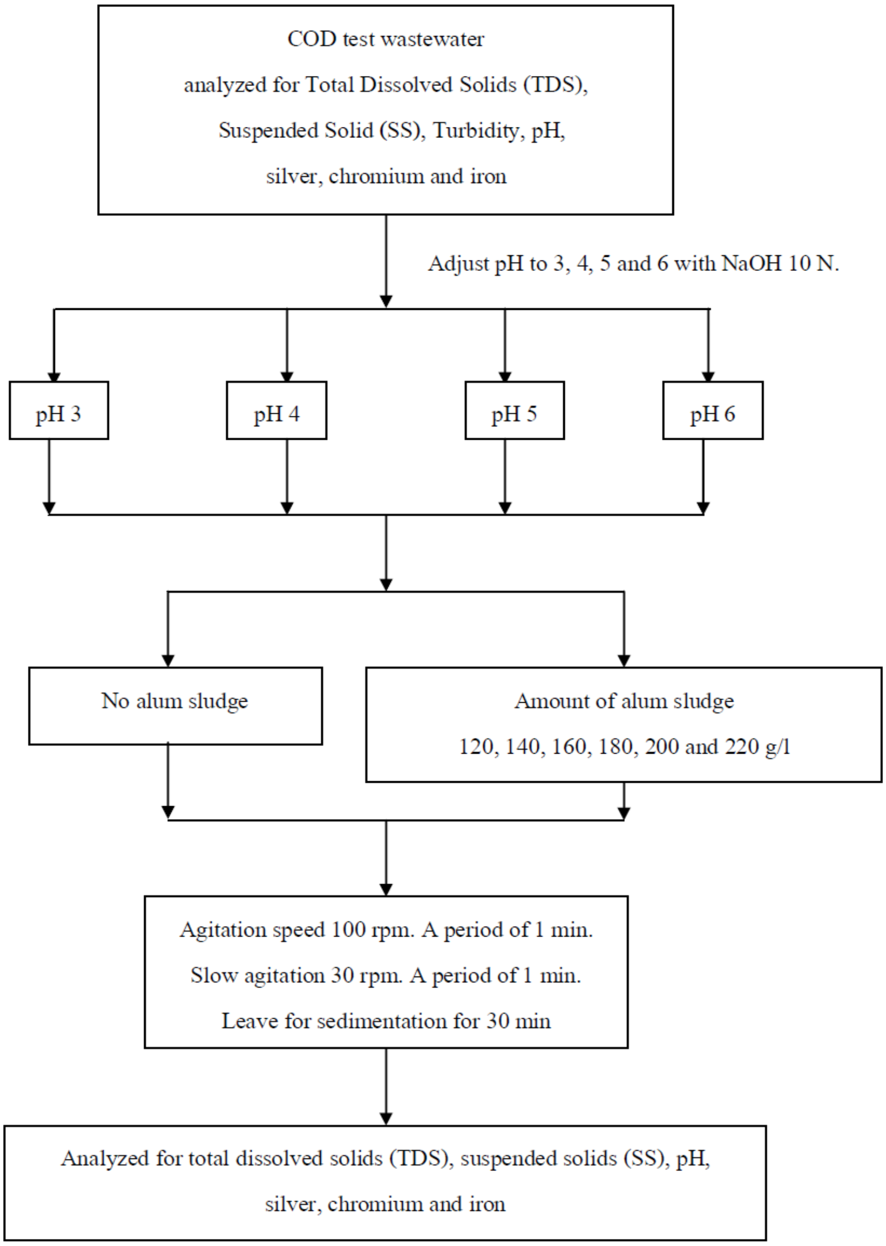


**Figure 2.** Test procedures for removing heavy metals from wastewater resulting from the COD test.

for total dissolved solids (TDS), suspended solids (SS), pH, silver, chromium and iron were analyzed before and after the experiment (Figure 2) by the standard method for the examination of water and wastewater (3).

**2.4 Data Analysis**

For data analysis, conventional descripttive statistics were used by calculated means, standard deviations and ranges. The Kruskal Wallis test was applied with a significant level of α 0.05.

## 3. Results and Discussion

### 3.1 Characteristics of wastewater after conducting the COD test

Effluent analysis showed a clear blue greenish solution of pH 0.8 ± 0.01 and NTU turbidity 0.37 ± 0.10, with an average amount of suspended solids of 53.51 ± 3.54 mg/l. The average total dissolved solids was 1,254.25 ± 1.60 mg/l, the average amount of silver was 1,007.90 ± 0.07 mg/l, and the average chromium and iron were 350.10 ± 0.20 and 888.55 ± 0.14 mg/l, respectively (Table 1). These results are congruent with those of Ranok, 2006 (4).

### 3.2 Efficiency of removal heavy metals by using alum sludge

For removing silver chromium and iron, the pH 6 was proofed to be most efficient over pH 5, 4 and 3. This is because heavy metals ($Ag^{+}$, $Cr^{3+}$and $Fe^{3+}$) are bound to hydroxide ($OH^{-}$) as metal hydroxide (AgOH, $Cr(OH)_3$ and $Fe(OH)_3$) and the reaction is best at basic conditions as provided by the sludge. The more sludge is added, the more the pH in the solution is increased and the more AgOH, $Cr(OH)_3$ and $Fe(OH)_3$ are precipitated. The addition of NaOH to adjust pH of wastewater together with alum sludge increased the efficiency of removal of silver chromium and iron (5). The process is very much dependent on the amount of alum sludge. The alum sludge enables the sweep coagulation. It acts like a large galantine net including anhydrous aluminum hydroxide, inorganic material, carbon, clay and sand (1), and has a porous surface (2). At pH 6 and 140 g/l of alum sludge, silver was removed to almost 100%, while 120g/l of alum sludge at pH 3 only removed silver to 86% (Table 2). At pH 6 and 120 g/l of alum sludge, chromium was removed to almost 100%, while 120 g/l ofalum sludge, chromium was removed to almost 100%, while 120 g/l of alum sludge at pH 3 only removed chromium to 89.35% (Table 3). At pH 6 and 120 g/l of alum sludge, iron was removed to almost 100%, while 120 g/l of alum sludge at pH 3 only removed iron to 89.35% (Table 4).

### 3.3 The mechanism for the removal of silver, chromium and iron

At a basic conditions, the metals

**Table 1.** Characteristics of wastewater derived after conducting the COD-tests

| racteristics of the wastewater | Min | Max | Mean | SD | Ranok (2006) |
|---|---|---|---|---|---|
| pH | 0.8 | 0.8 | 0.8 | 0.01 | < 1 |
| Turbidity (NTU) | 0.36 | 0.38 | 0.37 | 0.10 | - |
| Suspended solids (mg/l) | 50.15 | 57.09 | 53.51 | 3.54 | 44.78 |
| Total dissolved solids (mg/l) | 1,252.02 | 1,255.71 | 1,254.25 | 1.60 | - |
| Silver (mg/l) | 1,007.80 | 1,007.90 | 1,007.90 | 0.07 | 324.00 |
| Chromium (mg/l) | 350.08 | 350.13 | 350.10 | 0.20 | 215.90 |
| Iron (mg/l) | 888.35 | 888.70 | 888.55 | 0.14 | 534.50 |

**Table 2.** Efficiency of removal of silver by adjusting the pH of the alum sludge.

| Amount of alum sludge (g/l) | Efficiency removal of silver | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | pH 3 | | pH 4 | | pH 5 | | pH 6 | |
| | residual silver (mg/l) | (%) | residual silver (mg/l) | (%) | residual silver (mg/l) | (%) | residual silver (mg/l) | (%) |
| 0 (control) | 523.43 | 47.86 | 137.26 | 86.37 | 42.35 | 95.79 | 42.29 | 97.59 |
| 120 | 136.94 | 85.97 | 1.93 | 99.80 | 1.72 | 99.80 | 0.12 | 99.98 |
| 140 | 101.47 | 87.27 | 1.65 | 99.83 | 1.56 | 99.84 | 0.00 | 100 |
| 160 | 87.22 | 91.07 | 0.97 | 99.89 | 0.69 | 99.92 | 0.00 | 100 |
| 180 | 78.75 | 92.35 | 0.83 | 99.93 | 0.54 | 99.93 | 0.00 | 100 |
| 200 | 63.42 | 93.77 | 0.32 | 99.96 | 0.24 | 99.96 | 0.00 | 100 |
| 220 | 54.41 | 94.58 | 0.21 | 99.99 | 0.16 | 99.99 | 0.00 | 100 |

**Table 3.** Efficiency in the removal of chromium by adjusting the pH of alum sludge.

| Amount of alum sludge (g/l) | Efficiency in the removal of chromium. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | pH 3 | | pH 4 | | pH 5 | | pH 6 | |
| | residual chromium (mg/l) | (%) | residual chromium (mg/l) | (%) | residual chromium (mg/l) | (%) | residual chromium (mg/l) | (%) |
| 0 (control) | 185.40 | 47.04 | 72.46 | 79.29 | 2.31 | 99.33 | 0.45 | 99.95 |
| 120 | 37.06 | 89.35 | 1.23 | 99.64 | 1.20 | 99.65 | 0.00 | 100 |
| 140 | 26.77 | 92.25 | 1.01 | 99.70 | 0.99 | 99.71 | 0.00 | 100 |
| 160 | 21.21 | 94.03 | 0.65 | 99.81 | 0.54 | 99.84 | 0.00 | 100 |
| 180 | 16.19 | 95.94 | 0.53 | 99.84 | 0.38 | 99.88 | 0.00 | 100 |
| 200 | 13.90 | 96.02 | 0.40 | 99.87 | 0.18 | 99.94 | 0.00 | 100 |
| 220 | 11.59 | 96.68 | 0.24 | 99.92 | 0.07 | 99.99 | 0.00 | 100 |

precipitate best but in an acid solution the heavy metals remain dissolved in the wastewater (pH 3> 4> 5 and 6, respectively) (6) and will be discarded in the environment. Of importance is the optimum amount of alum sludge added to the process since it increases the area for sweep coagulation. Similar results have been obtained for chromium from Kaewlee, 2004 (7). The efficiency of removing silver, chromium and iron was dependent on the variation of the pH level (Table 5). In addition, an increase in the amount of alum sludge significantly ($p<0.05$) increased the removal of the heavy

**Table 4.** Efficiency in the removal of iron by adjusting the pH of alum sludge.

| Amount of alum sludge (g/l) | Efficiency in the removal of iron. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | pH 3 | | pH 4 | | pH 5 | | pH 6 | |
| | residual iron (mg/l) | (%) | residual iron (mg/l) | (%) | residual iron (mg/l) | (%) | residua l iron (mg/l) | (%) |
| 0 (control) | 545.90 | 38.54 | 12.39 | 98.60 | 1.16 | 99.84 | 0.73 | 99.92 |
| 120 | 15.04 | 98.29 | 1.52 | 99.82 | 1.08 | 99.89 | 0.00 | 100 |
| 140 | 11.64 | 98.68 | 1.15 | 99.86 | 0.83 | 99.90 | 0.00 | 100 |
| 160 | 9.72 | 98.90 | 0.71 | 99.91 | 0.76 | 99.91 | 0.00 | 100 |
| 180 | 7.08 | 99.20 | 0.59 | 99.93 | 0.58 | 99.93 | 0.00 | 100 |
| 200 | 6.09 | 99.31 | 0.5 | 99.94 | 0.45 | 99.94 | 0.00 | 100 |
| 220 | 4.79 | 99.46 | 0.32 | 99.96 | 0.24 | 99.97 | 0.00 | 100 |

**Table 5.** Comparison the efficiency of alum sludge with adjusting pH at different levels to remove heavy metals from laboratory wastewater derived from the COD test.

**Kruskal-Wallis Test**

**Ranks**

| | pH | N | Mean Rank | Chi-Square | df | Asymp. Sig. |
|---|---|---|---|---|---|---|
| silver | 3.00 | 21 | 13.19 | 54.794 | 3 | .000 |
| | 4.00 | 21 | 41.38 | | | |
| | 5.00 | 21 | 47.29 | | | |
| | 6.00 | 21 | 68.14 | | | |
| | Total | 84 | | | | |
| chromium | 3.00 | 21 | 13.57 | 63.982 | 3 | .000 |
| | 4.00 | 21 | 38.05 | | | |
| | 5.00 | 21 | 45.45 | | | |
| | 6.00 | 21 | 72.93 | | | |
| | Total | 84 | | | | |
| iron | 3.00 | 21 | 12.93 | 61.820 | 3 | .000 |
| | 4.00 | 21 | 39.79 | | | |
| | 5.00 | 21 | 45.81 | | | |
| | 6.00 | 21 | 71.48 | | | |
| | Total | 84 | | | | |

metals (silver, chromium and iron) from the laboratory's wastewater (Table 6). Optimum results, suitable for a wastewater treatment plant, are achieved at pH 3 with an amount

**Table 6.** Comparison the efficiency of removal heavy metals from the wastewater of the laboratory derived from conducting the COD test using different volumes of alum sludge.

**Kruskal-Wallis Test**

**Ranks**

| | Alum sludge | N | Mean Rank | Chi-Square | df | Asymp. Sig. |
|---|---|---|---|---|---|---|
| Silver | .00 | 12 | 16.17 | | | |
| | 120.00 | 12 | 36.29 | | | |
| | 140.00 | 12 | 41.13 | | | |
| | 160.00 | 12 | 45.71 | | | |
| | 180.00 | 12 | 48.04 | 22.332 | 6 | .001 |
| | 200.00 | 12 | 53.17 | | | |
| | 220.00 | 12 | 57.00 | | | |
| | Total | 84 | | | | |
| chromium | .00 | 12 | 23.46 | | | |
| | 120.00 | 12 | 36.75 | | | |
| | 140.00 | 12 | 40.17 | | | |
| | 160.00 | 12 | 43.83 | | | |
| | 180.00 | 12 | 47.25 | 13.382 | 6 | .037 |
| | 200.00 | 12 | 50.92 | | | |
| | 220.00 | 12 | 55.13 | | | |
| | Total | 84 | | | | |
| Iron | .00 | 12 | 22.04 | | | |
| | 120.00 | 12 | 36.04 | | | |
| | 140.00 | 12 | 39.08 | | | |
| | 160.00 | 12 | 43.96 | | | |
| | 180.00 | 12 | 48.71 | 15.921 | 6 | .014 |
| | 200.00 | 12 | 51.46 | | | |
| | 220.00 | 12 | 56.21 | | | |
| | Total | 84 | | | | |

of alum sludge of 200 g/l, which can remove silver, chromium and iron for 99.9%, 99.8% and 99.9%, respectively.

However, as illustrated a pH 3 and a total of 200 mg/l sludge are not really necessary to achieve sufficient results. Adding the amount of alum sludge of 160 mg/l and increasing the pH to 4, the removal of heavy metals already is remarkable in that silver was removed to 99.9%, chromium to 99.8% and iron for 99.9%. The residual concentration of chromium passed the water quality standards of the Ministry of Industry to be less than 0.75 mg/l.

The final pH of the wastewater and the total dissolved solids passed quality standards of the Ministry of Industry. The pH was 5.73 ± 0.06, while the standard requires pH of 5.5-9. The pH might increase even further due to the fact that through hydrolysis positively charged radicals increase. Total dissolved solids amount was 337.96 ± 9.12 g/l, while the standard allows not more than 500 mg/l. However, the suspended solids were still too high and did not fulfill the requirement of the quality standard of the Ministry of Industry. Suspended solids were 6,300 ± 398.49 mg/l but according to the standard not more than 30 mg/l are allowed. Total dissolved solids and the suspended solids increased because alum sludge incorporates anhydrous aluminum hydroxide, inorganic material, carbon, clay, and sand (1).

Cost effectiveness might be of interest for those operating a treatment plant.

Considering the optimum condition for the efficiency in removing silver, chromium and iron at pH 4 and with 160 g/l of alum sludge the expenses can be estimated on the basis of solidification of sludge disposal to lose 1 kg of the material. (Excluding wages)

1) Cement 4 kg @ 2.6 baht /kg
   price 10.4 baht
2) Sand 15 kg @ 1.8 baht /kg
   price 0.12 baht
3) Water 2.5 l @ 0.028 baht/l
   price 0.07 baht

Therefore, the total material cost would be 12.27 baht per 1 kg of sludge disposal.

## 4. Conclusion

The optimum condition for removing silver, chromium and iron from the COD wastewater was pH 4 and 160 g/l of alum sludge and under these conditions silver, chromium and iron were removed for 99.9%, 99.8% and 99.9%, respectively through precipitation. The residual concentration of chromium passed water quality standard of the Ministry of Industry (chromium less than 0.75 mg/l). However, the wastewater could not yet be drained because the suspended solid and the total dissolved solid did not fulfill the water quality standards as laid down by the Ministry of Industry. It will need further investigations to find ways and means to decrease the solid substances from wastewater after using alum sludge but one step further in the removal of heavy metal already had been achieved.

**Suggestions**

1) The level of a pH of 4 and 160 g/l of alum sludge create optimum conditions for the removal of silver, chromium and iron derived from the COD test.

2) In using the alum sludge for the removal of heavy metals from laboratory wastewater results in an increase of suspended solids and total dissolved solids. It will need time to explore ways and means to decrease the solid substances from wastewater after using alum sludge.

**5. Acknowledgement**

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