

Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse

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Abstract

There has been great demand for development of technologies that remove toxic heavy metal ions from wastewater. Chemical precipitation operation is known to remove heavy metal ions from water. In this study applicability of alkaline reagents such as $\text{Ca}(\text{OH})_2$ (lime) and NaOH (caustic soda) in removing copper and chromium ions were evaluated. Separation of heavy metals such as chromium compounds from petrochemical industries' cooling water wastes was achieved by conversion of hexavalent chromium, $\text{Cr}(\text{VI})$, to trivalent chromium, $\text{Cr}(\text{III})$. Maximum conversion occurred in the pH range of 2.0 and 2.3, adjusted by ferrous sulfate and sulfuric acid. Maximum precipitation of $\text{Cr}(\text{III})$ occurred at pH 8.7 with addition of $\text{Ca}(\text{OH})_2$, followed by mixing and 2-h sedimentation. At the end, the concentration of chromate was reduced from 30 ppm to 0.01 ppm. In the case of copper, which is found in the form of cupro-ammonia in ammonia plant wastes, it was observed that the presence of ammonia in wastewater prevents effective chemical precipitation. Therefore, the quantity of ammonia was reduced by aeration. The optimum aeration rate was determined to be 70 L/min, and it was found that ammonia concentration reached equilibrium after 5.0 h of aeration. Furthermore, hydroxide and carbonate methods were evaluated with respect to precipitation of heavy metals at bench scale, and the former was selected as the method of choice. The results obtained in the Jar test were then applied to pilot scale, and it was determined that the optimum pH for maximum copper precipitation was about 12.0 for both lime and caustic soda used in the hydroxide precipitation method. Lime was preferred due to economics and its high speed of precipitation. Finally, using established methods described here, the concentration of copper followed by coagulation with lime, mixing, 2-h sedimentation and filtration through Whatman 0.45 μm filters was reduced from 48.51 mg/L to 0.694 mg/L, which is below the environmental standards for water resources.

Keywords: Removal; Copper; Chromium; Lime; Pilot plant; Wastewater reuse

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1. Introduction

Copper and chromium are two of the most common metals found in wastewater discharge of petrochemical plants and also prevalent in run-off wastewater discharge from other industrial sites [1]. The effluent from these industries contains hexavalent chromium, Cr(VI), at concentrations ranging from tenths to hundreds of mg/L [2]. Water is the most commonly used cooling fluid for removal of unwanted heat from heat transfer surfaces. At present, some of the demand for better utilization of limited water supplies is supplied by recirculating cooling water systems at central utility stations; chemical, petrochemical, and petroleum refining plants; steel and paper mills; and all other types of processing plants [3].

Open recirculating cooling water systems continuously reuse the water that passes through the heat transfer equipment. However, these systems produce corrosion, scaling and micro-biological growth due to operation of these systems at high temperatures, for a long time and in the presence of high concentrations of dissolved solids.

Inhibitors are added to water cooling systems to alleviate these problems. Many heavy metals, particularly chromate, are standard corrosion inhibitors of choice and have a long history of successful commercial use due to their excellent effectiveness over a wide range of conditions.

Removal of excess heavy metal ions from wastewater is essential considering their extreme toxicity for aquatic life and humans [4]. For instance, Cr(VI) is considered by the International Agency for Research Cancer as a powerful carcinogenic agent that modifies DNA transcription processes causing important chromosomal aberrations. The National Institute for Occupational Safety and Health recommends that levels of Cr(VI) in water should be reduced to 10^{-3} mg/m³. Copper and its compounds are ubiquitous in the environment and are thus found frequently in surface water. Copper-bearing

mining wastes and acid mine drainage add significant quantities of dissolved copper into wastewater. Additional potential sources of copper-bearing wastes include plating baths, the fertilizer industry, paint and pigment industry, and municipal and storm water runoff [2,5]. Consequently, removal of heavy metals from industrial wastewater is a research topic of great interest.

Heavy metal ions from wastewater are commonly removed by chemical precipitation, ion exchange, reverse osmosis and uptake by micro-organisms [6,7]. Treatment methods differ depending on the conditions of the process and properties of wastewater. These methods have some disadvantages such as unpredictable metal ions removal, difficult precipitation and the necessity of extreme caution for their disposal. On the other hand, chemical precipitation is advantageous due to its speed and low operation costs.

Many chemicals in various forms can be applied in wastewater treatment to aid in sedimentation, nutrient removal, pH adjustment, odor control, disinfecting and sludge conditioning [8]. Chemical treatment is used for enhanced sedimentation, nitrogen, phosphorus, heavy metal removal and pH adjustment. The most widely used method for removing copper is precipitation as insoluble hydroxide at alkaline pH.

In this study ferrous sulfate and lime Ca(OH)₂ were used for pH adjustment and conversion of Cr(VI) to Cr(III) and Cr(III) precipitation, respectively.

2. Materials and methods

2.1. Chemicals

All primary chemicals used were of analytical reagent grade. HCl, HNO₃, NaOH, H₂SO₄, Na₂CO₃, Ca(OH)₂, 1,5-diphenylcarbazide, sodium sulfate, chromium, acetone and copper (II) were purchased from Sigma. Methyl orange and

phenolphthalein indicators were purchased from Merck.

2.2. Pilot-scale set-up

In order to evaluate the efficiency of precipitation of copper and chromium by chemicals, a pilot system including three tanks for storage, reaction and sedimentation were constructed as follows:

- storage tank: A stainless steel tank with 80×50×100 cm dimensions equipped with a 3/4" (1.89 cm) valve used for discharging effluent to the reaction tank
- reaction and sedimentation tanks: two cylindrical 60-L polyethylene tanks equipped with mixer, pH meter, chemical dosing pump and polyethylene pipe and connections.

2.3. Copper removal

Samples for a copper removal experiment were taken randomly at three different times. Properties of these samples are presented in Table 1. Samples A, B, and C were tested with the Jar test and at pilot scale. Samples containing ammonia were aerated for 5 h at 70 L/min before removal of copper. In jar scale, Ca(OH)₂, NaOH and Na₂CO₃ were separately added to reaction mixtures of samples A and B to adjust the pH of the mixtures at different values. Next, the sample was mixed at 160 rpm for 10 min for coagulation and sedimentation was achieved after 2 h. In pilot scale, a similar procedure was employed except that the reaction mixture of sample C was transferred to a sedimentation tank and left for 2 h. Prior to determination of copper concentration, 5 ml of nitric acid was added for digestion to each liter of sample, and final pH was determined to be 2.0. The mixtures were next filtered through 0.45 μm Whatman filters (Germany) and filtrate was assessed with respect to copper concentration by atomic absorption equipment (Shimadzu atomic absorption spectrophotometric (AA-680)

Table 1

Initial characterization of samples for copper removal experiments

Parameters	Samples		
	A	B	C
Cu conc., ppm	39.16	20,021	48.51
Alkalinity in CaCO ₃ , ppm	1650	1700	1850
pH	10.5	10.8	10.8
Volume, L	20	20	200

equipment, Bacharach, Coleman model (35). A standard curve was prepared using 5, 10 and 15 mg/L copper-containing solutions.

2.4. Chromium removal

Chromium was removed by conversion of hexavalent chromium to the trivalent form using ferrous sulfate, the amount which was used was determined based on the stoichiometric coefficient. However, due to precipitation of a portion of iron (III) ions precipitated in hydroxide form, the amount of required ferrous sulfate determined was 2.5 times the amount determined by stoichiometric calculation. Conversion of chromium was performed at different pH values adjusted through the addition of sulfuric acid. Chromium precipitation was next achieved by the addition of 4% lime and at different pH values and parameters such as Cr(III) and lime consumption and physical condition such as color were measured at each pH value to determine the optimum pH. The described procedure was also performed for 4% caustic soda instead of lime, and the results were compared.

In addition, the volume of sludge produced for both precipitating chemicals was determined by collection of 25-ml samples of each reaction mixture and sedimentation after 4.5 h. The specifications of the initial sample are given in Table 2.

Table 2
Initial properties of samples for chromium removal experiments

Parameters	Samples		
	A	B	C
Total alkalinity	Nil	Nil	Nil
TAC, ppm	36	33	35
pH	7.6	7.3	7.4
CrO ₄ ²⁻ , ppm	22.2	20.1	30

3. Results and discussion

Table 3 shows the effect of aeration on lime consumption and total alkalinity. Since the major reason for alkalinity in samples is the presence of large amounts of ammonia, its removal through aeration strongly reduces alkalinity. As depicted in Table 3, aeration has a marked effect on the amount of lime consumed for precipitation of copper ions, such that there is a fourfold decrease in lime consumption after aeration. Results of the Jar test for the removal of copper through adding lime followed by mixing and sedimentation are shown in Table 4. As can be observed, maximum efficiency in copper precipitation takes place at pH 11.5–12.0. The same experiment was performed with sample B (Table 5), the results of which confirm the previous data. More than 99% of copper was removed at pH 12.0 as depicted in this table. Fig. 1 shows the optimum pH (12) for minimum solubility of Cu(OH)₂ or maximum precipitation. Previous reports indicate that a concentration of copper compound in liquids increased at pH values less or more than 12.0 [9]. Another point to be considered is the advantageous effect of filtration on removal of small Cu(OH)₂ flocks (Fig. 2). To examine the effect of other alkalines such as NaOH on the removal of copper, the mentioned procedure for lime was performed with NaOH instead, and the results are illustrated in Table 6. Similar results were

Table 3
Effect of aeration on lime consumption to reach pH value of 12.0

Parameters	Before aeration	After aeration
Initial pH	10.5	9.5
TA, ppm	1650	168
Lime consumption, mg/L	6000	1500

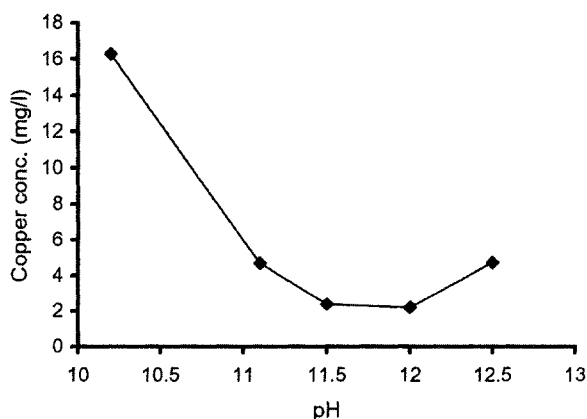


Fig. 1. Copper concentration change vs. pH by addition of lime to sample B.

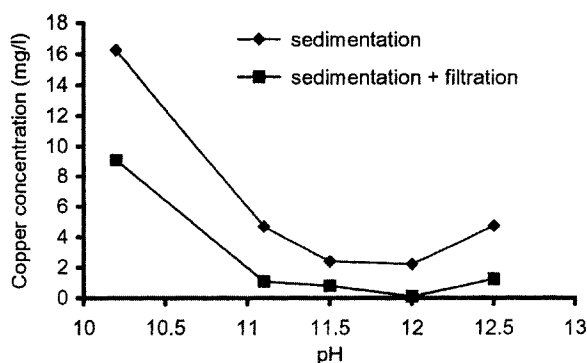


Fig. 2. Effect of filtration on copper concentration in lime precipitation operation.

obtained when NaOH was used to precipitate copper. Maximum precipitation occurred at pH 12.2 showing more than 95% efficiency in Cu(OH)₂ precipitation. Again filtration was more

Table 4
Copper concentration, pH change and lime consumption for sample A (initial cu conc. = 48 mg/L)

Parameters	Container				
	1	2	3	4	5
Lime consumption (mg/lit)	100	200	400	800	1800
pH	10	10.2	10.8	11.5	12
Cu conc. ^a , mg/L	4.92	4.82	2.69	0.63	0.36

^aCu concentration in supernatant after 2 h of sedimentation.

Table 5
Copper concentration, pH change and lime consumption after aeration for sample B (initial cu conc. = 20.021 mg/L)

Parameters	Container				
	1	2	3	4	5
Lime consumption, mgL	200	502	1000	2000	3200
pH	10.2	11.1	11.5	12	12.5
Cu conc. ^a , mg/L	16.28	4.69	2.40	2.21	4.75
Cu conc. ^b , mg/L	9.09	1.09	0.801	.0101	1.24

^aCu concentration in supernatant after 2 h of sedimentation.

^bCu concentration in supernatant after sedimentation and filtration.

Table 6
Copper concentration, pH change and NaOH consumption after aeration for sample B (initial cu conc. = 20.021 mg/L)

Parameters	Container				
	1	2	3	4	5
NaOH consumption, mg/L	440	672	1336	2632	7330
pH	11.2	11.6	12.2	12.5	12.7
Cu conc. ^a , mg/L	8.49	6.83	4.52	6.29	15.8
Cu conc. ^b , mg/L	2.088	1.254	0.994	1.525	4.705

^aCu concentration in supernatant after 2 h of sedimentation.

^bCu concentration in supernatant after sedimentation and filtration.

efficient for the removal of copper. The Jar test was scaled up to the pilot system operated on sample C with an initial copper concentration of 48 mg/l, results of which are given in Table 7. As

can be observed, similar results for optimum pH of precipitation were obtained in the pilot system as well. Maximum copper precipitation was seen at pH 12.1 and after filtration. As the operation

Table 7
Copper concentration, pH change and lime consumption in pilot system (initial $\text{Cu}(\text{OH})_2$ conc. = 48 mg/L)

Parameters	pH		
	11.6	12.1	12.5
Lime consumption, mg/L	100	135	170
Cu conc. ^a , mg/L	2.99	1.66	3.12
Cu conc. ^b , mg/L	1.25	0.65	1.72

^aCu concentration in supernatant after 2-h sedimentation.

^bCu concentration in supernatant after sedimentation and filtration.

was continued, change in wastewater color from blue to colorless and turbidity was markedly reduced resulting in almost clean water.

Similar finding have also been reported by others [6]. Table 8 shows the results of copper precipitation in the pilot-scale system by NaOH, indicating the optimum pH of 12 leading to maximum precipitation. However, a comparison of copper concentrations in the supernatant after 2 h of sedimentation in samples precipitated by lime and caustic soda shows that, due to the small size of copper compounds formed by the addition of NaOH, the concentration of copper in the samples precipitated by NaOH is higher than samples affected with lime. Nevertheless, filtration removed these small-sized flocks, and the end results were even more efficient compared with the lime system.

Sodium carbonate was also evaluated with respect to its copper removal ability (Table 9). As can be observed in this table, the addition of sodium carbonate increased the pH to 10.3. Further addition of carbonate did not have any effect on pH increase (Containers 1–3). HCl was added prior to carbonate to containers 4–6 to reduce the pH. Nevertheless, further addition of carbonate could only increase the pH to 9.5 in these containers. It is evident that the carbonate method has a poor performance on pH adjustment

Table 8
Copper concentrations and pH changes with NaOH addition for pilot (initial $\text{Cu}(\text{OH})_2$ conc. = 48 mg/L)

Parameters	pH		
	11.4	12.0	12.5
Caustic soda (33%) consumption 30 ml/L	14.5	25	40
Cu conc. ^a , mg/L	8.27	4.55	6.86
Cu conc. ^b , mg/L	2.63	0.53	1.21

^aCu concentration in supernatant after 2-h sedimentation.

^bCu concentration in supernatant after sedimentation and filtration.

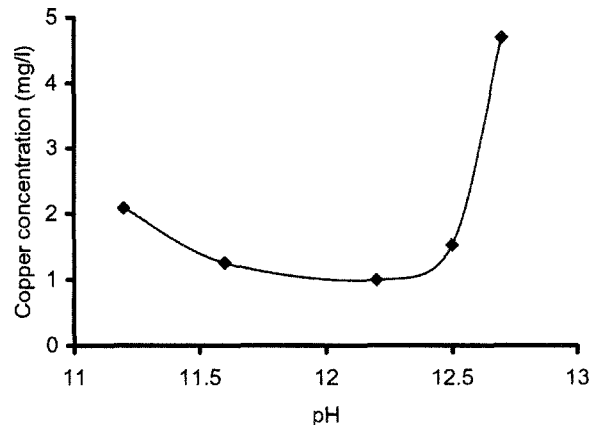


Fig. 3. Optimum pH for copper removal by NaOH.

and copper removal compared with hydroxide methods (Fig. 3).

Ferrous sulfate was used for reduction of Cr(VI) to Cr(III) (Table 10). The maximum conversion took place in pH values between 2.0 and 2.3. In this reduction Cr(III) appeared as both $\text{Cr}_2(\text{SO}_4)_3$ and free forms. When this reaction was performed at low pH, the concentration of $\text{Cr}_2(\text{SO}_4)_3$ was reduced, and Cr(III) was mostly present in its free form, which is more desirable. The same results are presented in Fig. 4, clearly indicating that a reduction of Cr(VI) to Cr(III) is mostly effective in the pH range of 2 to 2.3. The

Table 9
Effect of sodium carbonate on the copper removal

Parameters	Container					
	1	2	3	4	5	6
Sodium carbonate consumption, mg/L	400	800	1200	800	1400	2600
pH after sodium carbonate addition	10.0	10.2	10.3	8.5	9.0	9.5
Cu conc after filtration, mg/L	15.45	14.54	14.2	24.87	16.21	17.44

Table 10
Effect of ferrous sulfate addition on reduction of Cr(VI) for samples A, B and C

pH	Cr(VI), ppm			Cr(III), ppm			CR(VI) to Cr(III) conversion, %		
	A	B	C	A	B	C	A	B	C
4.6	5.0	4.9	6.8	6.2	5.1	7.9	27.9	25.3	26.3
4.0	2	1.8	1.9	10.8	9.5	13.8	48.6	47	46
3.5	1.4	1.2	1.5	14.1	12	18.6	63.5	59.7	62
3.0	0.6	0.6	1.0	16	14.9	22.3	72	74.2	74.4
2.5	0.4	0.3	0.5	18.4	16.9	25.5	83.8	84.1	85
2.3	0.02	0.02	0.03	19.7	17.6	26.7	88.7	78.5	89
2.0	0.01	0.03	0.01	20	18	27	90.1	89.7	90.0

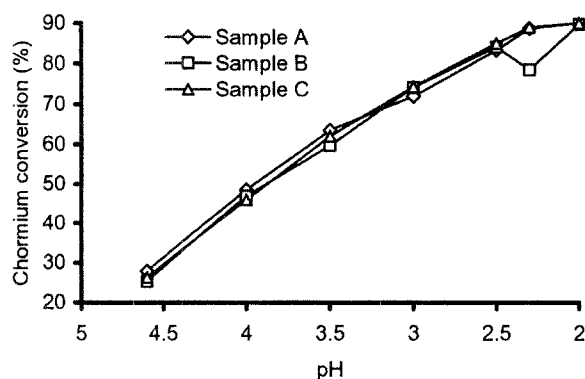


Fig. 4. Effect of ferrous sulfate on reduction of Cr(VI) for samples A, B and C.

next step in removing chromium was sedimentation of Cr(III) by alkaline methods using lime and caustic soda, results of which are presented in Table 11. The concentration of Cr(III) was

measured after alkaline mixing, coagulation and complete sedimentation in 2 h. Results indicate that the solubility of Cr(III) was very high at pH 7.5, and approximately all the Cr(III) was found in the solution and none was present in precipitated materials. However, a minimum solubility of Cr(OH)₃ was observed at the pH range of 8.0 to 8.5. Based on the obtained data, the optimum pH for precipitation of Cr(III) was found to be 8.7. An increase in TA and TAC following the addition of lime and caustic soda in samples A, B and C (Table 12) is caused by the presence of OH⁻ ions. This was also observed in an increase in pH. It was also observed that the volume of sludge in the lime addition process was more than the volume formed in the caustic soda operation. The volume of sludge for 30 L of waste after mixing and sedimentation was about 2.4 L in the lime operation, whereas in the latter the

Table 11
Effect of alkalines (lime and caustic soda) on Cr(III) concentration (ppm) for samples A, B and C

pH	Cr(III) concentration, ppm					
	Cu(OH) ₂			NaOH		
	A	B	C	A	B	C
7.5	20	18	27	19	18	26
8.0	3.6	3.2	4.9	4.2	3.8	5.4
8.5	0.08	0.07	0.12	0.1	0.09	0.2
8.7	0.04	0.03	0.06	0.05	0.04	0.08
9	0.09	0.08	0.14	0.13	0.1	0.18
9.5	0.26	0.2	0.4	0.3	0.3	0.4
10	4.7	3.8	7.5	5.6	5.2	7.9

Table 12
Comparison of initial and final properties for samples A, B and C following the addition of alkalines

Parameters	Initial value			After Ca(OH) ₂ addition			After NaOH addition		
	A	B	C	A	B	C	A	B	C
TA, ppm	Nil	Nil	Nil	12	10	17	10	8	15
TAC, ppm	36	33	35	40	35	48	35	32	45
pH	7.6	7.3	7.4	8.7	8.6	8.7	8.6	8.6	8.6
CrO ₄ ²⁻ , ppm	22.2	20.1	30	0.01	0.03	0.01	0.01	0.02	0.01

volume was 1.6 L. Furthermore, sedimentation in lime process was faster than that in the soda operation.

4. Conclusions

The present study demonstrated that lime is a cheap and excellent chemical for efficient coagulation and precipitation of copper and chromium ions from wastewater. The optimum pH for copper and chromium precipitation using lime are 12.0 and 8.7, respectively. The results showed that the optimum conversion of Cr(VI) to Cr(III) was achieved at pH 2.2. Due to the aeration effect, the alkaline consumption for pH adjustment was reduced.

The use of lime for the treatment of petrochemical wastewater containing heavy metals is gaining attention as a simple, effective and economical method of wastewater treatment. Lime is plentiful, inexpensive and readily available.

Finally, the results show that filtration has a critical role in the removal of small flocks of heavy metal compounds that are not easily sedimented.

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