

Removal Of Chromium From Electroplating Wastewater By Simple Chemical Treatment And Ion Exchange

Mahmood M. Barbooti¹ Nagham A. Ageena** & Manal A. Tooma**

Received on:24/3/2008

Accepted on:29/6/2008

Abstract

Wastewater from metal plating works was treated with lime - water suspensions at relatively small concentrations with continuous stirring. Experiments were designed to allow a direct contact of lime suspension with the wastewater constituents for a period of time followed by settling and filtration through a sand filter. The heavy metal content could be precipitated efficiently from the mother liquor by two mechanisms: reaction with calcium ions to yield calcium chromate and the precipitation of the chromium hydroxides in the alkaline medium. Various parameters were studied to reach the optimum conditions for the removal of chromium from the wastewater. It appeared that reasonable removal of chromium (80 – 85%) could be achieved with lime: wastewater ratio of 40 mg/ L and 50 min contact time. After the removal of most of the chromium from wastewater, the level of the pollutant needed to be reduced to the acceptable limit by passing water through ion exchange column. This final treatment gave treated water samples with chromium levels as low as 0.6 - 1.3 mg/L.

CaO : (80-85 %) .50min (40mg/L)
(0.6-1.3 mg/L)

Introduction

Chromium and its compounds are used for various purposes like the manufacturing of

stainless steel, staining glass, tanning leather, anodizing aluminum, and brick formation. Electroplating is among the industries in which

chromium is used widely. In addition to decorative plating, hard chrome plating is used to improve the surface properties. Chromium exists in all oxidation states from (III) to (VI) but only the trivalent and hexavalent Cr compounds are of practical importance. The Cr(III) is usually the most stable state of chromium in nature and its salts are generally insoluble in water in the pH range of 4-11. The Cr (VI) is a known carcinogen and a designated hazardous pollutant [1]. Contrarily, trivalent chromium in small doses is essential for good health. Lack of chromium in a human is associated with certain types of diabetes, cardiovascular diseases, and nervous system disorders [2]. In general, Cr(VI) compounds are more toxic than Cr(III) since it can pass through the cell membrane with greater ease and its compounds are also more oxidative. The toxic manifestations of chromium exposure are apparently determined by the bioavailability and biochemical interactions of specific chromium compounds, rather than by chromium per se [3]. Chromium is present in the wastes from five of the main steps in the electroplating process, namely, etching, pre-dip chrome, chrome tank, drag and the final rinse [4]. Sludge contaminated with chromium and other metals are known to be toxic. They are also known to be a valuable commodity.

The wastewater treatment methods vary depending on the pretreatment limits placed on incoming effluent. In most cases the characteristics of the wastewater will be high in metals, cyanides, and pH. In chrome plating, the use of a coagulant or flocculent, such as inorganic salt or polymer will create a solid sludge containing the metals which settles at the bottom of the holding container. The resulting hydroxide sludge will then be dewatered and sent for disposal. The sludge was used to recover (extract) metals to improve the economy of the method. Thus, the metallic waste turns from a hazardous landfill item to useful metal, avoiding the cost of dumping into a hazardous landfill, while supporting the cost of purchasing virgin chromium.

Chromium is reduced chemically prior to treatment or recovery. Many reduction methods

are used and it was concluded that, when a method is viable in one case they are marginally acceptable in another [1, 2]. Jing et al [5] described the preparation of nano-particles for the adsorption of heavy metals from wastewater utilizing the highly modified surface area of the particles.

Chemical precipitation using lime or magnesia is another attractive method for the removal of chromium from industrial waste-water [6, 7]. Huang [8] used a fluid sand bed with a simultaneous injection of carbonate solution to raise pH to induce nucleated precipitation of Cr on the sand surface. The removal efficiency was 65 to 75% for Cr (VI). Two mechanisms are involved, general, 25% of the metal removal is attributed to co-precipitation (forming CuCrO_4) and the remaining 75% by adsorption.

Ion exchange systems generally demonstrate the highest hydraulic capacity per dollar invested. Ion exchange units employ cylindrical columns of short or tall design, filled with polymeric beads with a chemical affinity for either cations (metallic) or anions. As the rinse is passed through the column packing (resin bed) the desired ions are extracted from the flow together with other ions of similar charge, which may also be present in the stream. The flow must eventually be interrupted and the resin bed regenerated. When ion exchange is applied to metal recovery, the metal values obtained from the regeneration process may not be suitable for return directly to the plating bath. Concentration and pH adjustment are frequently required before reuse. Much of the regeneration rinse waters are too dilute or otherwise unsuitable for reclaim; they will often require treatment in the wastewater system prior to discharge.

Experimental

Laboratory Experimental Units:

The experimental unit for the chemical treatment consists of a water bath of (60× 40 × 16 cm); a magnetic stirrer; a 3-neck round bottom flask of 1-L capacity, a thermometer and magnetic stirrer. The water bath was

employed only for studying the effect of temperature on the removal efficiency and removed in others. Thus, it was not shown in the schematic diagram of the experimental set up.

The lab scale sand filter was prepared by placing screened and washed red sand (Kerbala Sand) in a 15-cm wide Büchner funnel over beds of fine and coarse gravels. The washing of the sand was essential to remove soluble sulfates from the sand. The washings were tested by treatment with barium chloride until being free from soluble sulfates (no barium sulfate precipitate). However sand filter designs are very common in industry and companies utilize large area of land to construct the filter. The bottom of the filter is tilted to facilitate the flow of the filtered water towards on of the ends of the sand filter facility to end up with a pipe leading the water to the next stage of purification.

The filtrate was further purified by passing through columns packed with cation and anion exchange resins. The purification conditions are: Column length, 80 cm; column diameter, 3.0 cm; resin type, Duolite A-20 and flow rate, 1.0 L/min.

Chemical Analysis:

The determination of chromium in the water samples were carried out by atomic absorption spectrophotometer model SP 9-01 supplied from Buck, England (Ministry of Environment, Central Laboratories, Baghdad). The operating conditions were as specified by the manufacture. The chemical composition of the solid products was done by X-ray diffraction using a Philips P.W- 1840 Diffractometer (Material Research Center, Jadiriya, Baghdad). The activation energy was 40 KV at 20 mA. The Cu- α line was used (1.54 Å). For pH measurements, the universal pocket meter multi line P4, which consists of a pH combined electrode with temperature probe Sen Tix 41 was used.

Procedure

For the optimization, 500-mL aliquots of Wastewater were placed in a reaction vessel and various portions of lime water suspension of increasing volume were added and stirring

initiated for various periods of time. Meanwhile, samples of the water were taken at 10-min intervals and saved for chromium analysis. After 80 min, the stirring was stopped and the samples were allowed to settle for 30 min. A yellow precipitate was formed and the color of the solution was greatly reduced. A sand filter was prepared in a Buchner funnel to aid the removal of the precipitate. The yellow precipitate was entirely collected on the surface of the sand and the clear solution was taken for analysis and to be further purified by ion exchange method.

Results And Discussion

Preliminary experiments

Many preliminary experiments were carried out to reach the best performance within the designed work. The lime - water suspensions was among the important points studied. When the lime was suspended in water immediately before addition to the wastewater, the removal of chromium from wastewater was limited. Meanwhile, lime was suspended in water and stirred for reasonable time (e.g. 15-30 min) before addition to the wastewater. It gave improved chromium removal results. The previous soaking and stirring of calcium oxide in water resulted in complete disintegration and of the lime particles and rather certain degree of swelling. This expanded the surface area of the particles. The higher surface area of the particles improves both the dissolution of lime and the chemical reactivity of calcium hydroxide produced therein [9].

The process of removal and recovery of chromium values from the electroplating factory wastewater comprised contacting the acidic solution containing sulfate ion and trivalent chromium ion with at least about 4 millimoles of CaO against 3 millimoles of Cr(III). This aided acid neutralization to a pH value adequate for the formation of an amorphous, dense solid, grainy, easily settable precipitate. The water remaining after separation of the precipitate contains less than 50 mg/lit chromium which is close to some reported results [10]

The wastewater was treated with the lime-water suspension at various ratios of CaO

suspension to the wastewater ratios to reach the optimum amount of the lime necessary for the best removal of chromium. The results of the first set of experiments are given in Table 1. The best of the set was the 200 mg/L, where the chromium content of wastewater could be reduced to 25-30% of the original value. Fig. 1 shows the profile of chromium contents with mixing time at the high lime: wastewater ratios. After 40 min of mixing the 200 mg/L system attained the chromium level given by the 600 mg/L after 60 min. Thus, the increase of CaO contents lowered the stability of the precipitates. Such an effect is related to the increase of pH of the solution. The lowest (200 mg/L) ratio gave the best chromium removal possibility within this range. The high CaO content is expectedly associated with increase of pH of the solution. Consequently the solubility of the chromium hydroxide increases and hence the removal efficiency of chromium is lowered [2]. The mixing time is important in determining the removal efficiency. The chromium concentration decreases slowly down to the lowest value after 50 minutes of mixing and remains almost constant. Thus, it was not necessary to continue the mixing further.

Another set of experiments was carried out using low (≤ 100 mg/L ratios). The results are shown in Table 2. With these smaller ratios of lime: wastewater the removal could be highly improved and the chromium contents of wastewater were reduced down to 15-18%. Fig. 2 shows the effect of treatment time on the chromium removal efficiency from WW using the low lime: wastewater ratios. It appeared that the removal efficiencies were much better than those obtained in the high range treatment. The chromium contents of the treated wastewater decreased down to about 15% of the original value. The best removal efficiency can be obtained at a ratio of 40 mg/L. Thus, higher lime contents do not improve chromium removal. The mechanism of the removal, therefore, is not only a precipitation process. The pH of the effluent increases slowly with increasing the addition of CaO to 200 mg/L. The PH increased up to a value of 7.35 at 30 °C and a mixing period of 50 min.

Two factors seem to act on the removal mechanism: precipitation as chromium hydroxide and the precipitation as a calcium chromate compound. The chromium hydroxide solubility is affected by the pH of the solution [4].

At the end of mixing (after 80 min.) the chromium removal efficiency was plotted against the lime: wastewater ratio and the results are shown in Fig. 3. It is clear that the best removal efficiency occurs between 30 and 80 mg CaO / L WW and the highest was attained at 40 mg/L. Lime amounts lower than 40 mg/L were not enough to bring about the required stoichiometry of the formation of calcium chromate nor allowed pH to raise to the level required for the precipitation of $\text{Cr}(\text{OH})_3$. Meanwhile, lime amounts higher than 100 mg/L means that CaO exceeds the stoichiometric value to give the chromate and at the same time raises the pH to much high values at which the $\text{Cr}(\text{OH})_3$ is soluble returning thereby chromium to solution [2].

Filtration

Water emerging from the sedimentation basin is routed to the top of the filtration sand bed. The filtration unit traps those particles that did not settle in the sedimentation basin (because they were too small) or did not have sufficient time to settle and were carried along with the effluent out of the precipitation basin. Precipitates of faint yellow sludge containing calcium chromate and chromium hydroxide settle and stick on top of the sand bed. Water passes through the bed free of the metal ions load and hence became colorless. The first appearance of the filtered water reflects how successful the treatment was after the designed time. Filtration completes the metal treatment process. The pH of the water discharged from the sand filter was higher than the acceptable value for disposal and thus it has to be adjusted with calculated amount of mineral acid to be reused.

Depending on the pH of the reaction, the basicity of the chrome salt produced will vary:

At pH values less than 2.0, $\text{Cr}_2(\text{SO}_4)_3$ is formed;

At pH 3.0 - 4, $\text{Cr}_4(\text{OH})_6(\text{SO}_4)_3$ is formed;

At pH 6.5, $\text{Cr}(\text{OH})_3$ is formed.

At pH (8.0 - 9.9), $\text{Cr}(\text{OH})_3$ is virtually insoluble [11].

As filtration progresses and more metal hydroxides and other solids clog the filter material, pressure drop through the filter rises and some solids may pass through the filter. When either of these two situations occurs, the filter must be backwashed by reversing the flow of water through the filter. This backwash water is sent back to the rapid mix tank for mixing with the incoming water since it contains a significant concentration of solids from the dislodging that has occurred.

The filtrate, therefore, showed some chromium contents which is still higher than the permissible limits. The final chromium removal was aided by ion exchange purification. After passing through the ion exchange columns, the atomic absorption analysis of the samples showed chromium levels of 0.6 - 1.3 mg/L. However, only minor differences could be noticed in the results of analysis of the wastewater samples treated by the various amounts of lime-water suspension.

Sludge Treatment

The solids produced in the sedimentation stage (and possibly solids from filtration) are denoted as a sludge and periodically removed. In diatomaceous earth and fiber filters, the entire filter media (diatomaceous earth, filter cartridge) is dumped with the captured metal hydroxide solids. This sludge may be sent to a dewatering stage to remove excess water and leave only solids. The water from the dewatering stage may not be completely free of metals and should be piped to the rapid mix tank.

The sludge now contains the precipitated metal hydroxide solids, made up of identifiable quantities of heavy metals, which are regulated according to state and federal guidelines. The solids produced from heavy metal wastewater treatment must then be disposed of as a hazardous waste.

Incomplete removal of chromium is not a drawback of the method but a result of the presence of substances in the wastewater.

Compounds such as cyanide or ammonia can inhibit precipitation of metals, and limit their removal to the point where discharge limits can be exceeded [12].

However, the present, rather simple, treatment compares well with the results of Rao [13], who reported an efficient recycling of unused chromium as well as water with electro-dialysis technique using Selemion AMV and CMV membranes and a prototype electro-dialysis cell. Besides, it resulted in improved sludge properties in comparison with the system adopted by the European countries [14] which uses soda ash or some other alkali is added to promote the combination of the tanning agent with skin substance.

Conclusions

1. Treatment of electroplating wastewater with lime is a simple and cost effective method to strip off chromium in a sand filter.
2. During the chemical treatment, the operation pH increases and aids the removal efficiencies to exceed 85% which is higher than the reported removal efficiency [10].
3. Two mechanisms are found to contribute to the chromium co-removal: reaction with CaO to give insoluble CaCrO_4 , and precipitation of $\text{Cr}(\text{OH})_3$ due to increase of pH.
4. The presence of other substances in the wastewater of electroplating bath like cyanide and ammonia retarded the precipitation of the metal ions completely.
5. Further treatment with ion exchange resins is necessary in order to make the treated wastewater comply with the effluent standards.

References

- [1]. Nunno, T.; Palmer, S; Arienti, M. and Breton, M., "Waste Minimization in the Printed Circuit Board Industry - Case Studies", US Hazardous Waste Eng., R & D EPA/600/S2-88/008 Mar. 1988
- [2]. Ayres, D. M., Davis A. P. and Gietka, P. M., "Removing Heavy Metals from Waste-

water", Engineering Res. Cent. Rep., Univ Maryland, Aug. 1994

[3].Chang, L. Y., Chrome Reduction and Heavy Metal Removal from Wastewater - A Pollution Prevention Approach", WM'01 Conference, February 25-March 1, 2001.

[4].Anderer, F., Yang, D and Lee, J. H., Hazardous Waste Management, in "The Chromium Plating Process", Illinois Inst. Technol., Chicago, Illinois 60616.

[5].Jing, W. U.; Manchi, L. O. and Chen, G.H., US Pat. 60/752,883, 23 Dec 2005.

[6].Barbooti, M. M. ; Zablouk, M. A. and Al-Zubaidi, U., "recovery of chromium from waste tanning liquors by magnesium oxide", in press.

[7].Ismaeili, A; Alireza, M. and Reza, V., Amer. J. Appl. Sci., 2(10) (2005) 1471-3.

[8].Huang, J. C. , Nucleated Precipitation for Heavy Metal Removal and Resource Recovery, Science Council of Asia, May 12th, 2005

[9].Barbooti, M. M.; Al-Rikabi, B.; Ramadhan, H., and Mahmood, S., Proc. 1st Conf. Chemical Industries, Baghdad, 2002.

[10]. Hemming, D., Hahn, R.E., Robinson J.R. and John, W., Recovery of chromium values from waste streams by the use of alkaline magnesium compounds. U.S. Pat. No. 4108596, 1978.

[11]. Eckenfelder, W. W., Jr., "Industrial Water Pollution Control", McGraw-Hill, Inc., 1966.

[12]. Cotton, F.A. and Wilkinson, G., "Advanced Inorganic Chemistry", 4th Edn. Wiley, 1980.

[13]. Rao, J. R., J. Membrane Sci., 469 (2002) 215-224.

[14]. Poncet, T: "Sludge Landfill Model Site Manual", UNIDO, Vienna, 1978.

Table 1: Variation of chromium concentration in the treated wastewater at different lime concentrations (HIGH) with treatment time

Lime concentration, mg/L	Treatment time, min.								
	0	10	20	30	40	50	60	70	80
200	343	230	172	159	143	127	115	115	115
400	343	250	210	179	152	135	121	121	121
600	343	283	240	198	185	167	143	143	143

Table 2: Variation of chromium concentration in the treated wastewater at different lime concentrations (LOW) with treatment time

Lime concentration, mg/L	Treatment time, min.								
	0	10	20	30	40	50	60	70	80
20	343	190	155	140	121	114	100	100	100
40	343	128	105	88	78	68	63	53	53
60	343	180	168	151	138	120	106	87	87
80	343	172	151	139	128	116	100	78	78
100	343	160	147	128	117	95	86	67	67

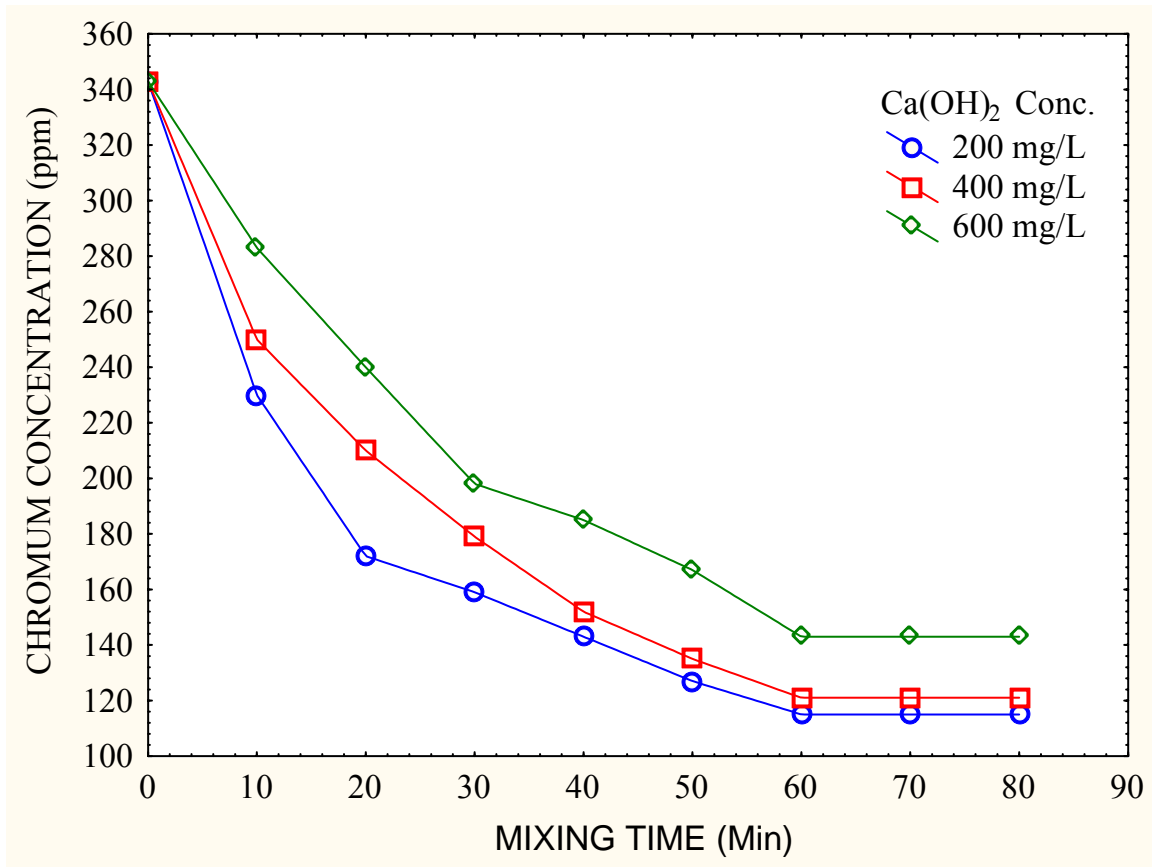


Figure 1: Chromium removal profiles for the high Lime : WW range.

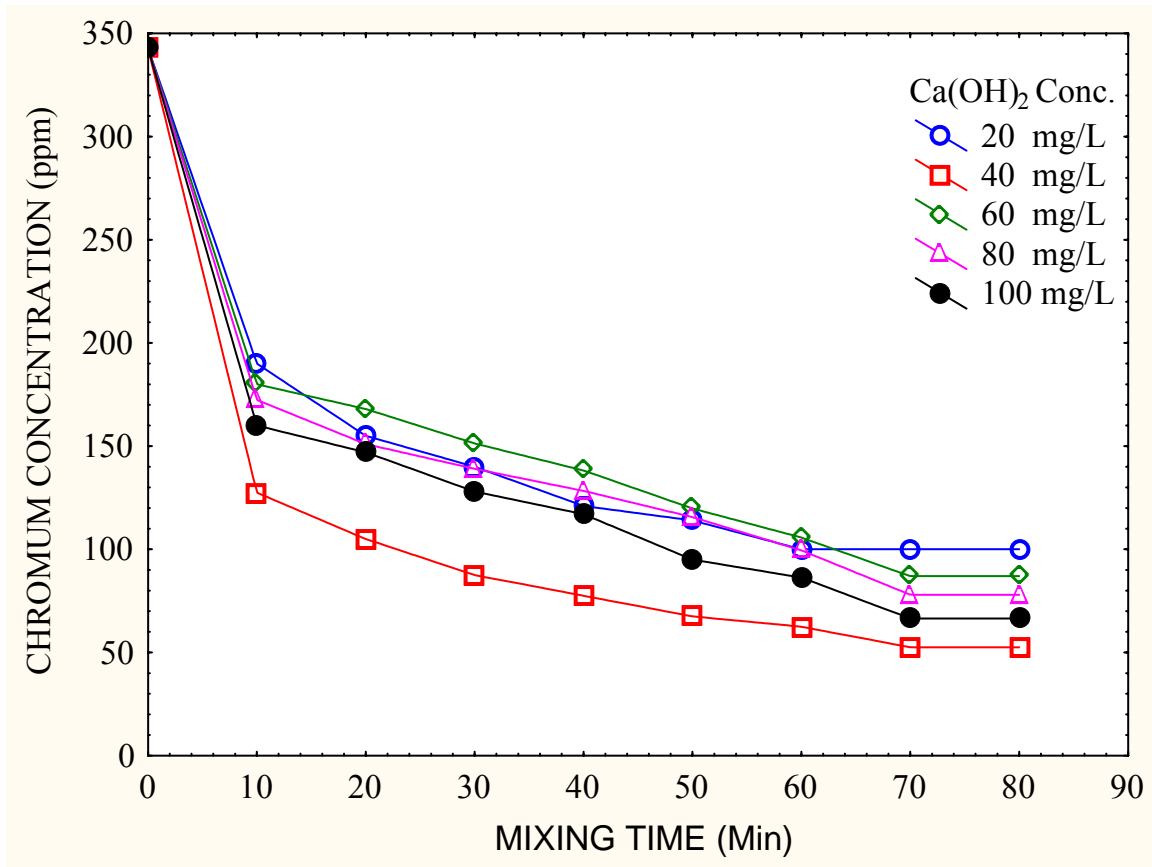


Figure 2: Chromium removal profiles for the low Lime : WW range.

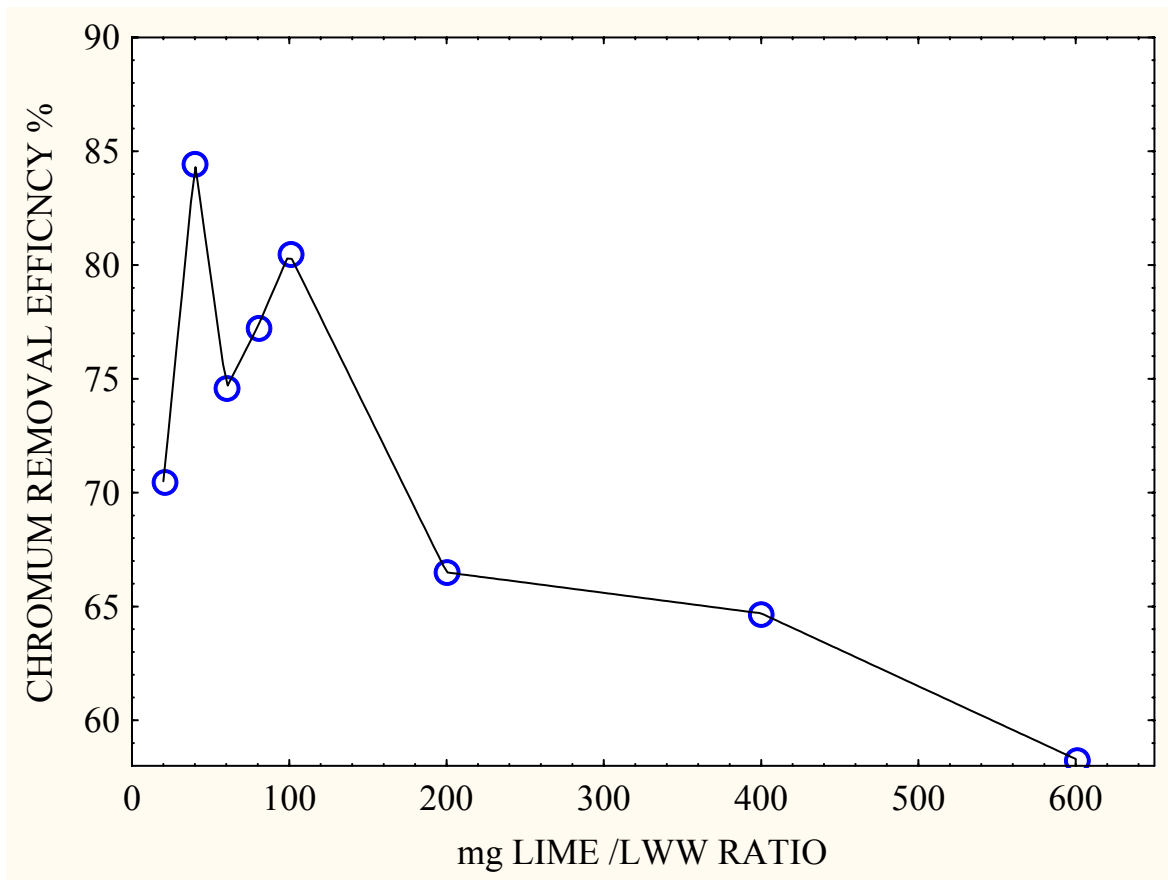


Figure 3: Chromium removal efficiency at various Lime: WW ratios.