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# Treating Waste with Waste : Utilization of Iron Powder for the Reduction of Chromium ( $\text{Cr}^{6+}$ ) in Metal Plating Industry Liquid Waste

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## Abstract

Metal plating industry waste is the main source of environmental pollution due to heavy metal chromium ( $\text{Cr}^{6+}$ ). The method commonly used in processing chromium metal waste ( $\text{Cr}^{6+}$ ) in industry is by means of reduction and coagulation. Chromium metal ( $\text{Cr}^{6+}$ ) is highly toxic because it is highly unstable compared to chromium ( $\text{Cr}^{3+}$ ). Therefore, chromium waste ( $\text{Cr}^{6+}$ ) must be reduced to chromium ( $\text{Cr}^{3+}$ ) before being discharged into the environment. The purpose of the study is to reduce the content of chromium ions ( $\text{Cr}^{6+}$ ) in liquid waste of the metal coating industry by the reduction and coagulation process using waste iron powder and calcium hydroxide. Liquid chromium waste ( $\text{Cr}^{6+}$ ) and iron powder waste are taken from the metal coating industry in Palur Karanganyar, Central Java. Iron waste is in the form of powder that comes from the sanding process that is no longer used. The parameters studied were the weight of iron powder, the addition of  $\text{H}_2\text{SO}_4$  2N, and the reduction time. The measurement of chrom ion levels ( $\text{Cr}^{6+}$ ) in all treatments was determined by UV-Vis Spectroscopy. The results of the study showed that the chromium level ( $\text{Cr}^{6+}$ ) of liquid waste of the metal coating industry was 749 mg/L. The optimum condition for reducing chromium ( $\text{Cr}^{6+}$ ) is to use 3 gr iron powder, 10 ml of  $\text{H}_2\text{SO}_4$  2N, and a reduction time of 7 minutes there is a decrease in chromium ( $\text{Cr}^{6+}$ ) levels by 100% with a chromium level ( $\text{Cr}^{6+}$ ) of 0 mg/L. This result meets the Regional Regulation of Central Java Province Number 5 of 2012 concerning Liquid Wastewater Quality Standards for the Metal Plating Industry which requires a maximum chromium level ( $\text{Cr}^{6+}$ ) of 0.1 mg/L.

**Keywords:** iron powder, chromium( $\text{Cr}^{6+}$ ), metal plating wastewater, reduction, coagulation

## Abstrak

Limbah industri pelapisan logam merupakan sumber utama pencemaran lingkungan akibat logam berat khrom ( $\text{Cr}^{6+}$ ). Metode yang biasa digunakan dalam mengolah limbah logam khrom ( $\text{Cr}^{6+}$ ) dalam industri adalah dengan cara reduksi dan koagulasi. Logam khrom ( $\text{Cr}^{6+}$ ) sangat beracun karena sangat tidak stabil dibandingkan dengan khrom ( $\text{Cr}^{3+}$ ). Oleh karena itu, limbah khrom ( $\text{Cr}^{6+}$ ) harus direduksi menjadi khrom ( $\text{Cr}^{3+}$ ) sebelum dibuang ke lingkungan. Tujuan penelitian adalah penurunan kandungan ion khrom ( $\text{Cr}^{6+}$ ) pada limbah cair industri pelapisan logam dengan proses reduksi dan koagulasi menggunakan limbah serbuk besi dan kalsium hidroksida. Limbah cair khrom ( $\text{Cr}^{6+}$ ) dan limbah serbuk besi diambil dari industri pelapisan logam di Palur Karanganyar, Jawa Tengah. Limbah besi berupa serbuk yang berasal dari proses pengamplasan yang sudah tidak terpakai lagi. Parameter yang diteliti adalah berat serbuk besi, penambahan  $\text{H}_2\text{SO}_4$  2N, dan waktu reduksi. Pengukuran kadar ion khrom ( $\text{Cr}^{6+}$ ) pada semua perlakuan ditentukan dengan metode Spektroskopi UV-Vis. Hasil penelitian menunjukkan bahwa penelitian adalah kadar khrom ( $\text{Cr}^{6+}$ ) limbah cair industri pelapisan logam adalah 749 mg/L. Kondisi optimum penurunan khrom ( $\text{Cr}^{6+}$ ) adalah menggunakan serbuk besi 3 gr, 10 ml  $\text{H}_2\text{SO}_4$  2N, dan waktu reduksi 7 menit terjadi penurunan kadar khrom ( $\text{Cr}^{6+}$ ) sebesar 100% dengan kadar khrom ( $\text{Cr}^{6+}$ ) 0 mg/L. Hasil ini memenuhi Peraturan Daerah Provinsi Jawa Tengah Nomor 5 Tahun 2012 tentang Baku Mutu Air Limbah Cair Industri Pelapisan logam yang mensyaratkan kadar khrom ( $\text{Cr}^{6+}$ ) maksimal sebesar 0,1 mg/L.

**Kata Kunci:** serbuk besi, krom(VI), limbah cair pelapisan logam, reduksi, koagulasi

## 1. Introduction

The metal coating industry is an industry that uses several chemicals. The chemicals used are metal solutions, so the waste produced is harmful to human health, both those directly involved with the activity, and those around the industry. One of them is chrome liquid waste. In the metal state chrome is not toxic but in the liquid state it causes cancer, corrosiveness and irritation[1][2][3][4][5][6][7].

Heavy metals cannot be broken down or destroyed. Heavy metals can enter the body of living things through food, drinking water and air. Heavy metals are harmful because they tend to accumulate in the body of living things. The rate of accumulation of heavy metals in the body is faster than the body's ability to dispose of them. As a result, their presence in the body is getting higher and higher and the longer it takes to have a damaging impact on the body[8][9][10].

Chromium (Cr) is a well-known heavy metal that has various applications in metal plating, leather tanning, metal corrosion inhibition, pigment production, textile industry, and wood preservation industry[2][3][5][6][7][11][12][13][14][15][16]. Chromium is stable in several valence states namely valence 3 ( $\text{Cr}^{3+}$ ) and valence 6 ( $\text{Cr}^{6+}$ )[17][18][19]. Chromium ( $\text{Cr}^{3+}$ ) is an important micronutrient in the biological activity of insulin, is relatively stable and has a low solubility in aqueous solution[20][21][22]. In contrast, chromium ( $\text{Cr}^{6+}$ ) is highly toxic, soluble, and active in water, classified as a potential carcinogen[23], mutagens[24], teratogens, and have acute toxicity to different biological systems[25][26][27][28][29][30]. The use of chromium in various industries has resulted in increasing amounts of chromium in the air, water and soil[31][20]. According to WHO, the maximum allowable limit of total chromium in drinking water is 50 ppb[32][33]. Meanwhile, according to Government Regulation No. 82 of 2001 concerning Water Quality Management and Environmental Pollution Control, the maximum acceptable limit for chromium ( $\text{Cr}^{6+}$ ) in drinking water is 0.05 ppm or 50 ppb[34].

Several techniques for chromium ( $\text{Cr}^{6+}$ ) removal such as precipitation[3][35][36][37], ion exchange[3][38][39], separation membrane[40][41][42], electrolysis[43][44], electrodialysis[37], bioremediation[14][30][38][45][46], adsorption[3][7][37][38][39][42], reduction, and coagulation[47][48] efforts have been made to remove chromium ( $\text{Cr}^{6+}$ ) in solution. Various efforts have been made to reduce chromium ( $\text{Cr}^{6+}$ ) ions, one of which is the coagulation process. In principle, coagulation is to agglomerate colloidal particles and suspended organic substances. The stages of this process are destabilization of colloidal systems, microfloc formation, and agglomeration. The effectiveness of the coagulation process is influenced by the type of coagulant, concentration, pH of the solution and the ionic strength of the solution. Coagulants used in the sewage treatment process can be natural coagulants or synthetic coagulants. Chemical coagulants commonly used as coagulants include alum, ferrosulfate, ferric chloride, zeolite, and others. This method is expected to reduce chromium ions ( $\text{Cr}^{6+}$ ) in the metal plating industry waste[2][3][47][48][49].

To reduce chromium ions ( $\text{Cr}^{6+}$ ) in this study using iron powder waste reductant. The iron powder waste used is in the form of powder derived from the sanding process in the metal coating industry process. Iron powder waste serves as a source of ferrous ions,  $\text{Fe}^{2+}$  which can be utilized to reduce chromium metal ions. ( $\text{Cr}^{6+}$ )[48][50][51][52]. Iron powder waste when dipped in a strong acid solution such as  $\text{H}_2\text{SO}_4$  [53][54][55], then the iron waste will release electrons. The strong acid added will serve a dual function, namely electron release and as a pH regulator. Iron waste is not too hard in texture, so that the release of  $\text{Fe}^{2+}$  can take place easily[7][47][50][56].

The general objective of this research is to reduce toxic and carcinogenic chromium ( $\text{Cr}^{6+}$ ) so as not to pollute the environment using iron powder produced from the metal plating industry followed by a coagulation process. The general objective can be achieved by answering the specific objectives, namely, 1) reducing and coagulating the content of chromium ( $\text{Cr}^{6+}$ ) after reduction with iron powder and coagulation with calcium hydroxide in the liquid waste of the metal coating industry, 2) knowing the content of chromium ( $\text{Cr}^{6+}$ ) before and after treatment with iron powder and coagulation using calcium hydroxide in the liquid waste of the metal coating industry.

## 2. Material and Methods

The tools used in this research are glassware, analytical balance, UV-Vis spectrophotometer. The materials used in this study were iron powder, 1,5-Diphenyl carbazide,  $\text{Ca}(\text{OH})_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , concentrated  $\text{H}_2\text{SO}_4$  made by Merck. Iron powder waste from the metal plating industry in Palur Karanganyar, chrome liquid waste, and mineralized water. Initial characterization of chrome liquid waste samples was carried out by taking 100 ml of chrome liquid waste from the metal plating industry, determining the concentration of chromium ( $\text{Cr}^{6+}$ ) using a Uv-Vis Spectrophotometer and measuring pH, color, and temperature.

### Sample Preparation

The samples used in the study were solid waste and liquid waste of the metal plating industry. Solid waste is iron powder left over from smoothing/sanding the coated iron, while liquid waste is water used for rinsing after chromium plating. The iron powder was cleaned of impurities, then filtered with a 40 mesh sieve size[57].

### *Physical Test and Determination of Chromium (Cr<sup>6+</sup>) Content of Liquid Waste from Metal Plating Industry*

Physical tests included organoleptical color and temperature measured with a thermometer, and pH tested using a pH meter. A number of samples that have been acidified, pipetted and put in a 50 ml measuring flask. Then added 2 ml of 1,5-Diphenyl carbazide solution. 0.2 N sulfuric acid was added to the volume until the limit mark. The mixture was stirred until homogeneous. The absorbance was measured at max, then the chromium (Cr<sup>6+</sup>) content was calculated based on the calibration curve[58][59].

### *Chromium(VI) Reduction with Iron Hill and Coagulation using Calcium Hydroxide*

Clean iron powder weighed in amounts of (1, 2, and 3) g was put into a glass beaker. 2 N sulfuric acid was added with a variation of (5, 10, and 15) mL. 50 mL of metal plating industry wastewater was added and stirred, with a reduction time of {3, 5, and 7) minutes. The mixture was filtered and put in a glass beaker. 10% Ca(OH)<sub>2</sub> lime solution was added to the beaker until pH 8.5. The mixture was filtered and the filtrate was measured for chromium content(Cr<sup>6+</sup>)[2][36][58][59].

### *Data Analysis*

The study was conducted with three replications. the percentage reduction of chromium (Cr<sup>6+</sup>) was carried out by the formula:

$$\% \text{ Chromium (Cr}^{6+}\text{) removal} = \left( \frac{C_{\text{initial}} - C_{\text{end}}}{C_{\text{initial}}} \right) \times 100\%$$

description:

C<sub>initial</sub> : initial chromium (Cr<sup>6+</sup>) concentration

C<sub>end</sub> : final chromium (Cr<sup>6+</sup>) concentration  
[36], [59]

Data processing was carried out with a three-way Analysis of Variance because it involved 3 parameters, namely grams of iron powder, ml H<sub>2</sub>SO<sub>4</sub> 2N and reduction time. If significantly different followed by LSD test.

## **3. Results and Discussion**

### *Physical Test and Determination of Chromium (Cr<sup>6+</sup>) Content of Liquid Waste from Metal Plating Industry*

The physical test results include temperature, colour, and pH measured by thermometer, colour observation, pH meter, and Uv-Vis spectra as shown in **Table 1**.

**Table 1.** Physical test results and chromium (Cr<sup>6+</sup>) content of metal plating industry wastewater effluent

No.	Parameters	Results of Observations	Quality Standard for Liquid Waste of Metal Coating Industry in Central Java Province Regional Regulation Number 5 Year 2012
1	Temperature (C)	28 <sup>0</sup>	-
2	Colour	Brown	-
3	pH	1,9	6,0-9,0
4	Chromium (Cr <sup>6+</sup> ) (mg/L)	749 mg/L	0,1 mg/L

**Table 1** shows that the chromium (Cr<sup>6+</sup>) effluent from the metal plating industry is brown in colour. The level of chromium (Cr<sup>6+</sup>) in the metal plating industry effluent is 739 ppm and this is still much higher than the quality standard permitted by the government according to the Central Java Provincial Regulation No. 5 of 2012 concerning the quality standard of liquid waste for metal plating industry activities for chromium (Cr<sup>6+</sup>), which is 0.1 mg/L[60]. This metal plating industry is located in the middle of a residential neighbourhood. The chromium (Cr<sup>6+</sup>) liquid waste is discharged into the sewer without any treatment process, causing pollution to the surrounding community[10][20][61]. The degree of acidity or pH of the solution is one of the important factors that determine the performance of the coagulant in the coagulation process. A pH value that is too high will make iron powder waste unable to work optimally as a reductant, because at high pH the metal will precipitate[2][3][47][48][49][62].

### *Reduction of Chromium ( $Cr^{6+}$ ) with Iron Powder and Coagulation with Calcium Hydroxide*

The results of the analysis of chromium ( $Cr^{6+}$ ) levels before and after treatment, treatment parameters, and percentage % reduction of chromium with iron powder and coagulation using calcium hydroxide as shown in **Table 2**.

**Table 2.** Pre- and post-treatment chromium ( $Cr^{6+}$ ) levels, treatment parameters, and % reduction in chromium levels ( $Cr^{6+}$ )

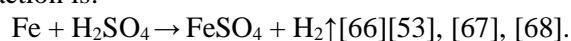
Before Treatment Average Initial chromium ( $Cr^{6+}$ ) level (mg/L)	Iron powder (g)	Processing Parameters Average Final chromium ( $Cr^{6+}$ ) content (mg/L)	Reduction Time	After Treatment Average Final chromium ( $Cr^{6+}$ ) content (mg/L)	Average reduction in chromium content ( $Cr^{6+}$ ) (%)
749	1	5	3	586,52	21,69292
			5	607,58	18,88117
			7	446,37	40,40454
		10	3	439,08	41,37784
			5	285,97	61,81976
			7	152,30	79,66622
		15	3	336,20	55,11348
			5	330,52	55,87183
			7	257,62	65,60481
		5	3	247,89	66,90387
			5	65,13	91,30441
			7	0,50	99,93324
	2	10	3	57,84	92,2777
			5	17,50	97,66355
			7	0,02	99,99733
		15	3	3,50	99,53271
			5	2,75	99,63284
			7	0,11	99,98531
		5	3	0,03	99,99599
			5	0,01	99,99866
			7	0,01	99,99866
	3	10	3	0,05	99,99332
			5	0,01	99,99866
			7	0,00	100
		15	3	0,00	100
			5	0,00	100
			7	0,00	100

**Table 2** shows that the more iron powder, 2N sulfuric acid and reduction time greatly affect the % reduction of chromium. ( $Cr^{6+}$ )[2][3][47][48][49][62]. Starting from the condition of iron powder as much as 3 grams of total waste), 5 ml of  $H_2SO_4$  2N and a reduction time of 5 minutes, the wastewater after chrome recovery has met the quality standards set in the [Regional Regulation of Central Java Province Number 5 of 2012](#) amounting to 0,1 mg/L[60]. Although the levels of chromium ( $Cr^{6+}$ ) have met the quality standards, heavy metal chromium ( $Cr^{6+}$ ) has accumulative properties, so it must be completely removed from the waters[8][10][20][23][26][46][63][64][65]. While starting the condition of iron powder as much as 3 grams, 10 ml of  $H_2SO_4$  2N and a reduction time of 7 minutes, wastewater after chrome recovery no longer contains chromium ( $Cr^{6+}$ ) so it is safe for the environment[8][10][20][23][26][46][63][64][65]. From this condition, the highest chromium ( $Cr^{6+}$ ) reduction result was 100% with a chromium ( $Cr^{6+}$ ) level of 0 mg/L. This result is in accordance with previously published research[1][47][48][56][62].

In the process of reducing chromium ( $Cr^{6+}$ ) by utilising iron powder waste through three stages, namely:

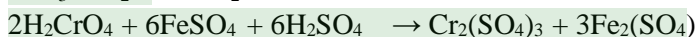
#### **a. Formation of $FeSO_4$**

In this process, dilute sulfuric acid (2N) dissolves iron and produces iron salts ( $Fe^{2+}$ ) and hydrogen gas. The reaction is:



## b. Reduction

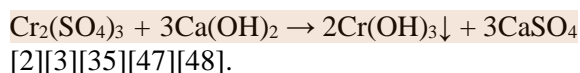
In the reduction process of chromium ( $\text{Cr}^{6+}$ ) a redox reaction will occur. If  $\text{FeSO}_4$  is used as a reductant,  $\text{Fe}^{2+}$  will be oxidised to  $\text{Fe}^{3+}$ , while chromium ( $\text{Cr}^{6+}$ ) is reduced to chromium ( $\text{Cr}^{3+}$ ) [13][35][36][47][48][51][56][69][70][71][72][73]. The reduction of chromium ( $\text{Cr}^{6+}$ ) to chromium ( $\text{Cr}^{3+}$ ) is indicated by the colour change from brown to green. In the reduction process that needs to be considered is the pH factor, because the reduction of chromium is very effective in an acidic atmosphere (pH 1 - 2) according to the following reaction:



Chromium ( $\text{Cr}^{6+}$ ) removal by reduction to chromium ( $\text{Cr}^{3+}$ ) using  $\text{Fe}^{2+}$  ions is often used in the chrome processing industry for concentration range in milli grams/litre [1][47][48][72].

## c. Coagulation/precipitation

After the reduction process is complete, the precipitation process is continued with lime solution because ferrous sulphate cannot be used as a precipitator. The precipitation of chromium ( $\text{Cr}^{3+}$ ) is optimum at pH 8-9. The precipitation reaction of chromium ( $\text{Cr}^{3+}$ ) with  $\text{Ca}(\text{OH})_2$  is:



From the results of the three-way Analysis of Variance, there were significant differences (95% confidence level) in the percentage reduction and coagulation of chromium ( $\text{Cr}^{6+}$ ) with various treatments. The parameters of iron powder weight, addition of 2N sulfuric acid and reduction time were significantly different on the percentage reduction of chromium ( $\text{Cr}^{6+}$ ). In addition, there is a relationship (interaction) between these parameters. Chromium loss can be caused by the precipitation process is not perfect, so it is included in the water. The reduction has been quite good, but efforts to increase the reduction need to be improved in the future [5][39][44]. To help address the problem of environmental pollution, the process of recovering/recycling waste into useful materials needs to be promoted by 3R. Particularly hazardous metal wastes, this effort needs to be prioritised as these metal compounds are required in many industries and most of them are still imported at a high cost [5][33][39][44].

## 4. Conclusion

The conclusion of the research is that the chromium ( $\text{Cr}^{6+}$ ) content of metal plating industry wastewater is 749 mg/L. The optimum condition for reducing chromium is using 3 grams of iron powder, 10 ml of  $\text{H}_2\text{SO}_4$  2N, and a reduction time of 7 minutes, there is a decrease in chromium ( $\text{Cr}^{6+}$ ) levels by 100% with chromium ( $\text{Cr}^{6+}$ ) levels of 0 mg/L. This result fulfils the Regional Regulation of Central Java Province Number 5 of 2012 concerning the Quality Standards of Liquid Wastewater for the Metal Coating Industry which requires a maximum chromium ( $\text{Cr}^{6+}$ ) level of 0.1 mg/L.

## 5. Acknowledgment

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## 6. Abbreviations

WHO	World Health Organization
%	Percentage
3R	reduce, reuse and recycle
ppm	Parts per million
ppb	Parts per billion

## 7. References

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