

## A STUDY OF SOIL ADSORPTION TOWARD CHROMIUM IN LIQUID WASTE FROM TANNING INDUSTRY

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### ABSTRACT

Tanning industry potentially produces waste containing heavy metals chromium (Cr) is harmful to the environment. One of the methods to decrease the Cr in liquid waste is using soil as adsorbent. Soil capacity to adsorb of heavy metal is determined by clay content, soil moisture, redox potential, pH, organic matter content and CEC. This research aimed to determine the soil capacity of Vertisol, Oxisol, Entisol, and Andisol to adsorb Cr in liquid waste from tanning industry. The experiment conducted in this research was to flow and saturate the liquid waste into soil column four soil samples. The adsorption capacity of each soil type was calculated by comparing Cr content in the soil with it in the filtrate. The results showed that the soil is a good Cr adsorbent and each soil type has different abilities in the adsorption of heavy metals Cr. At first saturating the soil is able to adsorb Cr about 99.92%, the second saturation at 99.64%, and the third saturation of the soil is able to adsorb Cr 97.17%. The adsorption capacity of Entisol and Oxisol was 0.174 mg/g, Andisol has an adsorption capacity of 0.175 mg/g, and Vertisol has adsorption capacity of 0.177 mg/g.

*Keywords: Chromium (Cr), Soil Adsorption, Tanning Industry.*

### INTRODUCTION

One of the negative effects from industrial development is the increase of industrial waste amount that is possibly harmful and hazardous. Heavy metals is categorized in B3 waste (Hazardous and Harmful Materials) that, in a specific content, can harm its surrounding environment because it is toxic for plants, animals, and humans.

Tanning industry is one of the industries that potentially produce waste containing harmful heavy metals such as Chromium (Cr). This is happened because the materials used in the process are mostly a mixture of  $\text{Na}_2\text{S}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NaCl}$ , dan Cr.

The maximum limit of Chromium allowed for Cr based on the State Minister for the Environment policy is 0.6 ppm. Meanwhile, according to research conducted by Fadilah (2011), characteristic of waste from tanning industry that has passed through Liquid Waste Processing Installation (IPAL) still contain Chromium of 41.37 ppm.

The prevention of heavy metals contamination to the environment can be performed in several methods. The most practical method is sedimentation which is followed by filtering, absorbing by using active carbon, natural zeolite and also soil.

The adsorption method by soil in solving the problem of waste contaminated by heavy metals is relatively simple and easy to be performed. In addition, soil has high adsorption capability, renewable, easy to get, and abundant.

### Objective

The objective of this research is to determine the soil capacity of Vertisol, Oxisol, Entisol, and Andisol to adsorb Cr from the liquid waste of tanning industry.

### Soil Contamination

Matters that can cause soil contamination are liquid waste or industrial chemical material leakage, use of pesticide, permeation of contaminated surface water into sub-surface layer, oil-contained vehicle accident, chemical substance, or waste; liquid waste from the waste dumping area, and also industrial waste that is dumped directly to the soil without obeying the regulations (Illegal dumping) (Sofyan, 2009).

The critical limit of heavy metal concentration in soil, water, and plant can be noticed in Table 1.

Table 1. The critical limit of heavy metal concentration in soil, water, and plant

Heavy Metals	Soil (ppm)	Water (ppm)	Plant (ppm)
Pb	100.00	0.03	50.00
Cd	0.50	0.05-0.10	5-30
Co	10.00	0.4-0.6	15-30
Cr	2.50	0.5-1.0	5-30
Ni	50.00	0.2-0.5	5-30
Cu	60-125	2-3	20-100
Mn	1500.00	-	-
Zn	70.00	5-10	100-400

Source : State Ministry for Population and Environmental of Indonesia (Dalhousie, 1992)

According to Palar (1994), soil has a significant role on the transfer and the washing of pollutant. Soil is also categorized as a pollutant carrier. The transfer process can be divided into three which are flow on, absorption, and leaching. If there is an accumulation from the metals, it will cause an environmental effect. The very last and highest accumulation of metals happens in the soil because of the forceful clay colloids absorption in the soil (Alloway, 1995).

### Tanning Industry

Tanning industry is an industry that process raw hides or skins into hides or leather by using tanning material (Zaenab, 2008). Tanning industry is one of the industries that have potential to harm the environment. The average amount of tanning industry waste



is 8,000 – 12,000 gallon per 1,000 pound of processed wet hides. The average content of waste is 8,000 ppm of total solids, 1,000 ppm of protein, 300 ppm of NaCl, 1,600 ppm of total hardness, 1,000 ppm of sulfide, 40 ppm of chromium, 60 pp of nitrogen, and 1,000 ppm of BOD. Those wastes have pH value between 11 and 12, and normally will produce 5 – 10% of sludge concentration because of chalk content and sodium sulfide. While in USA, from 1 tons of raw hides, it produces 600 kg of solid waste and contains 60,000 metric tons of high-content chromium (Cabeza *et al.* 1998).

Based on the research conducted by Fadilah (2011), the characteristic of tanning industry waste are as follow:

Table 2. The analysis result of physical and chemical factor of tanning industry waste

No	Parameter	Maximum Content (ppm)	Result (ppm)
1	BOD	50	102.3
2	COD	110	180.5
3	Chrome	0.6	41.37
4	TSS	60	107
5	Sulphide	0.8	0.02

Table 3 shows the standard of liquid waste that has to be fulfilled by all tanning industry made by State Ministry for the Environment No: KEP-51/MENLH/10/1995 about the standard of liquid waste for industrial activity.

Table 3. The standard of liquid waste for tanning industrial activity

Parameter	Tanning Process By Chrome		Tanning Process By Leaves	
	Maximum Content (mg/L)	Maximum Contamination Load (kg/tons)	Maximum Content (mg/L)	Maximum Contamination Load (kg/tons)
BOD	50	2	70	2.8
COD	110	4.4	180	7.2
TSS	60	2.4	50	2
Total Chrome	0.6	0.024	0.1	0.004
Oil/Fat	5	0.2	5	0.2
Total N	10	0.4	15	0.6
Total Ammonia	0.5	0.02	0.5	0.02
Sulphide (S)	0.8	0.032	0.5	0.02
pH	6.0-9.0		6.0-9.0	
Maximum waste discharge	40 m <sup>3</sup> /tons of raw material		40m <sup>3</sup> /tons of raw material	

### Soil as Heavy Metals Adsorbent

Soil has a limited ability or capacity in performing retention and accumulating the heavy metals. If this limitation is lapsed then the pollution will happen. Soil capacity in

performing retention, absorbing, and accumulating heavy metals is determined by clay content, soil moisture, redox potential, pH, organic material content and cation change capacity (CEC) (Bohn *et al.*, 1979 *cit* Jones dan Jarvis, 1981).

Soil reaction is an important controlling factor of chemical activity of metals and any other important process in the soil. By the increase of pH, the ionic form from micro unsure cation changes into hydroxide or oxide form. (Soepardi, 1983). Alloway (1995) also proposed that generally heavy metals cation moves easier in the sour condition and the increase of pH by calcification decrease the heavy metals availability for the living creature.

Organic material can reduce the negative effect that is possibly caused by heavy metals and maintain the plant in normal condition (Stevenson, 1994). Research by Ariyanto *et al.* (2005) proposed that from the metal content analysis, in this case is Chromium (Cr), the decrease of Cr content in the soil is followed by the result about higher organic material content.

Adsorption and cation change have a practical role which is very important in the nutrient adsorption of plant, soil fertility, nutrient retention, and fertilization (Tan, 1991). The soil clayey usually contains electronegative content which enables the cation change reaction. The CEC value is influenced by its negative content source and also by the soil texture and the amount of colloid in the soil. (Soepardi, 1983).

## MATERIAL AND METHODS

The soil sample used in this research was taken from several locations in order to get different soil types, which are:

- a. Andisol is taken from Dieng plateau, Wonosobo Regency.
- b. Oxisol is taken from Patuk Sub district, Gunungkidul Regency, Yogyakarta.
- c. Entisol is taken from Piyungan Sub district, Bantul Regency.
- d. Vertisol is taken from Donggubah, Wonosari Sub district, Gunungkidul Regency, Yogyakarta.

The soil sample was top soil and sub soil part. The tanning industry liquid waste was taken from tanning industry in the Sitimulyo Industrial Area, Piyungan, Bantul.

In the experiment, the liquid waste from tanning industries which was indicated to be contaminated by heavy metals Cr was flowed in the same volume and saturated on each soil type, and then the filtrate was contained. After the filtrate from the first saturation had been depleted and the soil had reached the field capacity, then the second saturation was performed followed by the third saturation. All treatments were performed three times on each soil type. Afterward, Chromium content in the filtrate produced from those saturations were analyzed in the laboratory.



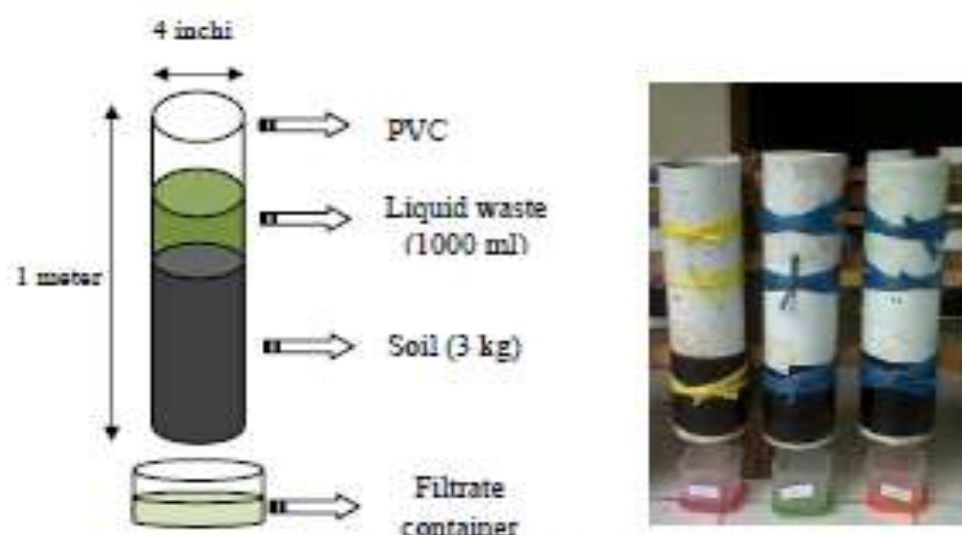


Figure 1. The Outline of Saturation Process of Liquid Waste from Tanning Industry

## RESULT AND DISCUSSION

These are data from the analysis result of liquid waste, filtrate, and soil adsorption capacity measurement in the first, second, and third saturation.

The data obtained in this research shows that the total Chromium content in the liquid waste from tanning industry that has not been processed is 530.43 ppm, while the maximum limit allowed is 0.60 ppm. This high Chromium concentration in the liquid waste is occurred because in the tanning process, it usually uses tanning material  $\text{Na}_2\text{Cr}_2\text{O}_7$  (Natriumdikromat) which is subsequently reduced by gas  $\text{SO}_2$  and formed into  $\text{Cr}(\text{OH})\text{SO}_4$ . This will be harmful for the environment and the living creature if it is flowed and spread just like that.

Table 4. Soil capacity to absorb Cr in the first saturation

Soil type	Cr-Total (ppm)		Saturation 1 (ppm)		Adsorption Capacity (mg/g)
	Soil	Liquid Waste	Cr-Filtrate	Cr-Adsorbed	
Vertisol Topsoil	0.4	530.4310	1.0613	529.3698	0.176457
Vertisol Subsoil	3.5	530.4310	0.0391	530.3919	0.176797
Oxisol Topsoil	0	530.4310	0.8119	529.6191	0.176540
Oxisol Subsoil	0	530.4310	0.0213	530.4097	0.176803
Entisol Topsoil	9.6	530.4310	1.2448	529.1862	0.176395
Entisol Subsoil	4.2	530.4310	0.1514	530.2796	0.176760
Andisol Topsoil	5.0	530.4310	0.0213	530.4097	0.176803
Andisol Subsoil	0	530.4310	0.0213	530.4097	0.176803

From the experiment, it is proved that soil can function as a good adsorbent for Chromium. This can be observed on Table 4, 5, and 6 showing that the soil adsorbing capacity from the three saturations still shows good result.

In the first saturation, the soil can absorb Chromium in the average of 99.92%. The Chromium concentration in the filtrate is still below the maximum limit allowed.

In the second saturation, the soil adsorption capacity is decreased into 99.64%. The vertisol and andisol capacity are stabile and not decreasing compared to oxisol and entisol. Moreover, the filtrate produced by these two soil type is still below the maximum limit allowed by the State Minister for the Environment.

In the third saturation, the soil adsorption capacity decreases again, but the basic adsorption capacity is still high in the range of 90%. This shows that the soil can accumulate huge amount of Chromium. From this experiment, the soil has accumulated Chromium more or less in the amount of 1,500 ppm.

#### **A. The Adsorption Capacity of Vertisol**

The physical and chemical characteristic of vertisol is very influential toward the soil capacity to absorb Chromium. In this case, high clay content and Cation Exchange Capacity (CEC) has a significant role in the Chromium adsorption. Vertisol has high clay content and also high CEC so that it supports the cation change process. Since clay colloid has negative charge while Chromium has positive charge, then the Chromium will be dragged toward the clay particle and bounded electro-statically on the clay surface. Clay has tiny particle and enormous surface area that enables to absorb great amount of Chromium.

Tan (1991) proposed that mineral montmorillonite is categorized as unique element from clay in the soil Vertisol, Mollisol, and Alvisol, and also found in several Entisol. Plasticity potential and high swelling-shrinking of this type of mineral causes these soils to have plasticity characteristic in wet condition and hard if it in dry. The high swelling-shrinking potential causes this mineral to be able to receive and fasten the ionic of the metal and organic compound. Besides, mineral montmorillonite also has specialty that adsorption by the clay surface can occur not only on the outer surface but also can penetrate into inter micelles area.

Vertisol here also has a small particle, so that the soil tends to be more compact and difficult to flow the liquid waste of tanning industry. The soil which has soft texture and is dominated by clay will have more total pore space and mostly constructed by micro pores so that it has higher water holding capacity. This high water holding capacity will have an influence toward the soil adsorption capacity because the soil will absorb more liquid waste from tanning industry.

The use of vertisol as adsorbent of Chromium will be more effective if the problem on the physical characteristic that is difficult to loosen the water can be solved. To solve these problems, vertisol characteristic can be improved by combining vertisol and other soil types for heavy metals adsorbent.



### **B. The Adsorption Capacity of Oxisol**

Although oxisol has a higher clay content than vertisol, due to different clay type contained it may caused the soil adsorption capacity of oxisol to be still lower than vertisol.

Oxisol in this research has higher organic content than vertisol and entisol. The high organic content in oxisol will affect the soil adsorption toward Chromium.

Stevenson (1982) in Ariyanto (2001) proposed that tar form organic material can control the availability of metal in the soil. The other evidence of chelating is the research conducted by Ariyanto *et al.* (2005), proposed that from the analysis of metal content, in this case Chromium, the decrease of Cr content occurs in the soil followed by the result about higher organic material content. From the analysis result, it can be concluded that the decrease of Chromium is caused by the chelating of organic material toward Chromium.

Although oxisol has higher organic material content, it has lower CEC compared to other types of soil. Besides, clay contained in oxisol is kaolinite type (1:1) with surface area range only between 7 to 30 m<sup>2</sup>/g and much smaller than any other types of clay. This can enable good oxisol adsorption capacity to absorb Chromium in the starting saturation, while in the second and third saturation, the adsorption capacity then been decreased.

### **C. The Adsorption Capacity of Entisol**

Entisol texture is dominated by sand fraction so that it has bigger soil particle compared to other soil types. With a bigger or coarse soil particle, it can create a bigger soil pore size as well. The effect is that the saturated liquid waste will be easier to pass soil column and less Chromium will be absorbed in the soil.

Entisol also has less organic material content compared to other soil types. This low organic material content and less clay content will reduce the amount of colloid in this soil. This enables the decrease of Chromium adsorption capacity and much faster to decrease.

### **D. The Adsorption Capacity of Andisol**

The characteristic of andisol is very dark, very porous, containing organic material and clay in the type of amorphous, especially allophane and also slight silica, alumina, or metal-hydroxide (Darmawijaya, 1990). Van Olphen (1977) *cit.* Tan (1991) proposed that specific surface area of allophane type is around 100 to 800 m<sup>2</sup>/g, so that andisol will have a wide cation adsorption area.

Organic material will form colloidal topsoil which has greater cation adsorption capacity than clay, so that the organic material contained in andisol has a crucial role in the process of Chromium adsorption.

The physical characteristic of andisol which has low bulk density and also high water holding capacity will be useful in the Chromium adsorption because in this research, Chromium contained in the liquid waste is saturated into the soil.



## CONCLUSION

Based on the research result, it can be concluded that soil is a good Chromium adsorbent. Vertisol, Oxisol, Entisol, and Andisol have different adsorption capacities toward Chromium. Vertisol has an adsorption capacity in the amount of 0.177 mg/g, Oxisol and Entisol in the amount of 0.174 mg/g, while Andisol in the amount of 0.175 mg/g.

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