

Critical Level of Chromium for Rice in Different Soil Types

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ABSTRAK

Meningkatnya jumlah industri dan buruknya pengolahan limbah akan merusak kesehatan lingkungan, termasuk lahan pertanian. Produk pertanian dari tanah yang terkontaminasi dapat mengandung logam berat berbahaya seperti kromium yang dapat membahayakan kesehatan manusia jika dikonsumsi. Pemeriksaan dan penentuan batas kritis logam berat kromium pada tanah sawah diperlukan untuk mengevaluasi ambang batas logam berat agar mengurangi distribusi ke tanaman padi. Penelitian ini bertujuan untuk mendapatkan batas kritis logam berat Kromium pada tanah bertekstur ringan dan berat dengan tanaman indikator padi. Uji adsorpsi krom menggunakan metode pendekatan Langmuir. Percobaan pot dilakukan di rumah kaca menggunakan rancangan acak lengkap dengan dua faktor yaitu konsentrasi logam berat (Cr) dan tekstur tanah (A) dan diulang sebanyak lima kali. Penyerapan kromium pada tanah bertekstur berat lebih tinggi dibandingkan tanah bertekstur ringan. Daya serap maksimum logam kromium pada tanah bertekstur ringan sebesar 87,719 mg kg⁻¹, sedangkan pada tanah bertekstur berat sebesar 204,082 mg kg⁻¹. Kromium total dalam tanah menurun setelah panen dan menurunkan hasil panen padi. Batas kritis Krom tanah bertekstur ringan pada padi adalah 0,861 mg kg⁻¹, sedangkan batas kritis Kromium tanah bertekstur berat pada padi adalah 1,012 mg kg⁻¹.

Kata kunci: Kromium, Batas kritis, Tanah sawah, Logam berat, *Oryza sativa*

ABSTRACT

The increasing number of industries and poor treatment of waste will damage environmental health, including agricultural land. Agricultural products from contaminated soil may contain hazardous heavy metals such as chromium which can harm human health if consumed. Examination and determination of critical levels of chromium in paddy soil are required to evaluate the threshold of heavy metals to disable their distribution into paddy plants. This study aims to obtain the critical level of chromium in light and heavy-textured soils with paddy as a plant indicator. The chromium adsorption test uses the Langmuir approach method. The pot experiment was carried out at the greenhouse using a completely randomized design with two factors, heavy metal concentration (Cr) and soil texture (A), repeated five times. Chromium sorption in heavy-textured soil is higher than in light-textured soil. The maximum sorption of chromium metal in light-textured soil is 87.719 mg kg⁻¹, while in heavy-textured soil is 204.082 mg kg⁻¹. Total chromium in the soil decreases after harvest and reduces rice yields. The critical level of light-textured soil chromium in rice was 0.861 mg kg⁻¹, while the critical level for heavy-textured soil Chromium in rice was 1.012 mg kg⁻¹.

Keywords: Chromium, Critical level, Paddy Soil, Heavy metal, *Oryza sativa*

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1. Introduction

The increasing national industrial development has positively impacted employment and increased community income. On the other hand, this can also have a negative impact on environmental pollution, one of which is an increase in metal pollution in the soil (Ogunkunle *et al.*, 2017). This environmental pollution is primarily due to the waste that comes from the factory, which is not adequately treated and managed. Environmental problems caused by poorly managed industrial wastewater include textile industrial wastewater in Kebakkramat

District, containing 0.26 - 0.99 mg kg⁻¹ chromium and polluting the surrounding rice fields between 1.20 - 5.20 mg kg⁻¹ (Rohmawati *et al.*, 2018). Paddy fields in Juwana District, Pati, polluted by electroplating industrial waste, contain 6.0-27.7 mg kg⁻¹ of chromium (Kurnia 2003). Cikijing river water, Rancaekek, was polluted by textile industrial wastewater with a high enough concentration of heavy metal chromium, which was between <0.02-0.07 mg kg⁻¹ (Komarawidjaja, 2016). The river water is used to irrigate rice fields in the Rancaekek sub-district, which has resulted in the contamination of rice fields with a

chromium content of 25.6-174.7 mg kg⁻¹ (Komarawidjaja, 2017). Chromium (Cr) compounds are toxic and detrimental to plant growth and development (Huffman & Alloway, 1973). Chromium has affected plant growth and production, characterized by abnormal growth. Chromium is also found in Juwana and Rancaekek Districts rice straws, respectively 0.16-1.29 mg kg⁻¹ and 0.67-4.52 mg kg⁻¹. In Juwana Regency, rice containing chromium was found from 0.33 - 1.15 mg kg⁻¹ (Kurnia, 2003), in Rancaekek, it was 0.99-17.1 mg kg⁻¹ (Suganda et al. 2003), and in Kebakkramat it was found grain containing chromium 0.30- 1.80 mg kg⁻¹ (Rohmawati *et al.*, 2018). Bioaccumulation of metals in the soil can be uptake by plants, which can increase metal levels in the food chain, thereby affecting human health (El-Kammar *et al.*, 2009). The accumulation of large amounts of chromium in the human body can be detrimental to health because chromium harms the liver and kidneys and is toxic to the protoplasm of living things. The nature of chromium metal, which is carcinogenic (cancer-causing), teratogen (inhibits fetal growth), and mutagens (Schiavon *et al.*, 2008), can interfere with human health in long-term exposure.

The chromium threshold in plants is 5 - 30 mg kg⁻¹ (Alloway 2010), while rice or rice flour must be free of chromium (*Dirjen POM 1989*). In Indonesia, there needs to be more accurate information regarding the critical level of heavy metals in agricultural land. This information is needed so that the assurance of food safety produced on that land can be monitored. Therefore, it is necessary to look for the critical level of heavy metal chromium in the soil so that rice production, mainly rice consumed, does not contain chromium. This study aimed to obtain the critical level of chromium on light and heavy-textured soils with rice as an indicator crop.

2. Material and Method

2.1 Location

This research was conducted in 2018 at the Indonesian Agricultural Environment Research Institute, Pati, Central Java. Soil properties and heavy metal content tests were analyzed at the Indonesian Agricultural Environment Research Institute Integrated Laboratory.

2.2 Tools and Material

The research materials consisted of light and heavy-textured soil samples, chemicals for heavy metal adsorption tests and soil properties analysis, rice seeds, urea, KCl, SP-36, plastic buckets, label paper, books, and plastic samples. The equipment used in this research includes soil sample drills, hoes, shovels, digital scales, glass tools, soil grinders, sieves, and Atomic Absorption Spectrometer (AAS).

2.3 Research procedure

Soil sampling

In this study, two soils with different textures were used, light and heavy-textured soil samples. A sampling of light-textured soil was taken in Ponggok Hamlet, Sidomulyo, Bambanglipuro District, Bantul Regency at coordinates - 7096'46,43" South Latitude - 110030'73,98" East Longitude. Heavy-textured soil samples were taken in Lamongan Regency at coordinates -7011 '53, 00" South Latitude - 112010'19,00" East Longitude. Soil samples were taken as a composite from the tillage layer (0-20 cm) as much as +/- 500 kg. The topography of the soil sampling location is in the lowlands with flat land contours dominated by rice plants.

Chromium adsorption test, analysis of physical and chemical properties of soil in the laboratory

The chromium adsorption test was carried out using the Langmuir approach method (Fox & Kamprath, 1970) by treating different concentrations of doses. Two grams of soil samples were added and put into a shaking bottle, then added 20 ml of 0.001 M CaCl₂ solution containing various doses of Cr concentration according to the treatment, namely 0 mg kg⁻¹, 25 mg kg⁻¹, 50 mg kg⁻¹, 75 mg kg⁻¹, 100 mg kg⁻¹, 200 mg kg⁻¹, 400 mg kg⁻¹. Each solution was incubated for six days and shaken twice daily (morning and evening), each for 30 minutes at a speed of 180 rpm. After incubation, each solution was filtered with Whatman filter paper no.41 to separate the clear extract and soil sediment. The clear extract was then measured for the heavy metal Cr concentration using AAS (atomic absorption spectrophotometer). The concentration of chromium adsorbed by the soil can be calculated using the Langmuir equation according to Fox & Kamprath (1970) as follows:

$$X = \frac{K \cdot X_{max} \cdot C}{1 + K \cdot C}$$

Information :

- X : The amount of heavy metal adsorbed per unit weight of soil (mg kg⁻¹);
- K : Constant relating to bond energy (L mg⁻¹);
- X_{max} : Maximum adsorption of heavy metal (mg kg⁻¹);
- C : heavy metal concentration in equilibrium (mg kg⁻¹).

From the Langmuir equation above, the buffering capacity of each soil against chromium can be calculated through the equation :

$$DS = K \cdot X_{max}$$

Information :

- DS : The buffering capacity (L kg⁻¹);

K : Constant relating to bonding energy (L mg⁻¹);
 Xmax : Maximum adsorption of heavy metal (mg kg⁻¹);

The physical and chemical characteristics of the soil analyzed in the laboratory include texture (pipette method), pH H₂O (1: 5), C-organic (walkey and black method), CEC (NH₄OAc saturation method 1 M pH 7, titration), and Chromium content (wet ash method, Hybrid-AAS).

Potted experiment for calibrating heavy metal soils in the greenhouses

Pot experiments to calibrate chromium were carried out in a screen house using a completely randomized design (CRD) with two different factors, namely the concentration of Chromium (Cr) and soil texture (A). Each treatment was repeated five times. The combination of treatments in this study is as follows (Table 1) :

Table 1. Research treatment

Chromium Concentration (Cr) mg kg ⁻¹	Soil Texture (A)	
	light-textured soil (A1)	Heavy-textured Soil (A2)
Cr 0 (0)	A1 Cr 0	A2 Cr 0
Cr 1 (25)	A1 Cr 1	A2 Cr 1
Cr 2 (50)	A1 Cr 2	A2 Cr 2
Cr 3 (75)	A1 Cr 3	A2 Cr 3
Cr 4 (100)	A1 Cr 4	A2 Cr 4
Cr 5 (200)	A1 Cr 5	A2 Cr 5
Cr 6 (400)	A1 Cr 6	A2 Cr 6

Preparation for planting and application of chromium is carried out by drying the soil sample until it reaches air dryness, then pounding and sieving. The pot is filled with 10 kg of the soil sample, then labeled according to the treatment to be given. Before being treated, the soil in the pot was flooded for two days. Furthermore, the treatment dose of chromium was added in each pot according to the treatment. Then the soil was stirred until it was homogeneous and incubated for ten weeks to achieve a heavy metal balance. At the incubation time, the water level was maintained at 2-5 cm by adding water every 1 or 2 days and covering the pot with aluminum foil. After incubation, an initial soil sample was taken to analyze the total chromium content.

Furthermore, rice seeds are planted in four seeds/pots. After seven days of planting, two plants that grow well are selected. The dose of fertilizer given is equivalent to 300 kg ha⁻¹ of urea, 50 kg ha⁻¹ of SP36, and 50 kg ha⁻¹ of KCl, and it was given at the age of 7 days (urea 75 kg ha⁻¹, SP36 50 kg ha⁻¹, and KCl 50 kg ha⁻¹), 21 days (Urea 150 kg ha⁻¹) and 42 days (Urea 75 kg ha⁻¹). Parameters were observed included: (1) total chromium concentration in paddy soil after incubation, (2)

total chromium concentration in roots, stems, and rice, (3) grain weight.

Data Analysis

The critical level for chromium was determined on the soil by using the relationship curve between the chromium content of the soil and rice. The maximum value of heavy metal contamination is defined in Indonesian National Standard (SNI) 7387: 2009 as the maximum allowable concentration of heavy metal contamination in food. Chromium contamination level reference in rice plants refers to SNI recommendations. Observation data for grain and straw weight will be analyzed using the ANOVA method followed by (Duncan's Multiple Range Test) DMRT test at the 5% level.

3. Results and Discussion

3.1 Soil Physical and Chemical Properties

The physical and chemical properties of each soil sample are presented in Table 2. The light-textured soil from Bantul has 8% clay content, while heavy-textured soil from Lamongan has a clay content of 80%. The low clay content in light-textured soil is followed by a very low organic content of 0.62%, while the organic content in heavy-textured soil is in a low category.

3.2. Chromium (Cr) Adsorption

Chromium in the soil is in the form of Cr (II), Cr (III), and Cr (VI) and is bound to iron oxides, aluminum, and organic matter. Cr (VI) is a form of chromium that are toxic, genotoxic, mutagenic, and carcinogenic effects on humans, animals, plants, and microbes (Murray *et al.*, 2005; Feng *et al.*, 2003; Turpeinen *et al.*, 2004). Soil characteristics affect the adsorption of heavy metals in the soil, such as pH, organic fraction, organic carbon, texture (clay), soil temperature, and buffering capacity (Zeng *et al.*, 2011). Chromium adsorption in the two types of soil studied varied widely. It is indicated by the absorption curve's shape, which is different in terms of both peak and slope (Figure 1).

The curve from left to right shows the lower chromium absorption rate. One of the factors that can determine the metal absorption rate is soil pH. Light-textured soil (Bantul) has a pH of 5.81, and heavy-textured soil (Lamongan) is 5.39. pH affects metal uptake through various mechanisms, such as changes in surface charge and hydrolysis of metals in solution. In general, the higher the soil pH, the higher the metal absorption. If the pH is below 5, metal mobility will increase due to increasing proton concentration (Rogers *et al.*, 2000; Paulose *et al.*, 2007).

Soil texture and soil mineral type play an important role in the mobility of metals in the soil. Clay has a high absorption capacity and a strong ability to bind metal elements due to its large specific surface area and high cation exchange capacity (CEC). In general, soils with higher clay

and humus content also have a high adsorption capacity of heavy metals. Meanwhile, sandy soils absorb heavy metals weakly due to their lower absorption capacity and larger pore sizes (Hasegawa *et al.*, 2015). Clay is a source of negative surface exchange in the soil and makes a major contribution to cation exchange. The type of clay soil can be seen from the CEC value. This is consistent with the adsorption results shown by the relationship curve between dissolved metal concentrations and the solid phase (Figure 2), chromium metal uptake in heavy-textured soil (Lamongan) is higher than in light-textured soil (Bantul).

Soil with a clay fraction dominated by clay type 2: 1 has a high CEC. It will also have a high maximum absorption of pollutants. This shows that each soil's ability is different in buffering pollutants depending on its physical and chemical properties (Tarradellas and Bitton 1997). Table 3 shows the maximum adsorption, bond energy constants and different buffering capacities in the two types of soil studied. The maximum uptake of chromium metal in light-textured soil (Bantul) is 87.719 mg kg⁻¹, while in heavy-textured soil (Lamongan), the maximum uptake of chromium metal in the soil is 204.082 mg kg⁻¹.

3.3. Total chromium in soil

Total soil chromium before planting (after treatment) was higher than after harvest (Figure 3). There has been the absorption of chromium from the soil by rice plants. The chromium content in the soil before and after harvest differed in the two soil types. The absorption ability of chromium in soil depends on the physical and chemical properties of the soil. Clay is classified as having high activity, as shown by its very large absorption capacity. The high clay content and absorption capacity predict the high-activity clay type. This is in accordance with the research results of Wijayanti *et al.*, (2018), who showed that the adsorption capacity of soil for chromium increases with increasing pH, cation exchange capacity, and the number of clay fractions in the soil. In soil types with high clay content, the adsorption capacity of chromium metal is also high. Due to the high chromium bonds in the heavy textured soil, relatively less chromium comes out than light textured soils (Figure 3).

3.4. Critical level of chromium with rice plants as indicators

Rice Yields

Land health conditions and the availability of nutrients in the soil strongly influence rice yields. Using agricultural chemicals can increase the growth and yield of rice plants. However, overuse can degrade product quality and pollute soil, water bodies, plants, and the air. This is detrimental to humans, livestock, and the

environment. These pollutants include heavy metals Pb, Cd, Cr, and Ni, which are dangerous toxic materials (B3). In excess, chromium and nickel are inhibiting factors for plant growth, which will affect yield.

The results of statistical analysis showed that chromium treatment had a significant effect on rice yields (Table 4). Soils contaminated with chromium experience a high reduction in rice yields, especially in chromium contamination above 100 mg kg⁻¹. Sundaramoorthy *et al.*, (2010) also revealed that rice production yields gradually decreased with increasing chromium concentrations. The growth of shoots, roots, total leaf area, fresh weight, and dry weight also decreased with increasing chromium concentration. Likewise, the absorption of macronutrients (N, P, K) and micronutrients (Mn, Cu, Zn, Fe) also decreased.

Critical Level of Chromium

Chromium metal in the soil will diffuse passively through the endodermis layer of plant roots. The accumulation of chromium in the plant endodermis causes a detoxification process by phytochelatin in the cytoplasm. The metal elements are then translocated into the plant canopy to the leaves through the xylem in the photosynthesis process. The results of photosynthesis are distributed to all plant organs.

In rice plants, the grain is a storage place for food reserves, so it becomes a place for chromium accumulation. Rice is consumed in grain, so it needs special attention. The chromium content in rice increases with the high concentration of chromium in the soil (Figure 4). In rice the accumulation of chromium in rice gradually increases with increasing chromium concentration (Sundaramoorthy *et al.*, 2010). The same result was also expressed by Xie *et al.* (2018) that the application of Pb, Cd, Cr, and Cu on rice growing media significantly affected the accumulation of Cd, Cr, and Cu in rice. Heavy metals are in rice through translocation to plant parts so that they can enter the food chain through rice consumption (Zhou *et al.*, 2014). Accumulation of Cr in threshold amounts in plant and seed parts is a serious problem for human health because it causes cardiovascular disease (dysfunction of the respiratory system through lung cancer and pulmonary fibrosis), kidney failure, and cancer (Peralta-Videa *et al.*, 2009).

The critical value of heavy metals in the soil can be estimated using a simple regression equation between the heavy metal content in the soil and the product, in this case, rice. The critical level for heavy metals in soil is calculated based on the critical level assumption in rice based on SNI 7387: 2009, which regulates the maximum contamination level for heavy metal chromium in rice, which is 0 mg kg⁻¹. The maximum level of contamination on rice in relation to heavy metals

in the soil will produce a critical level value (**Table 5**). The critical level of chromium in light-textured soils (Bantul) is 0.861 mg kg⁻¹, while in heavy-textured soils (Lamongan) is 1.012 mg kg⁻¹. The critical level of chromium in the soil is directly proportional to its clay content. The more clay it contains, the greater the critical level of chromium. The clay content linearly increases the critical level of chromium metal in the soil. The

greater the clay content, the greater the negative charge on the soil colloid, which can absorb the chromium, which has a greater positive charge by electrostatic forces on the clay surface. The accumulation of metals in plants depends not only on the metal content in the soil but also on the soil's chemical elements, types of metals, soil pH, organic matter, nutrient availability, and plant species (Jiwan & Ajay, 2011).

Table 2. Soil Characteristics

Soil Properties	Method	Value	
		Light-textured Soil (Bantul)	Heavy-textured Soil (Lamongan)
Texture :	Pipette		
Sand (%)		87	4
Dust (%)		5	16
Clay (%)		8	80
pH	H ₂ O	5.81	5.39
C-Organic (%)	Walkey and Black	0.62	1.19
Total N (%)	Kjeldahl	0.18	0.28
Available P (mg kg ⁻¹)	Olsen and Bray	139.35	74.69
Available K (mg kg ⁻¹)	Morgan	11.73	8.05
CEC (cmol ⁽⁺⁾ kg ⁻¹)	NH ₄ OAc 1 N pH 7	18	34.64
Cr (mg kg ⁻¹)	Wet Ash	2.56	2.36

The data source is processed from the analysis results in the IAERI laboratory

Table 3. Variables of chromium uptake in soil

Soil Uptake Variable	Light-textured soil	Heavy-textured soil
Constant (p)	0.1811	0.0924
Direction coefficient (q)	0.0114	0.0049
Maximum adsorption (b)	87.719	204.082
Bond energy constant (k)	0.063	0.053

The data sources were processed from the results of the IAERI laboratory test

Table 4. Statistical test results of grain and straw weight at each chromium contamination level

Contamination Level	Light-textured Soil		Heavy-textured Soil	
	Grain (g)	Straw (g)	Grain (g)	Straw (g)
0	138 a	299 a	142 a	355 a
25	133 a	276 b	136 a	338 b
50	130 ab	269 b	130 a	312 b
75	127 b	259 b	128 a	306 c
100	124 b	238 c	118 b	284 c
200	109 c	231 c	113 b	261 c
400	87 d	204 d	72 c	229 d

The data source is processed from the analysis results in the IAERI laboratory

*The numbers followed by the same letter for each variable were not significantly different based on the DMRT test at α=0.05

Table 5. The estimated critical level for Chromium in the soil based on a simple regression equation between chromium metal content in soil and rice

Soil Texture	Equation	Maximum residue level in Rice (mg kg ⁻¹)	Estimated critical level in soil (mg kg ⁻¹)
Light-textured soils (Bantul)	$y = -0.000x^2 + 0.036x + 0.861$	0	0.861
Heavy-textured soils (Lamongan)	$y = -5E-05x^2 + 0.031x + 1.012$	0	1.012

The data source is processed from the analysis results in the IAERI laboratory

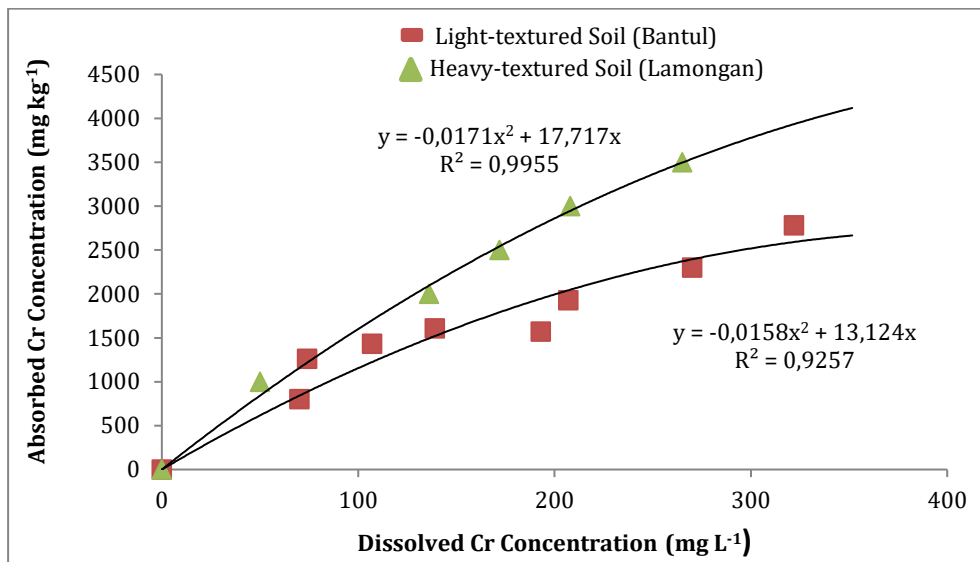


Figure 1. Chromium uptake curve in paddy fields

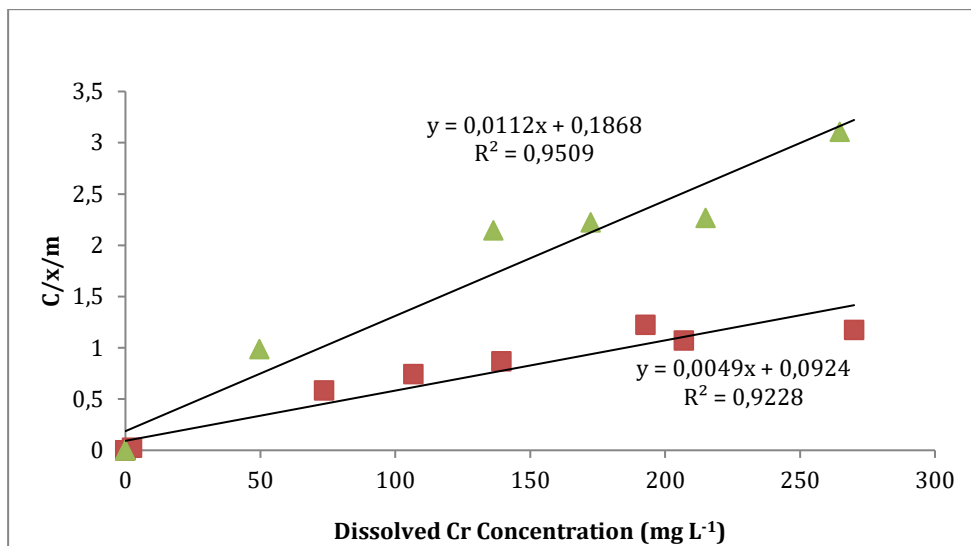
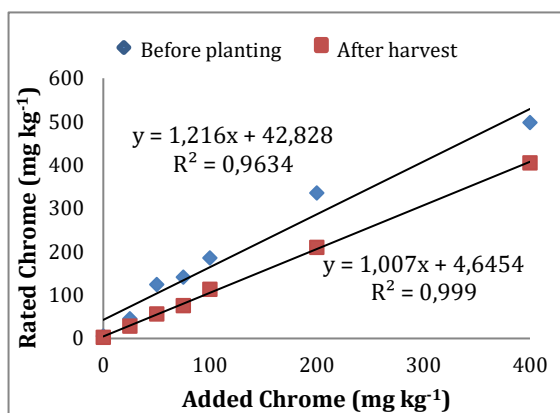
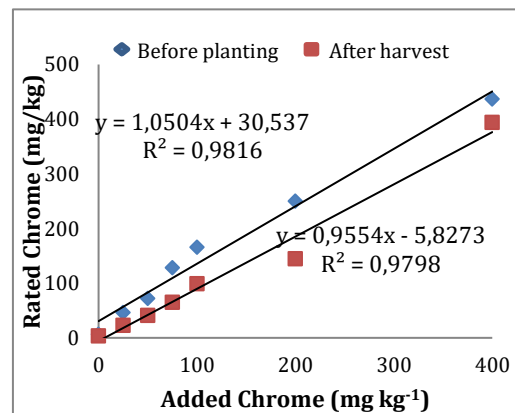


Figure 2. The relationship between C chromium and C/(x/m) in paddy fields

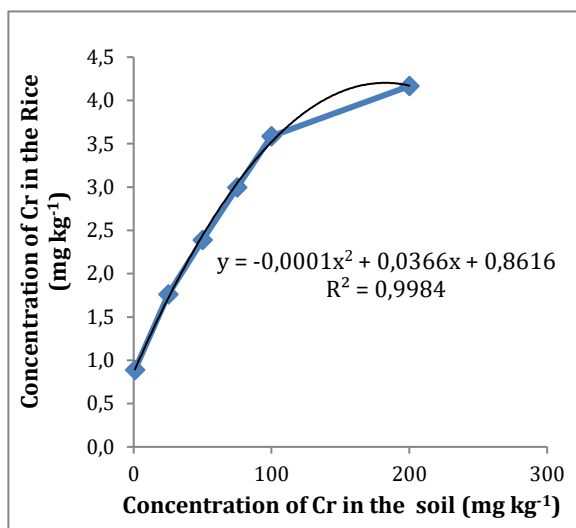


Light-textured soil (Bantul)

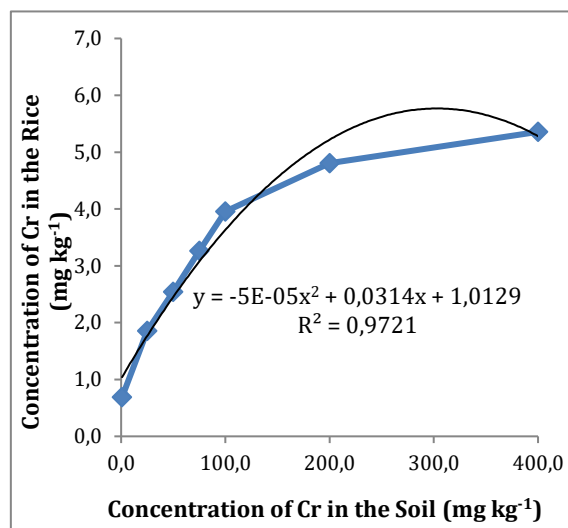


Heavy-textured soil (Lamongan)

Figure 3. Chromium content in the soil before and after harvest



Light-textured soil (Bantul)



Heavy-textured soil (Lamongan)

Figure 4. Chromium content in rice

4. Conclusion

Chromium absorption is influenced by soil pH, texture, mineral type, CEC, and soil organic C content. The maximum absorption of chromium in light-textured soil (Bantul) was 87.719 mg kg⁻¹, while in heavy-textured soil (Lamongan), the maximum absorption of chromium metal in the soil was 204.082 mg kg⁻¹. Soil contaminated with chromium will be absorbed by plants growing in the soil and accumulated in certain parts of the plant. The chromium content in rice increases with the high concentration of chromium in the soil. Accumulation of chromium in rice that exceeds the threshold can cause health problems for consumers.

The critical level of light-textured soil chromium in rice was 0.861 mg kg⁻¹, while the critical level for heavy-textured soil Chromium in rice was 1.012 mg kg⁻¹. In this study, only two types of soil texture were used, namely light and heavy textured soils. Future research can be supplemented by using medium-textured soils to improve the prediction of the critical chromium level to be complete. In addition, it is also necessary to research other potential commodities.

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