

Potential of Humic Acid from Soil to Reduce The Content of Heavy Metals

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Abstract. Humic acid is an important component for the qualities of soil with different properties or characteristics depending on the sources. The purpose of this study was to investigate the characteristics of humic acid produced from soil as a heavy metal adsorbent. This study used several methods to examine its adsorption pattern, including time incubations (20, 40, 60, 80, and 100 minutes), pH treatment (1-9), the adsorbent treatments (humic acid) with a weight ratio of adsorbent (1:2:3 and 4) also adsorption using five different heavy metals concentrations. The result showed that each treatment provides a different pattern of heavy metal uptake depending on the type of heavy metals. Humic acid from soil has good adsorption characteristics. They absorbed the greatest amount of heavy metals, particularly Pb (18.25%-98.06%), Cd (3.65%-70, 99%), and Cr (18.15%-97.52%). Furthermore, soil as a planting medium has potential to be used as a substance that can reduce heavy metal contain.

1 Introduction

Natural resources are abundant in the nation of Indonesia [1]. The abundance of natural resources, including the high potential of organic matter, might be a crucial resource for Indonesia's fight against environmental degradation. Although not abundant in the soil, this substance is crucial for the health of the soil. This is because the decomposition of these components will result in the production of nutrients and other elements that are crucial for plants, such as carbon and oxygen [2]. As of right now, materials for building materials and other important components can be derived from processes of decomposition of organic materials through mineralization and immobilization [3]. A more advanced process of decomposing organic materials can also yield valuable materials like humus, which has the function of providing plant with the elements that it needs [4]. The material in question may worsen nutritional deficiencies caused by plant and have negative effects on plant behaviour. Generally, humus is caused by humic material such as humin (which has a large molecular weight), humic (which has a medium molecular weight), and fulvat (which has a low molecular weight), all of which have important effects on soil health.

Today, the environment around us is polluted by many different types of contaminants. If it is not addressed right away, it could result in significant harm because the pollutants and

environmental variables that create this pollution can lead it to spread swiftly [5]. Metals, dyes, phenolic compounds, radionuclides, sulfur dioxide, carbon monoxide, particulates, and hydrocarbons are a few pollutants that are prevalent in the environment [6–8]. Heavy metals are pollutants that are created by a variety of human activities, including the mining, paper, textile, fertilizer industries, and may eventually turn into hazardous waste in nature [9].

It's crucial to use humic materials made from organic matter decomposition processes to decrease the concentration of pollution in the environment. In general, humic materials have been used extensively in research to minimize heavy metal content [10–12]. Adsorption is generally the most popular technique for lowering heavy metal content. Adsorption works by creating a complex between the metal and the functional groups that belong to the adsorbent. This is in line with [13] study, which found that an adsorbent surface rich in functional groups like -OH, -NH, -SH, and -COOH will be more effective at capturing and retaining substances. When it comes to the binding of metals by organic matter, humic substances are crucial because organic-metal complexes typically dominate metal speciation in wastewater. Based on this, it is still a fascinating topic to investigate how the characterization of humic components from soil affects the presence of heavy metals. This study's primary goal was to investigate the effects of humic acid from soil on the levels of the heavy metals Cr, Cd, and Pb. With the use of the information gathered, it is anticipated to describe the different uses for humic acid as a source of adsorbents that can help reduce environmental pollution. Also, this crucial information can support sustainable agricultural systems by assisting parties involved in agriculture, such as farmers, agricultural entrepreneurs, and the fertilizer business. In order to decrease the amount of pollutants in the soil, such as Cd, Pb, and Cr, this study set out to identify the features of the humic acid produced in the soil.

2 Materials and Methods

Samples of soil, chemicals for the extraction of humic acid and analyses of the chemical and physical characteristics such as NaOH, aquadest, buffer pH 4 and 7, HCl, H₂SO₄, KCl, K₂Cr₂O₇, standard of Cd, Pb and Cr, are among the materials employed in this experiment. GPS, a pH meter, a measuring flask, a measuring cup, an Erlenmeyer, a spray bottle, a shake bottle, a funnel, filter paper, a spectrophotometer, an AAS, UV-VIS, SEM-EDS, an XRD, and an FT-IR are among the equipment used for this experiment. The research design of this study used several methods to examine its adsorption pattern, including time incubations (20, 40, 60, 80, and 100 minutes), pH treatment (1-9), the adsorbent treatments (humic acid) with a weight ratio of adsorbent (1:2:3 and 4) also adsorption using five different heavy metals concentrations to see the pattern of heavy metal uptake such as Cr, Cd and Pb.

2.1 Physical and Chemical Analysis of Soil Properties

The analysis process was used to determine the soil's chemical qualities, which also included its pH value, organic-C content, nitrogen (N), potassium (K), phosphorus (P), calcium (Ca), magnesium (Mg), and sodium (Na), as well as its texture [14]. Humic acid is first produced through the method of extracting it from dry samples (humic acid, or HS). NaOH solution with a 10:1 ratio is used to extract this humic substance [15].

In the Cianjur Regency's Bojongpicung region, soil samples were collected. Using a land unit analysis, sample sites are chosen, and the analysis yields five representative land units. For each land unit, topsoil (0–30 cm) and subsurface samples were collected (30–60 cm) (Figure 1). Two sample sites are chosen to illustrate the state of the neighborhood for big land units. Each location point's coordinates were obtained using a GPS device (a Garmin 585) and shown on a map using desktop ArcGIS 10.2 software. Purposive random sampling was used to collect the samples. Figure 4 shows where the sampling points are located.

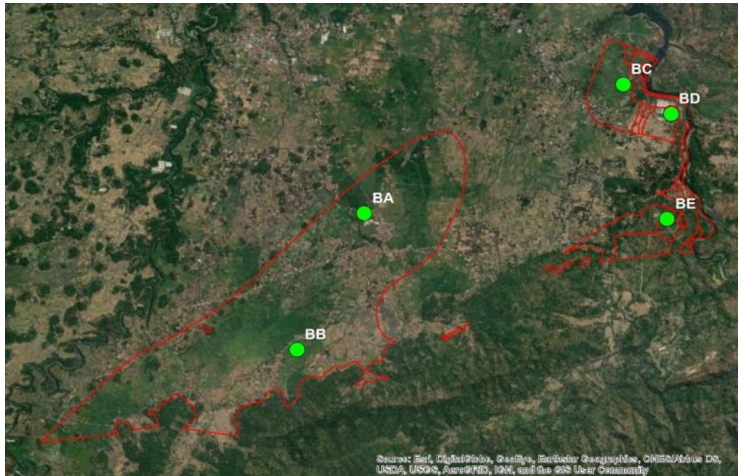


Fig.1. Soil Sampling Locations

The stages of this research were completed at the Padjadjaran University Faculty of Agriculture's Laboratory of Soil Chemistry and Plant Nutrition. The humic acid produced from soil was then examined for its adsorption pattern using a number of treatments, including time incubations (20, 40, 60, 80 and 100 minutes), pH treatment (1-9), heavy treatment of the adsorbent (humic acid) with a weight ratio of adsorbent (1:2:3 and 4) also adsorption use five different concentration of heavy metals. Using adsorbents made from humic acid from the soil, it is possible to explain the adsorption pattern between the heavy metals Cr, Cd, and Pb via all of these treatment modifications.

3 Results and Discussion

Tables 1 and 2 provide a general overview of the soil's chemical properties. Table 2 shows that the soil's Cation Exchange Capacity (CEC) is typically between 22.43 and 44.64 Cmol/Kg, with Ca content varying between 21.95 and 30.06 Cmol/Kg. The total base cations ranged from 36.60 to 50.43 Cmol/Kg, whereas the Mg content varied from 14.11 to 22.12 Cmol/Kg, the K and Na values from 0.08 to 0.81 Cmol/Kg and 0.27 to 0.68 Cmol/Kg, respectively.

Table 1. Base Cations and Total Base Cations from the CEC Analysis

Sample Code	CEC (Cmol/Kg)	Cation (Cmol/Kg)				Base Cation Total (Cmol/Kg)
		Ca	Mg	K	Na	
Sample I (0-30)	31.31	21.95	14.11	0.16	0.39	36.60
Sample I (30-60)	37.89	23.29	15.69	0.10	0.35	39.43
Sample II (0-30)	29.34	22.77	14.02	0.11	0.28	37.17
Sample II (30-60)	37.91	23.90	16.01	0.08	0.27	40.27
Sample III (0-30)	44.21	26.03	15.65	0.81	0.48	42.97
Sample III (30-60)	22.78	30.06	14.64	0.21	0.60	45.51
Sample IV (0-30)	22.43	26.08	16.83	0.64	0.47	44.01
Sample IV (30-60)	34.85	28.48	16.50	0.22	0.66	45.86
Sample V (0-30)	41.92	28.88	16.25	0.67	0.66	46.47
Sample V (30-60)	42.26	27.57	19.18	0.50	0.58	47.83
Sample VI (0-30)	44.64	28.92	16.58	0.41	0.57	46.48
Sample VI (30-60)	38.83	27.44	22.12	0.19	0.68	50.43
Sample VII (0-30)	40.01	29.41	14.48	0.61	0.63	45.13
Sample VII (30-60)	27.28	27.97	17.91	0.49	0.59	46.96

In general, the soil sample's characteristics such as CEC, cations, and total bases met the requirements, which ranged from low to very high. The CEC parameter has a significant impact on the properties of soil, particularly on its capacity to hold or retain cations. Thus that the mobility of nutritional components in the soil can be determined using CEC measurements as a reference [16].

Table 2. Shows the findings of the soil's humic acid, fulvic acid, and fulvic acid concentrations as well as the pH values.

Code	pH	Organic C (%)	Total N (%)	Humic Acid (%)	Fulvic Acid (%)
Sample I (0-30)	6.20	1.92	0.21	2.61	2.41
Sample I (30-60)	7.06	1.10	0.09	0.21	2.66
Sample II (0-30)	6.80	1.87	0.15	1.34	2.72
Sample II (30-60)	6.96	1.43	0.17	0.79	3.76
Sample III (0-30)	7.21	0.84	0.05	0.10	2.75
Sample III (30-60)	7.64	0.77	0.09	0.11	3.89
Sample IV (0-30)	6.98	1.61	0.20	1.89	2.99
Sample IV (30-60)	7.59	0.79	0.09	0.07	3.35
Sample V (0-30)	7.73	1.49	0.17	0.33	2.64
Sample V (30-60)	7.89	1.22	0.09	0.11	2.74
Sample VI (0-30)	7.84	1.05	0.09	0.12	2.79
Sample VI (30-60)	7.65	0.87	0.06	0.06	2.66
Sample VII (0-30)	7.40	1.52	0.13	0.46	2.68
Sample VII (30-60)	7.59	0.87	0.09	0.07	2.69

Table 2's analysis findings show that all samples had pH values between 6.20 and 7.89, which meet the criterion for neutral to slightly alkaline conditions. In general, environmental conditions have a significant impact on the acidity values of soil. This was clarified by [17] who noted that the pH value can dramatically rise throughout the growth phase of rice plants. The carbon content (C) is between 0.77% and 1.92%, falling into the category of "extremely low to low," and is often consistent with the amount of humic components present in the soil [18]. The overall N content ranges from 0.05% to 0.21%, and the C and N amounts are typically higher in the top soil layers.

3.1 Analysis Ratio of E4/E6

The results of measuring the E4/E6 ratio show that humic acid produced from soil give value 3.2. Analysis for self-standards yields of E4/E6 ratio was 3.82. The results of the E4/E6 ratio analysis using UV VIS from humic acid have shown the characteristics of humic acid by giving a peak in the range of 200 nm (Fig. 2). This is in accordance with the results of the study by [19], which stated that the characteristic of Natural Organic Matter (NOM), can be seen at UV light wavelengths of 220 nm – 280 nm.

In addition, this information on the value of the E4/E6 ratio suggests that the E4/E6 ratio increases with decreasing molecule size. This is consistent with [20] assertion that a higher E4/E6 ratio denotes a lower molecular size. While fulvic acid has an E4/E6 ratio ranging from 6-8.5, the E4/E6 ratios for humic acid still fall within the typical E4/E6 ratio for humic acids, which is 3-5. Based on [21] a humic compound's level of aromaticity can also be determined by this value. This is consistent with the study of [19]. A humic compound's level of aromaticity can also be determined by this value. According to study by [19], aromatic compounds typically have a UV light wavelength of 254 nm at different levels of activation.

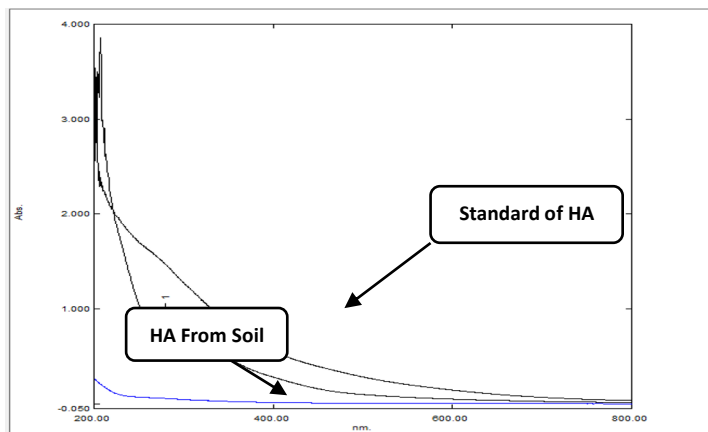


Fig. 2. Spectrum UV VIS of Humic Acid

3.2 SEM-EDS Analysis

Figure 3 displays the outcomes of humic acid analysis from soil using SEM-EDS. This analysis is performed to ascertain a material's composition and morphology aspect.

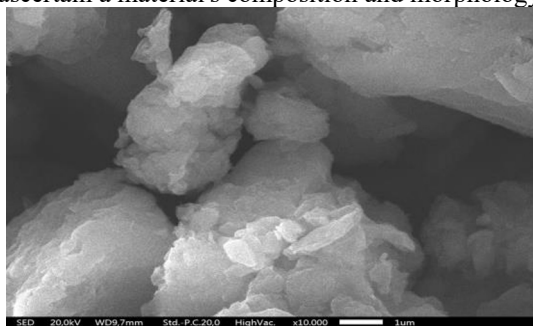


Fig. 3. Soil Humic Acid and SEM-EDS (magnification 10.000x)

The properties of humic acid from soil has an irregular morphology, as shown in Figure 3. In general, a material's surface might become more porous during the degradation process [21]. This may have an impact on the substance's capacity to bind heavy metals in solution. These humic acids have a variable of morphology, although the majority of them are granular and crumbly in texture. According to [22] study, which provided this information, This is consistent with the findings of a 2009 study by [22], who noted that humic acid from cow dung, vermicompost, silt, and sediment has a granular shape (in the form of aggregates such as crystals and various other forms). Table 3 shows the composition of the humic acid content based on the SEM-EDS study.

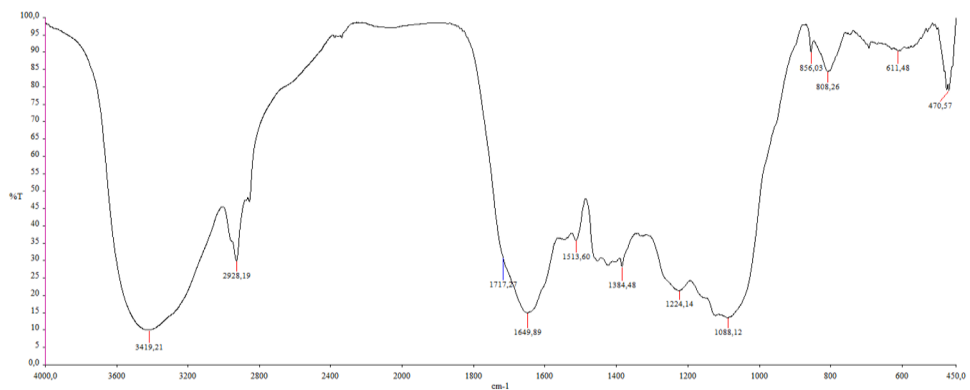
According to Table 3, the materials' composition, C and O make up the majority of the adsorbent. Furthermore, according to [23] research, the presence of C and O in all materials denotes the presence of polyelectrolyte macromolecules containing functional groups, such as carboxyl ($-\text{COOH}$).

Table 3. Humic Acid Composition of Soil Based on Analysis of SEM- EDS

Components	Contain (% Wt)
	Humic Acid from Soil
C	50.99
O	37.15
Si	5.13
Ca	-
Mg	0.25
Al	3.23
K	-
Cl	0.89
S	-
Fe	1.36
Na	0.86

3.3 FTIR Analysis

In Figure 4 displays, the outcomes of the humic acid FTIR study of the soil. As can be seen in Figure 4, the findings of the two analyses shows the characteristics humic acids from soil.

**Fig. 4.** FTIR Analysis from Humic Acids from Soil

Humic acid from the soil was revealed peaks in the 3419.21 area that indicate O-H stretching vibrations, the 2928.19 area that indicate aliphatic C-H stretching vibrations, the 1717.27 area that indicate C=O stretching vibrations, the 1513.60 peak that characterizes C-C stretching vibrations, the 1384.48 area that indicate C-H bending characteristics, and the 1224.14 and 1088.12.

Table 4. Results of the Analysis of the Absorption of Cr, Cd, and Pb by Soil Humic Acid

Contact Time	C Cr in Solution (mg/L)	Sorption Cr (mg/L)	C Cd in Solution (mg/L)	sorption Cd (mg/L)	C Pb in Solution (mg/L)	Sorption Pb (mg/L)
20 minutes	13.7404	1.2596	4.1340	0.0866	9.1493	0.8507
40 minutes	13.5760	1.4240	4.9160	0.0840	8.5872	1.4128
60 minutes	13.4260	1.5740	4.9481	0.0519	8.5088	1.4912
80 minutes	13.0316	1.9684	4.9316	0.0684	8.2519	1.7481
100 minutes	12.2774	2.7226	4.7076	0.2924	8.1733	1.8267

Explanation : C = Metal Concentration

In general, variations in contact times can result in a variety of absorption results; it is evident that the more time humic acid spends in touch with a metal, the more Cr, Cd, and Pb are absorbed. According to [23], the longer the contact period, the more heavy metals will be absorbed until they approach their maximum limit, at which point they will start to be absorbed less. It can be said that as the contact duration increases, the active side of the adsorbent shrinks, slowing the rate of adsorption until it reaches equilibrium.

3.4 Adsorption of Cr, Cd and Pb by Humic Acid from Soil Based on Variation of Acidity (pH)

The findings of the investigation of the absorption of the heavy metals Cr, Cd, and Pb show a similar pattern, showing that the absorption will be larger the higher the pH, specifically toward the base (Table 5). Of course, the degree to which humic acid can adsorb is a factor in this. Humic acid has been shown to dissolve in alkaline environments and to be effective at binding metals in solution. This method is consistent with how humic acids behave in general, which can segregate in acidic conditions and dissolve in alkaline situations [24]. The degree of ionization, speciation, and surface charge of the adsorbent are all connected to the mechanism of this reaction.

Table 5. Analysis Results of Cr, Cd and Pb Absorption by Humic Acid From Soil Based on pH Variations

Treatments pH	C Cr in Solution (mg/L)	Sorption Cr (mg/L)	C Cd in Solution (mg/L)	Sorption Cd (mg/L)	C Pb in Solution (mg/L)	Sorption Pb (mg/L)
pH 1	11.8876	3.1124	4.6400	0.3600	8.9245	1.0755
pH 2	12.7997	2.2003	4.6841	0.3159	8.0530	1.9470
pH 3	11.2603	3.7397	4.4432	0.5568	6.4895	3.5105
pH 4	9.8664	5.1336	4.1755	0.8245	5.1718	4.8282
pH 5	1.8199	13.1801	3.3702	1.6298	2.0638	7.9362
pH 6	1.7323	13.2677	2.5523	2.4477	0.6927	9.3073
pH 7	0.9549	14.0451	2.3531	2.6469	0.4830	9.5170
pH 8	0.8234	14.1766	1.8426	3.1574	0.2435	9.7565
pH 9	0.3800	14.6201	1.4066	3.5934	0.1867	9.8133

Information: C = Metal Concentration

3.5 Adsorption of Cr, Cd and Pb by Humic Acid from Soil Based on Variation of Humic Acid Amount

Table 6 displays the findings of the examination of the absorption of the heavy metals Cr, Cd, and Pb based on fluctuations in humic acid content. The table demonstrates that the absorption of heavy metals increases with the amount of humic acid supplied. The maximal adsorption power, which is typically regulated by environmental conditions, is what causes this. This is further supported by the assertion made by [25], who claim that surface activity and size are the two variables that can have an impact on the rise in interfacial adsorption power. Additionally, the structure of the adsorbent being utilized has a significant impact on this action. In addition, it is clear that Pb uptake by humic acids is higher than Cd uptake. This is because the carboxylic group, which is the main humic acid group and plays a significant role in metal-humic acid interactions that experience deprotonation so that Cd adsorption will be slower than absorption, plays a more active role in these interactions.

Table 6. Analysis Results of Cr, Cd and Pb Absorption by Soil Humic Acid Based on Humic Acid Variations

Treatments of Adsorbent	C Cr in Solution (mg/L)	Sorption Cr (mg/L)	C Cd in Solution (mg/L)	Sorption Cd (mg/L)	C Pb in Solution (mg/L)	Sorption Pb (mg/L)
0.03 g AH	11.9878	3.0122	4.9055	0.0945	8.2715	1.7285
0.06 g AH	11.7822	3.2178	4.8623	0.1377	8.2047	1.7953
0.09 g AH	11.8864	3.1136	4.8770	0.1230	8.1797	1.8203
0.12 g AH	11.7995	3.2005	4.8570	0.1430	8.1798	1.8202
0.15 g AH	11.6845	3.3155	4.8174	0.1826	8.1743	1.8257

Information: C = Metal Concentration

3.6 Adsorption of Cr, Cd and Pb by Humic Acid from Soil Based on Variation of Heavy Metal Concentrations

Table 7 provides an analysis of the absorption of the heavy metals Cr, Cd, and Pb. Metal concentrations 1 through 4 exhibited an increase in Cr absorption, followed by a decrease in metal concentration 5. It is believed that binding heavy metals causes the adsorbing substance to absorb at its maximum capacity, with Cr having the highest adsorption power at metal concentrations of 20 mg/L. This contrasts with the heavy metal Cd, which exhibits a linear pattern as its concentration rises. It is clear that the greatest metal concentration 10 mg/L produced the largest absorption, although for the heavy metal Pb, the adsorption tended to be uniform, falling between 20 and 21%. The heavy metal Pb has attained its maximal rate of absorption at a concentration of 5 mg/L to 15 mg/L at a ratio of 1:1000. These three diverse types of heavy metals differ from one another, demonstrating that each metal has unique mechanisms at play. This is in line with the study's findings, which showed that the mechanism of a bond's adsorption power would eventually reach an equilibrium point that is affected by the mechanism of the chemical reaction that takes place, the acidity of the solution, and other factors [25].

Table 7. Results of Cr, Cd and Pb Absorption by Soil Humic Acid Based on Metal Variation

Treatments of Heavy Metals	C Cr in Solution (mg/L)	Sorption Cr (mg/L)	C Cd in Solution (mg/L)	Sorption Cd (mg/L)	C Pb in Solution (mg/L)	Sorption Pb (mg/L)
Concentration 1	3.6405	1.3595	0.9197	0.0803	3.9070	2.0930
Concentration 2	7.2161	2.7839	2.5199	0.4801	5.8900	2.1100
Concentration 3	11.3247	3.6753	4.7980	0.2020	7.8210	2.1790
Concentration 4	16.1806	3.8194	6.9938	0.0062	9.9270	2.0730
Concentration 5	22.6651	2.3349	8.9957	0.0043	11.8708	2.1292

Information: C = Metal Concentration

Figure 5 shows the percentage of heavy metals Cr, Cd, and Pb absorption by humic acids from the soil that is removed. The % clearance (mass of additional humic acid) for each addition of adsorbent demonstrates that the absorption data rises with the addition of adsorbent. The range of the percent removal as a result of changes in the adsorbent's weight was different for Cr (20.08% -22.10%), Cd (1.89% -3.65%), and Pb (17.28% - 18.25%). In general, the % removal produced increased with the amount of adsorbent supplied. This is conceivable because humic acid adsorbent contains more active sites (C=O) and (-OH) that may adsorb heavy metals as adsorbent mass increases. In order to achieve the highest

absorption, an increase in the mass of the adsorbent also signifies an increase in the density of the adsorbent material in solution. The maximum absorption will be attained at a certain density that enables efficient interactions between metal ions and active groups since an increase in the mass of the adsorbent also signals an increase in the density of the adsorbent material in solution [26]. The mechanism of the adsorption process between heavy metals and humic acid from soil is influenced by soil characteristics, type of organic material and environmental conditions where the reaction occurs [27].

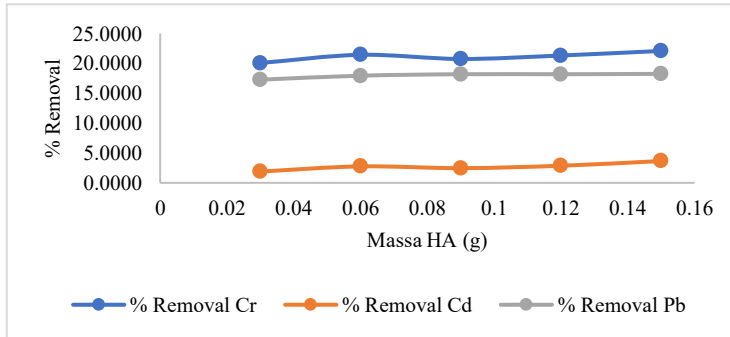


Fig. 5. Percent removal of heavy metal uptake of Cr, Cd and Pb by soil AH

4 Conclusion

Humic acid, which has good adsorbent characteristics can be produced in soil. Based on the type of heavy metals, each treatment generates a varied pattern of heavy metal uptake. The findings of the experiments show that there are good conditions that result in the highest rates of absorption for the three heavy metals, namely Pb (18.25% - 98.06%), Cd (3.65% -70, 99%), and Cr (18.15% - 97.52%). Because of the amount of organic matter in soil, it has the potential to be used as a product that can lower heavy metal concentrations in addition to serving as a planting medium. As a result, soil is important factor to support a sustainable agricultural system.

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