Mercury Adsorption Test On Several Large Groups Of Soils In West Sumbawa Regency, Indonesia

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Abstract.

Mercury is one of the heavy metals that has the highest toxicity in the global environment. Mercury can cause environmental damage and if it enters the food chain it can have negative impacts on human health. In overcoming the problem of mercury entering the food chain, it is very important to study the mobility and distribution of mercury in the soil. The presence of mercury (Hg2+) in soil is largely controlled by adsorption reactions with certain specific adsorption patterns. Therefore, it is very important to study mercury adsorption on several different types of soil in order to get an idea of how adsorption occurs in West Sumbawa Regency. The aim of this research is to determine the pattern and capacity of mercury adsorption on various large groups of soil in West Sumbawa Regency and the relationship between soil properties and mercury adsorption. The results of the research show that the adsorption isotherm pattern in the great soil groups Endoaquepts, Ustipsamments, and Udorthents more closely follows the Langmuir adsorption model, while the great soil groups Haplustepts, Hapludolls, Eutrudepts and Ustifluvents follow the Freundlich adsorption model. The major soil group that has the highest maximum mercury adsorption capacity in West Sumbawa Regency is Endoaquepts at 4,604 mg/g.

Keywords : *Mercury, Soil Properties, Adsorption, Langmuir and Freundlich.*

I. INTRODUCTION

Mercury is widely known as a toxic metal for the global environment (Bieser et al., 2023). This is because mercury has bioaccumulative properties, higher volatility than other metals and is very persistent in the soil (Hamzah, 2019). If the soil contains heavy metals that exceed the ability to digest these metals, it will result in soil pollution (Mirdat et al., 2013). Mercury that accumulates in the soil will enter the food chain and can have a negative impact on human health. Several reports state that mercury can pose a high risk to human health, such as motor nerve disorders, narrowing of vision, hearing, respiratory and digestive disorders, mental disorders and even death (Daniel Maramis et al., 2022; Hurum et al., 2023; Munawar et al. ., 2022).In overcoming the problem, mercury enters the food chain. It is very important to study the mobility and distribution of mercury in the soil. According to Schindler (1967) that the mobility and distribution of mercury in soil is largely controlled by the adsorption process with various adsorbents. The adsorption process occurs when Hg2+ metal contaminants are bound and adsorbed in soil colloids which act directly as adsorbents. The adsorption pattern will determine how strong the adsorbent bonds are to adsorb the adsorbate (Jasmal et al., 2015). It is known that there are two adsorption equation models that are often used, namely the Langmuir and Freundlich adsorption models. The Langmuir adsorption equation model follows chemical adsorption which has a strong binding force with adsorbate due to the presence of covalent bonds which cause each active site on the surface of the adsorbent to have the same energy and can only adsorb one specific molecule (Amanda, 2019).

Meanwhile, the Freundlich adsorption equation model follows physical adsorption which occurs due to the presence of Van Der Waals bonds which cause weak attractive forces between the adsorbate and the adsorbent surface (Maslukah et al., 2020).Therefore, it is very important to study mercury adsorption on several types of soil in order to get an idea of how adsorption occurs in West Sumbawa Regency. In this way, we can find out what type of soil is capable of absorbing higher levels of mercury. So that in the future soils that have high adsorption capacity can be used as natural remediation in mercury-contaminated areas in

West Sumbawa Regency. Apart from that, this research can also be used as a basis for information in preventing mercury contamination from entering the food chain in other areas. Several previous studies have studied mercury adsorption in soil (Jing et al., 2008; Ding et al., 2017; Wu et al., 2017; Olson et al., 2022) but mercury adsorption in several types of soil in Sumbawa Regency The West has never done it. Therefore, it is necessary to carry out research entitled "Mercury Adsorption Test on Several Large Soil Groups in West Sumbawa Regency".

II. METHODS

This research was conducted using descriptive methods with survey techniques. This research was carried out in November 2023-February 2024 in West Sumbawa Regency. Before taking soil samples, pre-survey activities are first carried out to see the condition of the research area and determine the location of the sampling location. The method used in selecting sampling location points was purposive sampling based on large soil groups in West Sumbawa Regency. Selection of soil sample points based on the distribution of major soil groups aims to provide an overview of how mercury adsorption occurs in several selected major soil groups. A total of 7 major soil groups have been selected by West Sumbawa Regency, namely Haplustepts, Hapludolls, Endoaquepts, Eutrudepts, Ustipsamments, Udorthents and Ustifluvents.

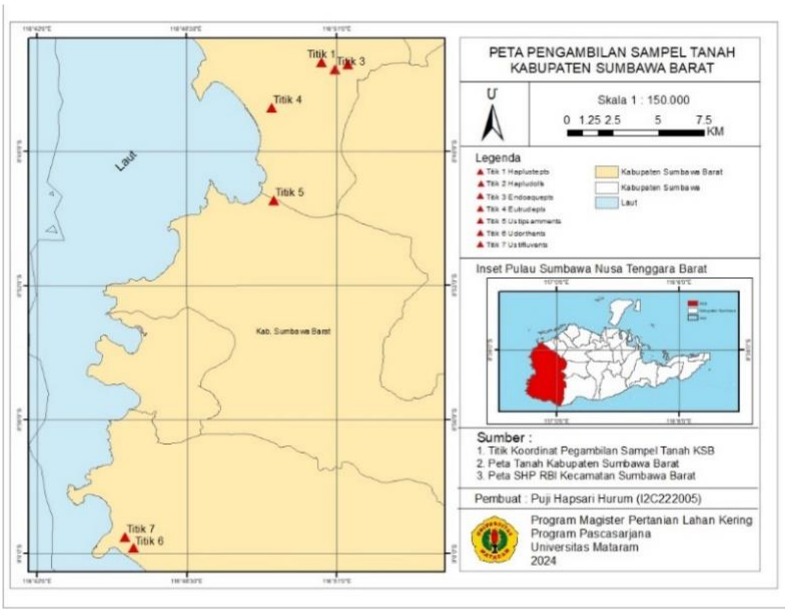

Fig 1. Soil Sampling Map of West Sumbawa Regency

Soil sampling was carried out at 7 points in the great groups of soil in 2 different soil layers with depths of 0-10 cm and 10-25 cm which were composited into one soil unit. Adsorption testing of soil samples is determined through adsorption isotherms. The mercury isotherm adsorption procedure was carried out in several stages, namely the weight of the soil used was 2 grams, then put into a shake bottle and 50 ml of 0.01 N KCl was added. Next, 10 ml of HgCl2 was added to each sample with a concentration of 0; 0.1 ; 0.2 ; 0.3 ; 0.4 ; and 0.5 ppm. After that, all samples were shaken at 200 rpm for 2 hours, then stored in a dark container for 22 hours (Jing et al., 2008). Adsorption was carried out on 7 soil samples for each Hg solution with repetitions 3 times. To determine the adsorption pattern of the Hg metal solution on the surface of the soil adsorbent, two isotherm adsorption models will be used, namely the Langmuir isotherm and the Freundlich isotherm (Apriyanti et al., 2018).

The Langmuir isotherm equation can be written as follows:

$$Ce/qe = 1/(qe)\ Ce + 1/(KL.qm)$$

Where:

Ce = equilibrium concentration (mg/L)

qe = equilibrium adsorption capacity (mg/g)

KL = Langmuir constant (L/mg)

qm = maximum adsorption capacity (mg/g)

The Freundlich Isotherm Equation is as follows:

$$\log (qe) = \log Kf + 1/n \log Ce$$

Where:

qe = amount of adsorbate on the surface (mg/g)

Ce = equilibrium concentration (mg/L)

Kf and n = constant

The obtained laboratory experimental data is plotted with ln (qe) as the y-axis and log Ce as the x-axis. The graph obtained is a linear line with slope = 1/n and intercept = log Kf

Data analysis was carried out using regression and correlation analysis with Microsoft Excel and adsorption calculations using Origin Pro 2024.

III. RESULTS AND DISCUSSION

Capacity and Efficiency of Mercury (Hg) Adsorption by Various Soil Groups in West Sumbawa Regency

Mercury adsorption capacity is described by the amount of adsorbate that is able to accumulate on the surface of the adsorbent (Asnawati, 2017). The success of adsorption is measured by the adsorption efficiency. Adsorption efficiency is the amount of solution absorbed divided by the amount of solution before it is absorbed(Salam et.al., 2023).

Table 1. Mercury Adsorption Capacity and Efficiency by Various Soil Great Groups at Various Concentrations

Ci (mg/L)	qe/E	Great Groups Land						
		Haplustepts	Happludolls	Endoaquepts	Eutrudepts	Ustipsamments	Udorthents	Ustifluvents
0.1	qe (mg/g)	0.262	0.250	0.180	0.245	0.135	0.213	0.281
	E (%)	52.41	50.53	36.81	49.77	27.23	42.84	56.53
0.2	qe (mg/g)	0.472	0.448	0.352	0.351	0.264	0.419	0.454
	E (%)	48.41	45.10	35.56	35.31	27.06	42.11	46.14
0.3	qe (mg/g)	0.691	0.642	0.505	0.528	0.394	0.538	0.696
	E (%)	46.64	43.48	34.49	35.58	26.72	36.34	47.04
0.4	qe (mg/g)	0.811	0.821	0.663	0.689	0.461	0.677	0.853
	E (%)	41.58	41.56	33.85	35.05	23.46	34.68	43.04
0.5	qe (mg/g)	0.884	1,000	0.839	0.757	0.590	0.785	0.933
	E (%)	35.67	40.59	33.83	30.84	24.14	31.88	38.10
Mean qe (mg/g)	0.624	0.632	0.508	0.514	0.369	0.526	0.643	
Mean E (mg/g)	45.11	44.25	34.91	37.31	25.72	37.57	46.17	

Information: Ci (Initial concentration); qe (Adsorption Capacity); E (Adsorption Efficiency)

Based on Table 1. Mercury adsorption (qe) by several major soil groups shows an increase as the Hg concentration increases, which means that the higher the Hg concentration added, the more Hg is adsorbed by the soil. According toSaputri (2020), adsorption is very small at low concentrations but adsorption will increase with increasing solution concentration. Mercury adsorption continued to increase from a concentration of 0.1 mg/L to 0.5 mg/L (Figure 2). This is because increasing the Hg concentration will cause more Hg ions to interact with the soil so that the mercury adsorption capacity increases. As reported by (Chen et al., 2020), the amount of adsorbate continues to increase with increasing concentration because the active sites on the adsorbent are still not filled so that they can accommodate a certain amount of adsorbate until all active sites are saturated with adsorbate (equilibrium condition).As presented in Table 1, the increase in mercury adsorption capacity is inversely proportional to its adsorption power (adsorption efficiency), which decreases as the Hg concentration increases. Theoretically, adsorption efficiency will decrease with increasing concentration added. This is because when the initial concentration is low the active site on the adsorbent is still available so that all the adsorbate can interact with the adsorbent, but after adding the highest concentration the active site is already saturated with the previous adsorbate (equilibrium phase) so that only some of the adsorbate can interact with the adsorbent.(Saputri, 2020).

The adsorption efficiency by various great groups of soils from highest to lowest is Ustifluvents, Haplustepts, Hapludolls, Udorthents, Edoaquepts, Eutrudepts and Ustipsamments. The highest adsorption efficiency by Haplustepts soil was at a concentration of 0.10 mg/L with an adsorption efficiency of52.41%Meanwhile, the lowest adsorption efficiency was by Ustipsamment soil at a concentration of 0.4 mg/L with an adsorption efficiency of only 23.46%.Ustifluvents soil is the soil that has the highest adsorption capacity compared to the other great soil groups, namely an average adsorption efficiency of 46.17%. The high adsorption capacity of Ustifluvents soil is estimated because this large group of soils contains organic matter, CEC and high levels of clay and sesquioxides. Increasing organic matter content will be followed by an increase in cation exchange capacity (CEC) and clay content. This is because soil that contains organic matter generally contains clay colloids. This clay colloid is able to bind cations in the soil (Fe and Hg). Organic matter is the main organic component in soil and plays an important role in Hg2+ adsorption. This is because Hg2+ has an affinity with the -O and N groups in organic materials. In addition, organic materials can provide important adsorption sites for Hg retention such as S-containing -S groups (Miretzky et al., 2005). A high CEC can provide a lot of negative surface so that a lot of Hg will be adsorbed on the adsorbent (Zhang et al., 2012).

Testing of Adsorption Models on Several Large Soil Groups in West Sumbawa Regency

The adsorption process by an adsorbent has a specific adsorption isotherm pattern. Every adsorbent that absorbs one substance with another substance will not have the same adsorption isotherm pattern. Testing the adsorption isotherm model on several great groups of soil aims to determine the adsorption isotherm pattern, whether the Hg2+ adsorption process by several great groups of soil fulfills the Langmuir equation or the Freundlich equation. Each of these equation models will determine the adsorption strength. To determine the Langmuir and Freundlich isotherm equations, calculate the values for Ce, qe, Log Ce and Log qe as in Table 4.16. Next, by mapping the graph by entering the values of 1/Ce and 1/qe, you will get the Hg adsorption isotherm pattern using the Langmuir model and entering the values of Log Ce and Log qe to get the Freundlich equation.

Table 2. Comparison of Langmuir and Freundlich Equation Models

Sample Point	Great group	Langmuir Isotherm Model		Freundlich Isotherm Model	
		Equality	R2	Equality	R2
1	Haplustepts	y=0.1519x+0.5965	0.9593	y=0.5909x+0.2588	0.9837
2	Happludolls	y=0.1761x+0.4929	0.9949	y=0.7750x+0.4041	0.9994
3	Endoaquepts	y=0.3384x+0.2172	0.9996	y=0.9202x+0.3589	0.9994
4	Eutrudepts	y=0.1595x+1.0584	0.9210	y=0.6188x+0.1654	0.9591
5	Ustipsamments	y=0.5124x+0.3407	0.9978	y=0.8776x+0.1423	0.9918
6	Udorthents	y=0.2326x+0.5639	0.9941	y=0.7180x+0.2483	0.972
7	Ustifluvents	y=0.1271x+0.7153	0.9719	y=0.6472x+0.3237	0.9781

Information: R2 (Coefficient of Determination)

Testing of the Langmuir and Freundlich adsorption equations is proven by a good linearization graph and has a coefficient of determination R2 $\geq$ 0.9 (close to 1). Based on Table 4.2, the adsorption of Hg2+ by several great soil groups of Endoaquepts, Ustipsamments, and Udorthents more closely follows the Langmuir isotherm adsorption model as evidenced by the coefficient of determination (R2) which is closer to 1 with the respective R2 values being 0.9967, 0.9996, 0.9978 and 0.9720. This indicates that the adsorption process that occurs is chemisorption (chemical adsorption) and Hg adsorption only takes place in one layer. Chemical adsorption is irreversible, specific, and depends on the surface chemistry, activation energy, and pressure of the adsorbent.As explained by Rahman (2018), chemical adsorption (chymissorption) occurs due to the interaction between the active site of the adsorbent and the adsorbed substance. In the Langmuir isotherm there is a certain number of active sites which is proportional to the surface area of the adsorbent. At each active site there is only one molecule that can be adsorbed, in other words, each active site can only adsorb one molecule.(Ghabbour & Davies, 2011). The Langmuir isotherm model assumes that the adsorbent surface is homogeneous and the amount of adsorption energy is equivalent for each adsorption site(Amanda, 2019). This is what causes the Langmuir isotherm to have a strong bond between the adsorbent and the adsorbate substance.

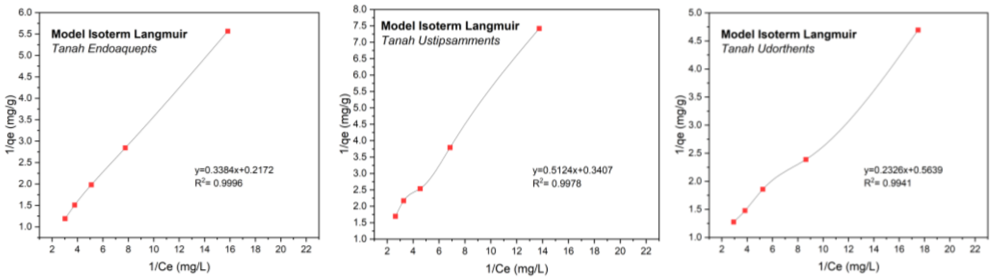

Fig 4. 3 Langmuir Isotherm Patterns in the Great Soil Groups of Endoaquepts, Ustipsamments and Udorthents in West Sumbawa Regency

Meanwhile, the great soil groups Haplustepts, Hapludolls, Eutrudepts and Ustifluvents more closely follow the Freundlich isotherm adsorption model because they have coefficient of determination values that are close to 1, namely 0.9837, 0.9994, 0.9591 and 0.9781. This indicates that the adsorption process occurs via physisorption (physical absorption). Physisorption is an adsorption event that occurs due to physical forces (Madina et al., 2017). As reported bySari et al. (2017)that in physical adsorption the physically adsorbed molecules will not be strongly bound (have weak bonds) on the surface and usually occurs in a fast, reversible process, so they are easily replaced with other molecules. This is confirmed by the opinion of Jasmal et al., (2015) that physical adsorption occurs due to the presence of Van Der Walls bonds, namely the weak attractive force between the adsorbate and the surface of the adsorbent.

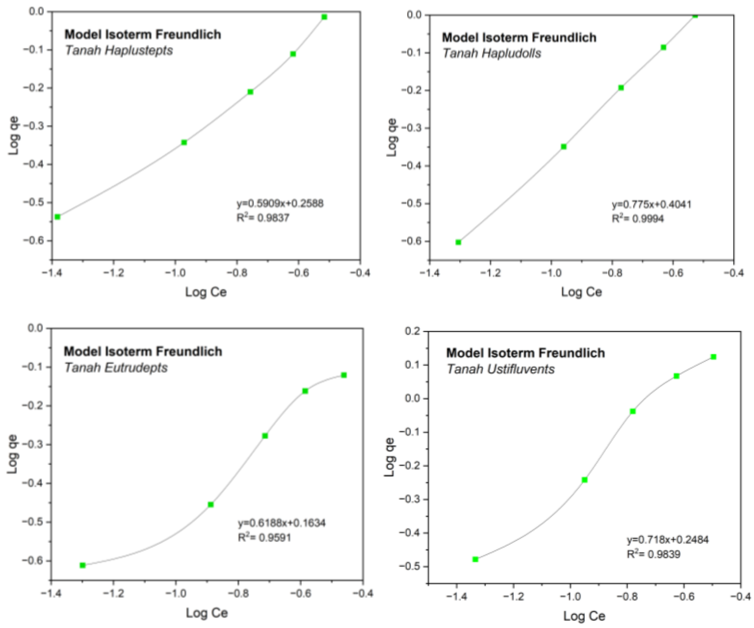

Fig 4. Freundlich Isotherm Pattern in the Great Soil Groups Haplustepts, Hapludolls, Eutrudepts and Ustifluvents in West Sumbawa Regency

The Freundlich equation model states that there is more than one surface layer and the sides are heterogeneous, so that there is a difference in bond energy on each side. As reported byAtkins (1999)that the Freundlich approach assumes that adsorption occurs on the surface of the adsorbent which is heterogeneous and the adsorption forms many layers. This allows the adsorbate to move freely until the adsorption process takes place in many layers. However, the adsorbate is not strongly bound to the adsorbent so that the adsorbate can move from one part of the adsorbent surface to another. So that the surface left by the adsorbate can be replaced by other adsorbate.From the linear equation obtained by graphing the Langmuir and Freundlich isotherms, it can be used to determine the maximum adsorption capacity and adsorption affinity by determining the Langmuir parameters (KL and Qm) and Freundlich parameters (KF and 1/n). Maximum adsorption capacity refers to the maximum amount of adsorbate that can be adsorbed by an adsorbent under ideal conditions when all adsorption sites are active and available. The maximum adsorption capacity can be obtained after optimizing the parameters that influence adsorption(Miri & Narimo, 2022). The Qm value is obtained from the calculation results (1/a) while the KL value is obtained from the calculation (1/(Qmxb). The KF value is obtained from the calculation results (log a) while the 1/n value is obtained from the b value. where a and b are intercepts. and slopes.

Table 3. Langmuir Isotherm Parameters

Parameter Langmuir	Great Groups Land		
	Endoaquepts	Ustipsamments	Udorthents
qm (mg/g)	4,604	2,935	1,773
KL	0.64	0.66	2.09
R2	0.9996	0.9978	0.9941

Information: qm (Maximum Adsorption Capacity); KL (Langmuir Constant); R2 (Coefficient of Determination)

Table 4.3 shows the highest maximum adsorption capacity by Endoaquepts, namely 4,604 mg/g, while the lowest maximum adsorption capacity is by Udorthents soil, namely 1,676 mg/g. In research conducted byJasmal et al. (2015) explained that the qm value obtained from the Langmuir isotherm illustrates that the bond between the adsorbent and Hg2+ forms a significant amount of monolayer and shows maximum or saturated absorption capacity where all sorption sites are full, with the formation of a layer on the surface of the adsorbent. The KL value indicates the level of affinity between Hg2+ and the adsorbent surface, where if the KL value <1 then adsorption indicates a weak level of affinity between the Hg2+ metal and the adsorbent. In this study, the soil of Endoaquepts and Ustipsamments had a KL value <1 which indicates a weak level of affinity between Hg2+ metal and the adsorbent. Meanwhile, Udorthents has a strong affinity between Hg2+ metal and the adsorbent because it has KL>1.

Table 4. Freundlich Isotherm Parameters

Parameter Freundlich	Great Groups Land			
	Haplustepts	Happludolls	Eutrudepts	Ustifluvents
KF (mg/kg)	2,054	2,535	1,411	1,808
1/n	0.65	0.77	0.71	0.60
R2	0.97317	0.99939	0.94582	0.9830

In Table 4.4, the maximum adsorption capacity in the three great soil groups from highest to lowest is Hapludolls>Haplustepts>Ustifluvents>Eutrudepts. The highest maximum adsorption capacity in the Freundlich model is Hapludolls with a value of 2,535 mg/g, while the lowest maximum adsorption capacity is Eutruddepts soil, namely 1,411 mg/g. In research conducted by(Wijayanti et al. (2018)stated that the adsorption coefficient KF can be roughly used as an indicator of maximum adsorption capacity and 1/n is the adsorption intensity. In general, the higher the KF value, the higher the adsorption capacity. Meanwhile, the exponent value 1/n provides an indication that supports adsorption, the value 1/n<1 represents adsorption with normal intensity and is highly preferred.

The 1/n value indicates the level of affinity between Hg2+ and the adsorbent surface, where if the 1/n value is <1 then the adsorption intensity occurs normally and indicates a high level of affinity between the Hg2+ metal and the adsorbent. On the other hand, if 1/n > 1 then the adsorption intensity occurs abnormally and indicates a weak level of affinity between the Hg2+ metal and the adsorbent. In this study, all Haplustepts, Hapludolls, Ustifluvents and Eutrudepts soils had a value of 1/n <1 which indicated that the adsorption process occurred normally and had a strong affinity between the Hg2+ metal and the adsorbent.

IV. CONCLUSION

Based on the objectives and discussion above, it can be concluded that:

1. The isotherm adsorption pattern in the great soil groups Endoaquepts, Ustipsamments and Udorthents follows the Langmuir adsorption model, while the great soil groups Haplustepts, Hapludolls, Eutrudepts and Ustifluvents follow the Freundlich adsorption model as evidenced by the coefficient of determination $R2 \geq 0.9$ (close to 1) .
2. The major soil group that has the highest maximum adsorption capacity in the Langmuir adsorption model is Endoaquepts of 4.604 mg/g. Meanwhile, the great group of soil that has the highest maximum adsorption capacity in the Freundlich adsorption model is Hapludolls at 2.535 mg/g.

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