Determination of Pb(II) ion Adsorption Isotherm Model by Regenerated Spent Bleaching Earth (RSBE)

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Abstract. Waste water from several industries such as paint plant, printing, tin smelting, plastic factory, also fuel leaking from ships and ship welding are the main causes of the presence of Pb(II) ions in the water. Lead is a heavy metal that can adversely affects all organisms in the waters and can accumulate in the food chain, it is harmful to human and animal if exposed to it. Adsorption is one of the technologies for separating dissolved metal ions in liquid that easy handling and very effective. The concentration of heavy metal ions in solution can be reduced by using an adsorbent, such as zeolite, activated charcoal, regenerated spent bleaching earth (RSBE). Spent bleaching earth (SBE) is a disposal from edible of the bleaching unit in oil refinery industries, it can be regenerated to a adsorbent RSBE. The treatment SBE into RSBE, oil of SBE is separated by the solvent extraction method at 72°C for 5 hours with n-hexane as a solvent, followed by washing it with HCl 3%, then physically activated at 470°C for 12 hours. The goal of this study are to increase SBE value and reduce the level of Pb(II) ions in solution with RSBE. Several works done in this study, namely characterization of SBE and RSBE, determination of the absorption capacity of RSBE against Pb (II) ions at equilibrium conditions, and an adsorption isotherm model of Pb (II) ion by RSBE. Results, RSBE has a specific surface area of 165.88 m²/g, a total pore volume of 0.21 cc/g with an average pore diameter of 6.90 nm. Based on these values, RSBE is categorized as a mesoporous adsorbent. The adsorption of Pb (II) ion by RSBE reaches equilibrium after 150 minutes contact time. The adsorption Pb (II) ion by RSBE is follows the Langmuir isotherm adsorption model with a correlation coefficient (R²) value of 0.9935 and a maximum adsorbing capacity value of 4.29 mg Pb (II)/g RSBE.

1. Introduction
Spent bleaching earth (SBE), a disposal from edible of the bleaching unit in oil refinery industries. It ignites spontaneously, this fire hazard resource has been handled by landfill, unfortunately it requires more lands and larger spaces. In Indonesia, the demand of cooking oil is always increasing by time, also the number of refinery industries [1], so the amount of SBE is increasing as well. The goal of this research is to increase the SBE value and reduce the concentration ion Pb(II) in solution by RSBE. Several works done in this study, namely characterization of SBE and RSBE, determination of the absorption capacity of RSBE against Pb (II) ions at equilibrium conditions, and an adsorption isotherm model of Pb (II) ion by RSBE. Results, RSBE has a specific surface area of 165.88 m²/g, a total pore volume of 0.21 cc/g with an average pore diameter of 6.90 nm. Based on these values, RSBE is categorized as a mesoporous adsorbent. The adsorption of Pb (II) ion by RSBE reaches equilibrium after 150 minutes contact time. The adsorption Pb (II) ion by RSBE is follows the Langmuir isotherm adsorption model with a correlation coefficient (R²) value of 0.9935 and a maximum adsorbing capacity value of 4.29 mg Pb (II)/g RSBE.
determined by using Pb (II) ions in aqueous solution and Atomic Absorption Spectrophotometer (Varian-Spectra AA 220). Furthermore, SBE's regenerated (RSBE) was applied for an adsorbent to reduce a heavy metal Pb (II) in aqueous solutions [6 - 8].

The main cause of increased lead levels in waters are waste water from several industries such as paint plant, printing, tin smelting, plastic factory, also fuel leaking from ships and ship welding [9 - 12]. Lead exposure at a concentration of 25.06 mg/l in tilapia can cause edema, necrosis, secondary lamellar hyperplasia, and lamellar fusion in the gills and can also cause death in Prochilodus lineatus [13]. Lead can interfere with the male reproductive system by reducing the quality of semen [14] suggesting that lead exposure of 5.29–7.25 µg /dl can reduce semen quality in men. When the blood lead concentration is greater than 20 µg / dl it can decrease hemoglobin and increase the risk of developing anemia [15 - 17]. Other investigators reported that 28 out of 33 workers (84.8%) in metal casting suffered from impaired liver function [18]. In principle, the content of heavy metal ions in solution can be reduced by using adsorbents, such as zeolite, activated charcoal [19, 20].

Adsorption is one method to reduce the levels of dissolved metal ions in waste water, because it is easy to handle and very effective, does not cause toxic side effects and is inexpensive compared to other methods [21], so it is widely used in industries. Research on the adsorption of Cr (VI) ions by zeolite has been carried out and the adsorption isotherm model was determined [19]. In this study, the determination of the Pb (II) ion adsorption isotherm model by RSBE were examined by the Freundlich adsorption isotherm method, Langmuir isotherm, BET isotherm, Sigmoidal Chapman isotherm, and thermodynamic adsorption model. The pattern of the Pb (II) ion adsorption isotherm model by RSBE was determined from the results of the adsorption isotherm model and the linearity of the curve indicated by the highest R^2 value. The highest acceptable R^2 price is ≥ 0.95 or ≥ 95% of the sediment in an area depends on the condition of igneous rocks (bedrock) around the area. If bedrocks are exposed on the surface, it can be concluded that the sediment in the area is very thin, and even in a certain place the sediment cannot be found. The size of this sediment thickness becomes an important variable to determine how much the amount of groundwater can be stored in the sediment, so that in areas with igneous rocks that are in shallow depths, the possibility of groundwater should be cultivated from the fractures of the bedrocks. However, the exploration of groundwater in the shallow bedrock area is needed in order to obtain the water resources for the certain purposes.

2. Methods

All reagents were applied, such as CH\textsubscript{3}OH (impure), n-hexane (impure) and acetone (impure), H\textsubscript{2}SO\textsubscript{4} (± 98.99% purity, Merck), NaOH pellet (± 99.95% purity, Merck) and HCl (37% fuming, Merck). There were several steps have been done in this research, firstly SBE sampling, SBE characterization, oil separation of SBE, regeneration of SBE to RSBE, characterization of RSBE, determination of the equilibrium time between RSBE and Pb (II) ionic, determination of the adsorption power of RSBE and determination of the adsorption isotherm model.

Spent bleaching earth was collected at the point of its disposal from edible Oil refineries in Industrial Area- Dumai, Riau-Indonesia. Samples from eight point of SBE's landfill area were mixed together in the one place. Then the SBE was screened to obtain a particle size of 100 mesh.

Oil separation of SBE has been done by using solid-liquid extraction method such as Soxhletation. Firstly, at soxlethation process, 500 ml solvents was heated at a certain temperature and it converted to gas form, then this gas flew through 100 g SBE of sample chamber. The oil was separated from the extractant at a certain temperature and vacuum condition. This process is finished if KmnO\textsubscript{4} solid was contacted with gas and it’s colour turn over from purple to blue. N-hexane soxhletation heated at ± 72°C.

SBE was characterized proximate and ultimate, also pH. Some of the proximate analyzes carried out were the determination of pH (Mettle-Teledo), moisture content, bulk density (SNI 01-2891-1992), ash content, volatile material content (British 1016 Part 104.3: 1998) and bound carbon content (British 1016 Part 104.1: 1999). To determine the levels of the element carbon and elemental sulfur,
the ultimate analysis was carried out using the thermal conductivity and infrared methods on the absorption spectrum of the area ranging from 1000/cm - 4000/cm.

In addition, SBE’s residue from soxlethration process was rinsed with HCl 3%. The 3% HCl solution was contacted with SBE in a beaker with an SBE / HCl ratio of 1: 5 (m / v) for 60 minutes while stirring using a mechanical stirrer at a speed of 250 rpm. The SBE is then separated from the acid by filtering. Then, it was washed until the wastewater rinse’s pH neutral. After that, it was activated by heating it under temperature 470 °C for 12 hours (Nabertherm (R)). After activation process was finished, there was Regenerated Spent Bleaching Earth (RSBE) obtained as an adsorbent. SBE and RSBE were characterized by using Brunauer-Emmett-Teller Analysis (BET Analysis) for it’s surface area, mean pore diameter (nm), total pore volume.

Determination of the adsorption equilibrium time between Pb (II) ions and RSBE, as much as 100 ml of 20 ppm of Pb (II) solution was put into 250 ml Erlenmeyer, then added 1 g of RSBE. This mixture is stirred using a hotplate equipped with a magnetic stirrer with a speed of 300 rpm for a certain time. After that, separated RSBE with Pb (II) fluid. The concentration of Pb (II) ion in the liquid is determined with the aid of an Atomic Absorption Spectrophometer (AAS). This experiment was carried out with variations in the adsorption time of 30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 minutes at a temperature of 40 °C. Based on the data obtained, a curve of the adsorption time versus the absorption power of RSBE to Pb (II) ion was made.

The absorption of RSBE to Pb (II) ion was determined by batch. 100 ml of Pb (II) ion solution was put into Erlenmeyer, then 1 g of RSBE was added. The mixture was stirred at 300 rpm for 150 minutes. After that, the RSBE residue was separated from the Pb (II) liquid. Determination Pb (II) ionic concentration of filtrated was measured by Atomic Absorption Spectrophometer (Varian-Spectra AA 220). Adsorption number of RSBE (Qe) at Pb (II) ionic were estimated by using this equation (1).

\[ Qe = \frac{Co - Ce}{m} v \]  

Where, \( Co \) is Pb (II) ionic concentration initially, \( Ce \) is Pb (II) ionic concentration after adsorption process, \( v \) is Pb (II) ionic volume initially, and \( m \) is the amount of RSBE before adsorption process. Equilibrium time of this adsorption was calculated based on adsorption number data obtained. In this experiment, it was carried out using variations in the concentration of Pb (II) ions (20, 30, 40 ppm) and the adsorption temperature (40, 50 and 60 °C). Based on the data obtained, the Pb (II) ions adsorption isotherm model by RSBE is determined according to Freundlich, Langmuir, BET, Sigmoidal Chapman.

3. Results and Discussion

| Parameter                        | SBE          | RSBE         |
|----------------------------------|--------------|--------------|
| Surface area (m²/g)              | 15.94        | 165.88       |
| The mean pore diameter (nm)      | 2.63         | 6.90         |
| The total pore volume (cc/g)     | 0.05         | 0.21         |
| Water content                    | 3.19 %       | 3.19 %       |
| pH                               | 6.98         | 6.88         |
| Bulk density at room temperature | 0.67 g/cm³   | -            |
| Volatile matter content          | 1.09 %       | 0.04 %       |
| Ash content                      | 62.19 %      | 22.23 %      |
| Fixed Carbon                     | 31.57 %      | 31.57 %      |
| Carbon element content           | 20.33 %      | 21.35 %      |
| Sulphuric element content        | Not detected | Not detected |
Table 1 shows the result of SBE and RSBE characteristics for several parameters. Both SBE and RSBE are not corrosive materials because it’s pH neutral, also this material are less reactives. Fixed carbon content of these materials are quite high 31.57% and it will increase SBE’s caloric value. In addition, based on ultimate analysis results by thermal conductivity and infrared methods, the carbon element that contains in SBE and RSBE are quite high, then a sulfuric element of these materials are not detected.

Some researches reported that SBE is a potential oil resources to reuse because of these properties [3], others report that RSBE is a good adsorbent to reduce heavy metals in solution [3, 7]. The regeneration process of SBE into RSBE greatly influences the characteristics of RSBE (Table 1). The surface area, the mean pore diameter, and the total pore volume in RSBE were significantly greater than SBE. In this study, the resulting RSBE has a specific surface area of 165.88 m$^2$/g, an increase of about 1000% from before SBE was regenerated (15.94 m$^2$/g). This value is greater than the results of other researchers [22] who have a specific surface area of 121.70 m$^2$/g. The specific surface area of the porous adsorbent ranges from 100 to 1000 m$^2$/g [23]. The specific surface area of the RSBE obtained has a value close to that of natural bleaching earths or in studies conducted by Plata et al. (2019) is called VBE (Virgin Bleaching Earth) which has a value of 168.11 m$^2$/g.

Apart from the surface area, the average pore diameter and the total pore volume are important characteristics to know for a porous material. According to the International Union of Pure and Applied Chemistry (IUPAC) there are 3 classifications for pore diameter, namely micropores (diameter <2 nm), mesoporous (2 nm <diameter <50 nm) and macropores (diameter> 50 nm). Based on the pore diameter classification, SBE and RSBE have an average pore diameter of 2.63 nm and 6.90 nm, respectively, including the mesoporous type because the average pore diameter is in the range of 2 to 50 nm. The average pore diameter size of RSBE is greater than that of SBE, this is due to the activation process in SBE which causes impurities in SBE to be released [23]. Thus with the total pore volume, RSBE has a greater value than SBE, namely 0.21 cc / g and 0.05 cc / g, respectively, the increase in total pore volume is due to the dissolution of impurities that fill the SBE pore system at the time. acid dissolving process [24].

**Results of Determination of Equilibrium Time**

The adsorption equilibrium time is the time there is no more Pb (II) ions uptake by RSBE or the absorption power of RSBE is constant. This is indicated by the absence of a change in concentration in the solution with increasing contact time. Determination of the equilibrium time is the first step in the adsorption equilibrium experiment because all data on the absorption of Pb (II) ions by RSBE are determined at the time of adsorption equilibrium. The curve of the results of the timing of the adsorption equilibrium of Pb (II) by RSBE is presented in Figure 1 and the number of Pb(II) ions adsorbed (uptake) by RSBE can be seen from the equilibrium data.
At the adsorption time of 0-30 minutes, there was an increase in the absorption of Pb (II) ions by RSBE which was very significant compared to the next adsorption time. This is due to the rapid absorption of Pb (II) ions by RSBE at the beginning of adsorption (0-30 minutes) because the RSBE pores are still empty, which are used to absorb Pb (II) ions (Sari, 2009). In the adsorption time range of 60-120 minutes, the increase in the absorption of Pb (II) ions by RSBE was not that big compared to that at 30 minutes. This shows that the Pb (II) ion adsorption process is close to equilibrium time. This efficiency increase occurs until 150 minutes, after which there is no significant change in the efficiency of the adsorption process, so it can be concluded that the adsorption time of 150 minutes is the time when the adsorption rate is the same as the desorption rate or the adsorption equilibrium state of Pb (II) ion by RSBE has been reached.

**Result of Determination of RSBE Absorption Power**

The absorption power of RSBE against Pb (II) ions at various conditions of Pb (II) ion concentration and adsorption temperature can be seen in Table 2.

| Pb(II) concentration before adsorption process (ppm) | Pb(II) concentration after adsorption process (ppm) | Removal (%) |
|---------------------------------------------------|---------------------------------------------------|-------------|
| 40°C                                               | 50°C                                               | 60°C        |
| 20                                                 | 1.31                                              | 1.23        | 1.12        | 93.41 | 93.82 | 94.35 |
| 30                                                 | 1.73                                              | 1.53        | 1.39        | 94.22 | 94.89 | 95.33 |
| 40                                                 | 2.19                                              | 2.01        | 1.82        | 94.51 | 94.95 | 95.43 |

The concentration of Pb (II) ion adsorbate is one of the factors affecting the absorption process of Pb (II) ions by the RSBE adsorbent (Table 2). The higher the concentration of Pb (II) ions, the greater the number of Pb (II) ions adsorbed by RSBE. This is because the adsorbate is absorbed a lot by the adsorbent, with the higher the adsorbate concentration, the more adsorbate ions diffuse and interact in the adsorbent cavities or pores.

Overall, activation temperature of RSBE are affected to RSBE's adsorption power (Table 2). Adsorption power increases as the level up of activation temperature of RSBE. At activation temperature 60°C, the maximum adsorption power of RSBE on Pb (II) ionic is 38.18 mg Pb (II) / g. It removed a heavy metal Pb (II) in aqueous solution very significantly with removal percentages 95.43%. wt. At higher temperatures, the kinetic energy of the molecule for the collision will be greater, so that the ability of the adsorbent to adsorb Pb (II) ions will also increase, so the efficiency of absorption of Pb (II) ions by RSBE also increases. As is the case with research conducted by Rahayu and Purnavita (2014) which states that at higher adsorption temperatures, the kinetic energy of the molecules for the collision will be greater, so that the ability of the adsorbent to adsorb will also increase. It can be concluded, RSBE is a material which has strong adsorption power for Pb (II) ionic in aqueous solution found that RSBE could adsorption Cu (II) ionic highly ± 98% [7].

**Pb (II) Ion Adsorption Isotherm Equilibrium Model by RSBE**

Determination of the Pb (II) ion adsorption equilibrium model by RSBE was determined by linear regression method for variations in temperature and concentration. The equilibrium models reviewed are the Freundlich, Langmuir, BET equilibrium model and the Sigmoidal Chapman equilibrium model. The adsorption pattern is determined by comparing the linearity of the curve shown by the R² price. Acceptable R² rates are ≥ 0.95 or ≥ 95% [25]. The results of the Freundlich and Langmuir adsorption isotherm equilibrium can be seen in Figure 2 and 3.
Figure 2. Freundlich Model Equilibrium Curve

Figure 3. Langmuir Model Equilibrium Curve

Figure 4. BET Model Equilibrium Curve

Figure 5. Chapman Model Equilibrium Curve

According to Freundlich, every porous solid object has potential as an adsorbent, and the adsorbent adsorbs molecules / adsorbates in the form of a monolayer and the adsorption event is physical adsorption. Freundlich's isotherm equation is as follows;

\[ Q_e = K C_e^{1/n} \]  \hspace{1cm} (2)

\[ \log Q_e = \log K + \frac{1}{n} \log C_e \]  \hspace{1cm} (3)

Where, \( Q_e \) is the amount of mg Pb (II) / g RSBE, \( C_e \) is Pb (II) ionic concentration at time of equilibrium, \( K \) is a constant at equilibrium, \( n \) is a Factor heterogeneity. Based on the straight line equation \( y = 0.6687x + 0.1401 \), the slope is \( 1/n = 0.67 \) and the intercept is \( K = 1.38 \) which is the Freundlich constant (Figure 2).

In the Langmuir isotherm theory, it is assumed that the adsorbent has a homogeneous surface and can adsorb one adsorbate molecule and there is no interaction between the adsorbed molecules. The adsorption is in the form of a monolayer, the general equation isotherm Langmuir, namely;

\[ Q_e = \frac{Q_0 K C_e}{1 + K C_e} \]  \hspace{1cm} (4)
The straight line equation \( y = 1.2436x + 0.2326 \) with slope \( = 1/Qo.K \) (0.77), and Intercept \( = 1 / Qo \) (0.23), then the Langmuir K constant is the intercept/slope of 0.18 (Figure 3). The BET theory assumes that the adsorption of substances by the adsorbent is multilayer, and the BET isotherm equation is as follows;

\[
Q_e = \frac{Q_o K \frac{C_e}{C_o}}{1 - \frac{C_e}{C_o}} \left[ 1 + (K - 1) \frac{C_e}{C_o} \right] \tag{5}
\]

Curve \( \frac{Q_e \left( 1 - \frac{C_e}{C_o} \right)}{C_e} \) versus \( Ce/Co \), then the equation is obtained.

The equilibrium results of the Chapman adsorption isotherm can be seen in Figure 5. A summary of various models of adsorption isotherm equilibrium is presented in Table 3. It is concluded that the equilibrium model of the Pb (II) ion adsorption isotherm by RSBE is according to the Langmuir adsorption isotherm equilibrium model. Langmuir adsorption equilibrium model has the highest value of relation coefficient (R2) 0.9935 compared to the others, the absorption value of 4.29 mg Pb (II) / g RSBE is the maximum absorption value. This explains that the process occurs on a homogeneous surface, the adsorption process that occurs in this study is in the form of a monolayer and the type is chemical adsorption.

**Table 3. Summary of Adsorption Model Equilibrium**

| Adsorption Isotherm Equilibrium Model | Constant Equilibrium Abbreviation | Value     |
|--------------------------------------|----------------------------------|-----------|
| Freundlich                           | K                                | 1.38      |
|                                      | n                                | 1.49      |
|                                      | R²                               | 0.9739    |
| Langmuir                             | Qo                               | 4.29      |
|                                      | K                                | 0.18      |
|                                      | R²                               | 0.9935    |
| BET                                  | Qo                               | 1.69      |
|                                      | K                                | 15.33     |
|                                      | R²                               | 0.9591    |
| Chapman                              | α                                | 3.55      |
|                                      | γ                                | 2.51      |
|                                      | β                                | 28.58     |
|                                      | R²                               | 0.9913    |

Another evidence that the adsorption of Pb (II) ions by RSBE is chemical adsorption is based on the heat of the reaction which is calculated by the equation \( E = \Delta G^{ads} = - R T \ln K \), namely; \( E = (1.987 \text{ kcal/mol.}^°\text{K}) \times (300 \text{ }^°\text{K}) \times (\ln 0.02917) = 21.038 \text{ kcal/mol.}^°\text{K} \). This value indicates that the
adsorption that occurs is chemical adsorption with the heat of adsorption ranging from 20-100 kcal/mol.

**Thermodynamic Model**

Apart from the four equilibrium models above, this thermodynamic model analysis aims to determine the processes that occur in the adsorption of Pb (II) ions by RSBE. Thermodynamic analysis was performed to determine the enthalpy (ΔHo), entropy (ΔSo) and Gibbs free energy (ΔGo) obtained by plotting ln Kc vs 1/T at each temperature, the graph can be seen in Figure 6.

![Figure 6. Thermodynamic Model Curves](image)

The results of plot of ln Kc versus 1/T, the values of ΔHo, ΔSo, and ΔGo are obtained during the adsorption of Pb (II) by RSBE, as shown in Table 4.

| Temperature (K) | ΔGo (kJ/mol) | ΔSo (kJ/molK) | ΔHo (kJ/mol) |
|----------------|--------------|---------------|--------------|
| 313            | -1.41        |               |              |
| 323            | -1.70        | 0.03          | 22.38        |
| 333            | -2.04        |               |              |

Based on data of Table 4, it is obtained that ΔGo <0, then the Gibbs energy increases towards the negative side as the temperature increases and the reaction goes on spontaneously. The ΔHo value is obtained at 22.38 kJ/mol, which indicates an endothermic reaction, namely the transfer of heat from the environment to the system. The endothermic process identifies that the process that occurs in the uptake of Pb (II) ions by RSBE is chemical adsorption [25]. The enthalpy value also indicates that the adsorption occurs chemically because ΔH0 is greater than 20 kJ/mol [25]. The ΔSo value obtained is 0.03 kJ/mol.K, indicating that the disturbance to the system is very small. Thus, adsorption takes place chemically, is endothermic and spontaneous.

**4. Conclusion**

In this study, the adsorption equilibrium time of Pb (II) ion by RSBE was reached at the adsorption time of 150 minutes. The adsorption mechanism of Pb (II) ion by RSBE is in accordance with the Langmuir isotherm model, namely chemical adsorption. SBE can be a potential material resource reused as adsorbent RSBE and it can remove a heavy metal in aqueous solution very significantly.

**Nomenclature**

A = ash content of SBE
$Ce$ = Cu(II) ionic concentration after adsorption process

$Co$ = Cu(II) ionic concentration before adsorption process.

$FC$ = the fixed carbon content

$IM$ = water content of SBE

$m$ = amount of RSBE (Regenerated Spent Bleaching Agent) before adsorption process.

$v$ = Cu (II) ionic volume before adsorption process

$VM$ = volatile components.

$K$ = Adsorption Equilibrium

$n$ = Heterogeneity Factor

$R^2$ = Relation Coefficient

$Qo$ = Maximum Absorption Capacity (mg/g)

$\alpha$ = Maximum Absorption Capacity (mg/g)

$\gamma$ = Constant Equilibrium

$\beta$ = Constant Equilibrium

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