Bangka’s Tin Sea Sand-Fe$_3$O$_4$ as A Removal of Heavy Metals in By-Product of Tin Ore Processing

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Abstract— An experiment to investigate the adsorbent capacity of tin sand from Bangka Island Indonesia toward the lead/Pb(II) ion in lead aqueous solution either non-modified sand and magnetite-coated sand were studied using adsorption method. The adsorbent was activated with sulfide acid (H$_2$SO$_4$) and showed that the tin sand with the highest porosity is the sand with the low activation temperature and the fast activation time, the lowest porosity was reached with the high activation temperature and 2 hours activation time. Both of the tin sand with the highest and lowest porosity were successfully covered with magnetite (Fe$_3$O$_4$) using the ferrite chloride aqueous (FeCl$_3$) (pH=13) and was found that the more amount of Fe ions coated tin sand with the higher temperature, the more Pb(II) ions were absorbed in artificial solution. It occurred in 1 hour and resulted 83.44% at the highest porosity sand and 96.67% at the lowest porosity sand. The adsorption capacity of tailing decreased and only reached 71.76% of adsorption capacity. Moreover, Bangka’s Tin Sea Sand-Fe$_3$O$_4$ can be used as a reusable material for adsorbing Pb$^{2+}$ ions. The desorption result showed Bangka’s Tin Sea Sand-Fe$_3$O$_4$ could be suitable separated in pH 2 and can re-prepare to derive the new adsorbent.

Keywords: tin sand, tailing, heavy metals adsorption, magnetite-coated

I. INTRODUCTION

Tin ore mining activities in marine poses many problems in Bangka Belitung Province, Indonesia. By-product from the processing of tin ore contains sludge which can caused sedimentation, turbidity and its heavy metal ions pose serious damages to the ecological marine environment. Tailings that were discharged into seawater from the cutter suction dredges attacks the oceanic life. It contains lead (Pb), cadmium (Cd) and chromium (Cr) and however, the heavy metals could increase if the tailing continuously is dumped to sea water without filtering [1]. Pb ions are one of the toxic pollutant that are recharged from cutter suction dredges into marine environment.

Febrianto [2] also state there were differences of lead concentrations in seawater among the areas contained tin mining activities and the areas without mining activities. It was observed that the concentration of lead in mining activities are about 0,11 mg/L, while Indonesian Minister of the Environment have decided that the maximum of lead concentration in sea is 0,008 mg/L (Kep 51/MENLH/2004). The high concentration of lead ions are caused by associated heavy metals from by-product of washing tin ore which were not used but were dumped to seawater.

II. RESEARCH ON SEA SAND AND MAGNETITE AS AN ADSORBENT

Tin mining industry in Bangka Belitung Province is facing new challenges due to the reclamation era. The increasing of tailings/by-product from tin ore processing in marine are seriously damaged the oceanic life. Besides the turbidity, heavy metals are apparently one of the major problems towards the contamination to seawater. This heavy metal ions is really concerning because the living organisms and the environment can get severe damage from its pollution [1]. Tailing which is a by-product from tin ore processing contains lead (Pb), cadmium (Cd) and chromium (Cr) and however, the heavy metals could increase if the tailing continuously being dumped at sea without filtering [2]. There are methods in practice today for treatment of heavy metal contaminants like lead/Pb$^{2+}$ions in aqueous solution and tailing from tin ore processing.
Bangka’s Tin Sea Sand is the natural resources that are easily found in lots of places in Bangka Belitung Archipelago. Nowadays, Bangka’s Tin Sea Sand is used as raw materials of tin metals both in Bangka and Belitung. Besides that, Bangka’s Tin Sea Sand is one of the unique sand which contains rare earth elements (e.g. lanthanide). Lanthanide can be used as high performance magnetic materials [3] and it has the good molecular magnetic properties [4]. Hence, it is essential to understand the magnetic material of Bangka’s Tin Sea Sand through its performance to adsorb heavy metal ions in aqueous solution.

One of an essential class of conventional oxides, are ferrites. It has magnetic compounds and varies in the crystal structure. The structure of ferrite and their diverse chemical compositions are highly promising. Some of ferrites have high thermal characteristics, good mechanical and chemical stabilities, large specific surface area, high magnetic permeability, tunability in chemical composition, controllable magnetic characteristics, and chemical and corrosive stability [5,6,7]. One of the composite of spinel ferrites that used in this study is made from Bangka’s Tin Sea Sand. The sand will be generated as adsorbent and spinell ferrites composites. Currently, spinell ferrites composite have been widely used as adsorbent to remove metal ions from water. These materials was focused to remove the lead, arsenic, mercury and chromium, which are known to cause severe damage and diseases to human populations [8].

Besides retrieving the heavy metal ions from aqueous solution or wastewater using adsorbents is an important step, desorption of the loaded heavy metal ions from the adsorbent, to recover the adsorbent and to discard the pollutant is also important [9,10]. Henceforward, Bangka’s Tin Sea Sand-Fe3O4 will be prepared as reusable adsorbent, showing high desorption capacity and high performance towards realising heavy metal ions from the material’s surfaces.

III. RESEARCH METHOD

A. Preparation

Bangka’s Tin Sea Sand is washed using distilled water and then dried. The next stage is the immersion of sea sand using 1% nitric acid for 24 hours in order to make the sea sand clean from impurities. After soaking, sea sand was rinsed with distilled water to obtain a neutral pH or equal to 7. Drying of sea sand carried out by heating at a temperature of 105ºC for 12 hours. Sea sand sieved with a 100 mesh sieve to obtain a size of 0.149 mm of sea sand.

B. Activation

Activation with sulfide acid (H2SO4) by varying parameters such as H2SO4 concentration (2 mol/L, 4mol/L), duration (1, 2 and 3 h), and temperature (30,45,60ºC);

C. Measuring Surface Sand’s Porosity

To determine the porosity of Bangka’s Tin Sea Sand, use this following formula:

\[ \phi = \frac{(V_{\text{liquid}} + V_{\text{sand}}) - V_{\text{bulk}}}{V_{\text{liquid}} + V_{\text{sand}}} \]

C. Coating Sand with Iron Oxide (Fe3O4)- Magnetite

Coating magnetite (Fe3O4) is used with aqueous ferrite chloride (FeCl3) onto the sand (with pH=13), 10% up to 20% concentration of FeCl3 and also varying coating temperature with 30,45 and 60ºC and duration from 1, 2 through 3 hours.

D. Adsorption Experiment

The experiment is used two types of adsorbents, namely:

- sea sand without activation and without magnetite-coated (non-modificated sand), and

Fig. 1. The procedures of making Bangka’s Tin Sea Sand-Fe3O4.
IV. RESULTS

A. Characterization

Bangka’s Tin Sea Sand were sieved in mesh (100#) to obtain the distribution of minerals and its magnetic compounds.

The characterization was analyzed in PT. Timah using a manual microscope. Bangka’s Tin Sea Sand contains the main minerals; Quartz (53.68%) and Cassiterite (30.94%). Other associated minerals are Tourmaline > Ilmenite > Pyrite > Zircon > Monazite. Bangka’s Tin Sea Sand contains many metal compounds hence it is named as magnetic sand.

Bangka’s Tin Sea Sand basically is normal sand but things that make its unique is because the associated mineral contained inside. Cassiterite or SnO$_2$ is the most abundant mineral after quartz or SiO$_2$. Other associated minerals such as ilmenite (FeTiO$_3$), monazite (Ce,La)PO$_4$ and pyrite (FeS$_2$) also have abilities to make attraction among pollutants especially heavy metal ions in wastewater.

B. Activation Process and Measurements

Porosity

Activation is an important process that occurred in adsorption method. The activation will increase the surface of the sand so that it can be more powerful to capture heavy metal ions. Other elements which could influence activation process are the concentration of the sulfide acid solution (H$_2$SO$_4$) and the temperature of the stirring process.

Based on the analysis in Fig.1 And Fig.4 showed that the tin sand with the highest porosity was the sand with the low activation temperature and the fast activation time, whereas the lowest porosity was reached by high activation temperature while activated in 2 hours. Activation treatment using acid solution can dissolve the material’s impurities so that the pore of Bangka’s Tin Sea Sand pores become more extended and increased. This increasing area can improve the ability Bangka’s Tin Sea Sand adsorption process towards heavy metal ions [11].
C. SEM Analysis in Activated Sand

SEM analysis results showed a decline in the number of Sn and Ca elements after sands are activated. The more acidic sands are, Sn content value will be reduced, this is because Sn is dissolved in a solution of pH less than 1. The value of magnetic force in sands is reduced and the ability to adsorb metals will also lower. Whereas, the decreasing of Ca elements could cause higher magnetic force in material. It showed that the activation process on tin sand can lead to decreased levels of Sn and its associated minerals in tin sand. And it directly caused lower adsorption capacity. However, Sn was indicated to be an adsorption toward dyes in water pollution. [12] Other researcher states that SnFe2O4@activated carbon can absorb crystal violet with a high capacity (158.73 mg / g).

D. Fe3O4-coated and Adsorption Percentage

The high adsorption capacity was attained when Fe-coated process occurs in 3 hours and when the sand was coated with 20% FeCl3. The pure Bangka’s Tin Sea Sand (non-modified sand) still showing the higher adsorption capacity due to the mineral contents of tin in the sand. Moreover, the non-modified sand didn’t undergo any damages while dissolved with the acid.

E. SEM Analysis in Activated and Magnetite-Coated Sand

Fig. 5 Bangka’s Tin Sea Sand in Scanning Electron Microscope

Fig. 7 A) high porosity sand with 10% of FeCl3; B) low porosity sand with 10% of FeCl3; 2A) high porosity sand with 20% of FeCl3; 2B) low porosity sand with 20% of FeCl3

Fig. 8 A) high porosity sand with 10% of FeCl3; B) low porosity sand with 10% of FeCl3; 2A) high porosity sand with 20% of FeCl3; 2B) low porosity sand with 20% of FeCl3

Fig. 9 The mapping result of Bangka’s Tin Sea Sand coated by Magnetite (Fe3O4) showed that Fe was successfully covered silica and both of them sorbed lead ions.
TABLE 1. THE ADSORPTION CAPACITY OF NON-MODIFIED TIN SAND, HIGHEST POROSITY AND LOWEST POROSITY SAND AGAINST THE PB (II) AQUEOUS SOLUTIONS

| No treatment | Artificial | 71.15 | 3.125 | 42.51 | 95.60 |
|--------------|------------|------|-------|-------|-------|
| High Porosity (2A60,3) | Artificial | 71.15 | 11.78 | 37.10 | 83.44 |
| Low Porosity (2B60,3) | Artificial | 71.15 | 2.363 | 42.99 | 96.67 |
| Optimum Value | Tailing | 3.262 | 0.921 | 1.170 | 71.76 |

Based on the analysis in Table 1, the equilibrium sorption capacity of Bangka’s Tin Sea Sand as a removal of lead was 42.99 mg/g. This value is comparable with previous research using adsorbents derived from lead waste, e.g., 42.96 mg/g for biological sludge [13]. The adsorption capacity in tailing decreased and only reached 71.76%, it might be derived that the adsorbent sorbed other heavy metals ion in tailing such as Cr and Cd. Its comparable with previous observation [14] which has been demonstrating magnetite and rare earth element with other toxic dissolved metal such as cadmium (99.7 mg/g) and chromium (49.8 mg/g) in adsorption capacity.

a. XRD Analysis

Fig 10 shows that Quartz and Cassiterite were the main crystalline phases in Bangka’s Tin Sea Sand. The iron compounds of Fe₃O₄ were identified in calcined sand which was coated with Fe before. Whereas sand after the adsorption process showed new peak of PbO. Lead ions which was sorbed by the adsorbent formed PbO compound, deriving a formation between Pb and SiO₂ or Pb and Fe₂O₃. Similar result has derived that PbO was the major precipitate of ferric-activated sludge-based adsorbent. The precipitation would contribute to the removal of Pb²⁺ ions from solution by sludge and ferric activated sludge [15].

The mechanism of Pb(II) removal from aqueous phase by adsorption which was observed by other researchers [16]. The reaction may have two models with Pb(II) hydrolysis reaction:

1. Pb²⁺ + OH = Pb(OH)⁺
2. Pb(OH)⁺ + OH = Pb(OH)₂

b. FT-IR Spectral Analysis

The FTIR spectra of Bangka’s Tin Sea Sand, Bangka’s Tin Sea Sand-Fe₃O₄ coated and Pb-loaded adsorbents show the result in Fig. 11. The broad band at around 3400-2400 cm⁻¹ represents –OH. The treatment of HNO₃ in the surface of Bangka’s Tin Sea Sand, formed Si-O-H [16]. After Pb adsorption, the broad band shifted slightly due to the activation process with sulfide acid (H₂SO₄) but still provides –OH. The broad band in range of 1600-1540 cm⁻¹, which is corresponds to C==C vibration [17] shifted after Pb adsorption. The change of the new peak shape might be due to the complexation of Pb²⁺ with C==C (π-electrons) band [18].

For the before-after adsorption (activated and Fe₃O₄-coated sand), shifted respectively from 584-439 cm⁻¹ to bands at 551-445 cm⁻¹ while it can be assigned to the Fe-O bonds [13,19,20]. For the Pb desorption, the peaks of Fe-O vibration were shifted to 607 cm⁻¹ and 511 cm⁻¹. It indicates that some lead ions were released from the surface
of Bangka’s Tin Sea Sand-Fe₃O₄ coated. From the FTIR spectral analysis, it is proven that Bangka’s Tin Sea Sand-Fe₃O₄ coated possesses a significant number of functional groups for capturing heavy metal ions such as Pb(II) ions.

**F. Desorption**

Desorption or known as sorbent regeneration are important properties of the loaded adsorbent. As shown in Fig. 12, the desorption rate of different pH for the Pb-loaded adsorbents increased from pH 1-2, but decreased in higher pH. This indicates that some lead adsorption on tailings or aqueous solution could be separated with only low concentration of H⁺ ions. H⁺ ions are essential properties to desorb Bangka’s Tin Sea Sand-Fe₃O₄ coated. Therefore, when using deionized water in pH 5 and pH 7 lead ions do not completely desorb because it does not contain any H⁺ ions in solution. Likewise another eluents such as NaOH with pH 12, the result seems lower because it contains abundant of OH⁻. The result suggested that pH 2 on 88% desorption percentage was suitable for desorbing the toxic metal Pb²⁺ ions from the adsorbents.

**V. CONCLUSION**

In this study, Bangka’s Tin Sea Sand-Fe₃O₄ can be used as a highly efficient adsorbent for the adsorption of Pb(II) from lead solution and by-product of tin ore processing (tin tailing). The results showed that inspite of the low porosity of sand, the higher capacity was reached to sorb lead ions (96.67%) and even more better than the high porosity (83.44%). It is caused, the activation process will decrease cassiterite and its associated minerals, whereas they can enhance the ability in adsorption. The increased surface area and iron compounds of Bangka’s Tin Sea Sand-Fe₃O₄ promoted the removal of Pb(II) heavy metal ions. From the desorption results, this material can be a reusable adsorbent. Showing 88% desorption percentage in pH 2 has made this material can be re-prepared to adsorb lead ions in another solutions or wastes. Bangka’s Tin Sea Sand-Fe₃O₄ to adsorb Pb(II) is a simple and cost-effective way to implement in Bangka’s mining practice related to its natural magnetic materials and a short way to meet future regulations for water and tailing management.

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