Combination of activated allophane-effective microorganisms for bioremediation of iron and manganese on pharmaceutical industry wastewater

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Abstract. Climate change has become a crucial problem for the water resources of the pharmaceutical industry in Wonogiri district, Central Java, Indonesia, as the industry uses surface water of several adjacent rivers for its processes and results in high Fe and Mn concentration in its wastewater. Iron and manganese in pharmaceutical industry wastewater should be reduced to 1.0 and 0.5 ppm to implement the Indonesian Ministry of Environment Law No 5 of 2014. The study aims to evaluate the effectiveness of combined activated allophane adsorption and biofiltration of Effective Microorganisms 4 (EM4) for reducing Fe and Mn concentrations in pharmaceutical industry wastewater. Allophane of Lawu volcano, Central Java, Indonesia is activated using NaOH and the EM4 is attached to bio ball media. Bio balls were seeded with 2 ml EM4, inserted into allophane tube, then submerged into the wastewater from a herbal Pharmaceutical industry in Wonogiri district, Central Java on November 2017. The combined of bioreactor system operated in aerobic batch condition. The bioreactors were set for 0, 6, 12, 18, 24 hours at 28, 32, 37 and 46 ^{o}C. The analysis of iron used o'phenanthroline method and manganese was examined using Persulfate method. The results showed a decrease from 0.591 to 0.175 ppm of iron, and manganese from 0.721 to 0.441 ppm at 37 ^{o}C for 24 hours.

1. Introduction

The quality of water is a global issue. Industrial and agricultural wastes, hospital and home sewage are discharged into water streams as lakes and rivers without proper treatments in every year. A lot of people die from unsafe water than all forms of violence, including war. The greatest impacts are on children under the age of five. Water contamination weakens or destroys natural ecosystems that support human health, food production, and biodiversity. Moreover, during the past few decades, climate change has gradually exacerbated the pressure on the hydrologic system and induced potential risks for drinking water safety [1]. Climate change has also become a global agenda since its dominant influences on water quality of the pharmaceutical industries, especially herbal medicine industries sources and processes. Besides producing essential medicines, the industries produce wastewater, controlling its wastewater and pollution are of prime activities.

In Indonesia, drinking water service operates mainly in urban, managed by Municipal Waterworks (*Indonesian*: PDAM) and covers only about 16.08% of needed. In areas without government drinking water supplies, people utilize groundwater, river, rainwater, natural spring water, and other sources [2]. At present, the water supply of urban areas is diminishing. For instance, Surakarta City with its 554.387 inhabitants in 44,04 km^2 has a very limited water source with a rainfall rate of 2.362 mm per year and run-off coefficient by 0.61. Most of rainfall water flows as surface water with only small parts infiltrate then dissolve iron as well manganese in the soils and fill the aquifer as a source of shallow groundwater wells. Deep groundwater wells serve only 5 L of water per second. The PDAM Surakarta only supplies 53.26 % of the water needed and hardly get support from adjacent districts. Therefore, they have tried to process surface water of Bengawan Solo and the Pepe River of Karang Anyar District. The quantity of the surface water is sufficient but the quality is questionable since Bengawan Solo, Pepe River and their smaller rivers collect unsafe wastewater from textile, pharmaceutical and other industries. The river water needs to be processed before use as safe waters by PDAM Surakarta [2].

Climate change influences the quantity of surface water, especially in adjacent areas of Wonogiri. During the rainy season, the quantity of surface water is sufficient but the quality is questionable since Bengawan Solo, Pepe River and their smaller rivers collect unsafe wastewater from textile, pharmaceutical and other industries. The river waters need to be processed before use as safe waters for the target pharmaceutical industry [2].

An established well known herbal pharmaceutical industry has built a modern well-equipped laboratory in Wonogiri District, Surakarta. The laboratory also built a Wastewater Treatment Plant (*Indonesian*: IPAL) but certified red according to the Regulation of the Minister of Environment of the Republic of Indonesia no. 06 The Year 2013 [3] by the Central Java Province Government. The certification indicated that there was malpractice of the IPAL. Preliminary study revealed that the concentrations of iron and manganese were 0.591 and 0.721 ppm respectively. This research tries to reduce the high concentrations of iron and manganese to meet the standard of 1.0 and 0.5 ppm [4].

A number of specialized processes have been developed for the removal of metals from water and waste discharges. These unit operations include chemical precipitation, coagulation/ flocculation, ion exchange/ solvent extraction, cementation, complexation, electrochemical operation, biological operations, evaporation, filtration, membrane processes and adsorption [5]. Adsorption is the process by a solid adsorbent can attract a component from the aqueous phase to its surface and thereby form an attachment via a physical or chemical bond, thus removing the component from the aqueous phase [6]. The biological operation uses effective microorganisms to remove iron and manganese [7].

This study aims to evaluate the effectiveness of two techniques consisting of adsorption by activated allophane and biofiltration by Effective Microorganisms 4 (EM4) on bio ball media. Adsorption of heavy metals by activated allophane proved to be an efficient technique [8]. However, biological treatment is energy saving and environmentally friendly as it converts the wastes into harmless end products. A hybrid treatment technology appears to be a wise solution as long as considering local social-economic conditions, effectiveness, simple application, availability of materials, and environmentally friendly. After surveying the local social-economic conditions in Wonogiri district, this preliminary study has been selected: a combination of physicochemical adsorption and biological treatments.

2. Materials and methods

The research was conducted at the Sub-laboratory of Chemistry, Central Laboratory Sebelas Maret University, Surakarta, Indonesia for 6 months, started from November 2017 until April 2018 in the rainy season.

2.1. Instrumentation and materials

The main materials used in the study were allophane taken from Lawu Volcanic Mount, Central Java, Indonesia, distilled water, electronic pH meter (Eutech Instrument pH 700), UV-Vis Shimadzu UV-1601PC, electronic thermometer, electronic analytical balance, electrical heater, Erlenmeyers, pipettes, burette sets, cellulose membranes, aerator with debit of 4 liter air/minute, glass aquarium with dimensions of 40x40x20 cm, *bolacin* type bio ball, EM4 solution for waste product and toilet produced by Songgolangit Persada Co. Ltd., Jakarta, Indonesia. The materials for iron and manganese examination such as standard solutions, nitric acids, H_2O_2, $(NH_4)2S_2O_8$, Nessler tubes, isopropyl ether, etc. are provided.

2.2. Preparation of allophane clay.
Allophane nanoclay was taken from andisol soil at Mount Lawu, cleaned from impurities, washed with aquadest and air-dried. The soil was then crushed and sieved with a 150-mesh filter. Soils getting through the sieve was soaked in distillate water and sieved again, dried for 4 hours at a temperature of 105^0C [8][9].

Allophane nanoclay was activated chemically using NaOH and physically by heating at 600 ^{o}C. The purpose of this activation was to clean allophane from organic and inorganic impurities which clot allophane pores so that the pores were opened and increase its surface width and increase its sorption capabilities. After activation, allophane was molded into a tube by a local craftsman with 23 cm height, the outer diameter of 6.5 cm, and the inner diameter of 5.2 cm. Allophane pellets of about 1.5 cm diameter were also prepared.

2.3. Preparation of media bio ball.
2 ml of EM4 was poured into 1 L of distillate water beaker and stirred homogenously. The solution showed pH of 5,9. Into this solution, 18 bio balls were soaked and incubated at temperature 28 ^{o}C for 96 hours. After incubation, the bio balls were air-dried at 28 ^{o}C.

2.4. Preparation of iron and manganese wastewater
Iron and manganese wastewater were collected from the effluent of the herbal medicine industry in Wonogiri district several times from November 2017 to April 2018. The wastewater samples were preserved in a 4 ^{o}C refrigerator. Furthermore, the temperature and pH were monitored before preservation, during batch and aerobic process.

2.5. Preparation of the system process
The system process used batch and aerob methods. Each allophane tube filled with media bio balls and allophane pellets. Media bio balls were arranged in both one third space ends of the tube with allophane pellets in the middle space. To prevent bio balls and pellets fall out, the tube covered with gauze on both sides. This filled allophane tube was dipped into a glass aquarium containing a 10-liter sample solution, and an aerator. Iron concentrations were examined according to O'phenanthroline methods and manganese following Persulfate methods for every 6 hours, which are 0, 6, 12, 18, and 24 hours at 28, 32, 37 and 46 ^{o}C. The arrangement of allophane tube, media bio ball, allophane pellets and aerator in the system process was presented below.

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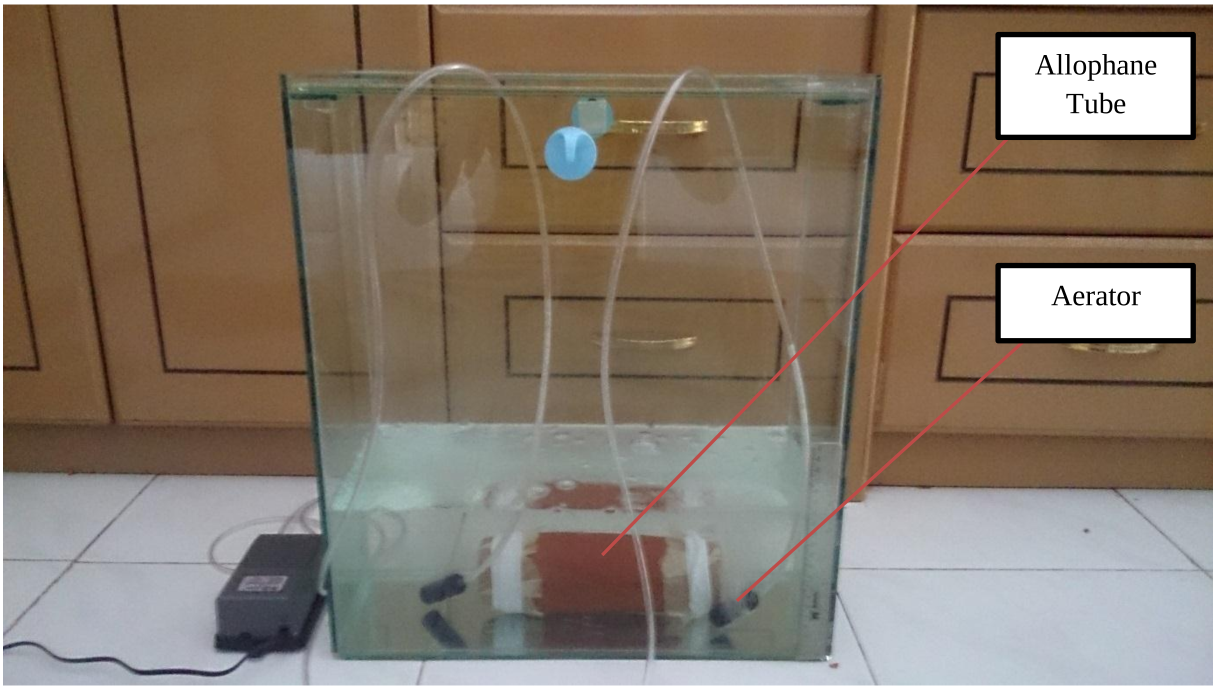

Figure 1. Batch and aerobic system of the bioreactor process.

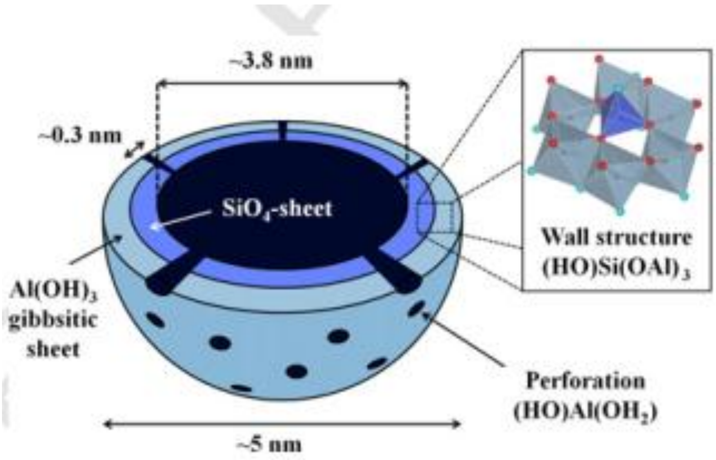

Figure 2. Theoretical allophane nanoclay structures [10].

3. Results and Discussion

The bioreactor system process for the pharmaceutical wastewater operated at temperatures of 28, 32, 37, 46 ^oC. Fe concentrations were examined using the O'phenanthroline method at 0, 6, 12, 18 and 24 hours, respectively. The initial concentration of Fe is 0.591 ppm and the pH of the waste is 5.8. Data analysis showed that the optimum conditions for the reduction of Fe concentration occurred at 37 °C pH 6.1 for 24-hour contact time. At these optimum conditions the concentration of Fe was reduced to 0.175 ppm or with an efficiency of 70.3%. Data on the decrease of Fe concentration in optimum condition can be seen in Table 1. Complete data of iron reduction, temperature, pH and contact time during the process are available on request.

Table 1. The decrease of Fe concentrations at 37 °C, pH and contact times

Contact Time (Hour)	pH	Fe Concentration (ppm)
0	5.8	0.591
6	5.8	0.461
12	5.9	0.354
18	6.0	0.222
24	6.1	0.175

Manganese removal in the pharmaceutical wastewater operated at temperatures of 28, 32, 37, 46 °C for 24 hours in the bioreactor system. Manganese levels were examined using the Persulfate method at 0, 6, 12, 18 and 24 hours. The initial concentration of manganese was 0.721 ppm and the pH of the wastewater was 5.7. Data analysis showed that the optimum conditions of the removal of manganese occurred at 37 °C at a contact time of 24 hours. At these optimum conditions, the Mn concentration was successfully reduced to 0.441 ppm or reached an efficiency of 38.8%. Data on the reduction of manganese levels in optimum conditions can be seen in table 2 below. Complete data of manganese reduction, temperature, pH and contact time during the process are available on request.

Table 2. The decrease of Mn concentrations at 37 °C, pH and contact times

Contact Time (Hour)	pH	Mn Concentration
0	5.7	0.721
6	5.9	0.601
12	5.9	0.554
18	6.1	0.482
24	6.2	0.441

Combination process of adsorption and biofiltration using batch and aerobic methods succeeded in decreasing Fe concentration from 0.591 to 0.175 ppm (70.3% efficiency), Mn concentration 0.721 to 0.441 ppm (38.8% efficiency), and it fulfilled the quality standard requirements of wastewater before disposal to the water body.

The removal process of iron and manganese in this system was successful because of adsorption and biological processes occur simultaneously. Further, the effectiveness of adsorption by allophane and biofiltration (oxidation) by EM4 in this system were supported by immobilization of type 4 effective microorganisms (EM4) on bio balls; adequate oxygen supply for microorganisms from the optimal oxygen flow of 4 liter/minute; and a long path of the wastewater through allophane pellets and bio balls.

A research concerning the efficiency of allophane adsorption from Mount Papandayan, West Java, Indonesia on Fe in distilled water gave a reduction of 99.9%, and allophane from Mount Wilis, East Java, Indonesia on Mn in distilled water gave a reduction of 88.8% [8]. Whereas this application of a combination of allophane adsorption and biological EM4 systems for pharmaceutical wastewater effluent results in lowering of Fe concentration with an efficiency of 70.3% and lowering of Mn concentration with an efficiency of 38.8%. Pranoto et al. [8] used a single technique of adsorption by allophane applied to Fe and Mn removal in the distillate water, whilst this research used a hybrid technology system applied to wastewater containing many organic pollutants and heavy metals other than Fe and Mn.

Another research by Desica [11] studied the application of a combination of adsorption by zeolite and biofiltration by EM4 attached to bio ball media on wastewater from Prambanan public hospital. However, the efficiency of Fe and Mn removal [11] were not investigated yet. With a similar combination system but the allophane adsorbent, this hybrid system extended its application to examine the efficiency of Fe and Mn removal.

The efficiency of a biological system for groundwater Fe removal of concentration ranging from 1 mg per L to 5 mg per L succeeded in reaching 93% to 95.25% removal. Whilst the efficiency of Mn removal with concentration ranging from 1 mg per L to 5 mg per L reached 92.25% to 95% [12]. The efficiency of this allophane adsorption and biological EM4 combination system for pharmaceutical wastewater effluents reached 70.3% Fe removal and 38.8% Mn removal. The efficiency results of the two types of research are different because the biological system [12] was applied to the groundwater while this hybrid system was applied to wastewater containing many organic pollutants and heavy metals other than Fe and Mn.

McClellan's study [13] using a biological system successfully achieved the efficiency of Fe and Mn removal up to 98% at pH 9.0 in drinking water, and Mn removal reached 90% at pH 6.5. The study in Tobiason et al. [7] showed that pH is very influential in biological systems. This study of the hybrid system also observed the pH fluctuation during the process of decreasing Fe and Mn, which ranged from 5.7-6.2. Differences in pH in the process and differences in the conditions of Fe and Mn, in wastewater and in drinking water were factors that differentiate removal efficiencies.

Kasim [14] cited that a biological iron and manganese removal in artificial conditioned water succeeded in removing Fe with efficiency ranged from 52.33-97.18%. Whereas Mn was successfully removed at 12.5-60%. The research [14] showed the efficiency of biological manganese removal is significantly lower than Fe. Results of this hybrid system operation gave the same pattern of removal efficiency: Fe was higher than Mn although this hybrid system operated in wastewater.

4. Conclusion

The combination system process of adsorption and biofiltration for pharmaceutical wastewater in rainy season optimally occurred at a temperature of 37 ^oC, pH 6.1 and contact time of 24 hours for iron, and 37 ^oC, pH 6.2 and contact time of 24 hours for manganese. This bioreactor with aerobic condition and batch method, iron and manganese in wastewater experienced physicochemical and biological process simultaneously.

The hybrid technology system succeeded in innovating a new adsorbent that was activated allophane and extending its application and proved that wastewater pH in the bioreactor influenced the efficiency of Fe and Mn removal; and also managed to match the efficiency of a biological system for removing Fe and Mn in simulated conditioned water. This result made this combination system worthwhile to be developed further.

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