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Synergism of Allophanic Andisol Adsorption and EM-4 Biosorption for Remediation of Iron and Manganese in Wastewater

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ABSTRACT
A pharmaceutical industry wastewater in Wonogiri district, Central Java, Indonesia, contains high Fe and Mn concentration that should be reduced to1.0and 0.5 ppm to implement the Indonesian Ministry of Environment Law No 5 of2014. This study aims to evaluate the effectiveness of combined activated allophanic andisol adsorption and type 4 Effective Microorganisms (EM-4) biosorption for Fe and Mn remediation. The allophanic andisol of Lawu volcano, Indonesia is activated using NaOH and molded into a tube, and theEM-4 is attached to bio balls then inserted into the allophanic andisol tube. This combined bioreactor system is submerged into the wastewater and operated in aerobic batch condition and set for 0, 6, 12, 18, 24 hours at 28, 32, 37and 46^{o}C. The concentrations of iron were detected using the Indonesia National Standard Method (SNI) No.6989-4-2009and manganese by SNI No. 03-6855-2002.The results showed a decrease from 1.684 to 0.188 ppm of iron, and manganese from 0.993 to 0.148 ppmat37^{o}C after 24 hour operation.

Keywords: synergism,Biosorption,Waste Water
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INTRODUCTION
Nowadays, water quality has become a major environmental concern as each year huge quantity of water from industrial, agricultural, hospital and home wastes are released into fresh water bodies without having any recycling. That causes deaths even more than all types of violence including wars. Children under five years age are most effected. Water pollution has detrimental impact on all types of natural ecosystems that are essential not only for human health, but also for food chain, and ecological biodiversity.
During recent past, dangerous pollutants and non biodegradable heavy metals, that remain in the environment and biological systems, have gradually aggravated the pressure on the water system and captivated risks for the safety of water use for drinking purposes(Salem et al., 2012).
For example, presence of Fe and Mn heavy metals in high concentration in water can cause aesthetic, economical, technological and health issues. These heavy metals normally exist in groundwater in their soluble forms and remain as Fe2+ and Mn2+having atomic radii of 0.208 nm and 0.217 nm respectively (Ghosh and Biswas, 2002). These metals are colorless in water during their soluble form but turn into insoluble as Fe3+ and Mn4+, on oxidation and make the water red-brown in color (Kasim and Mohammad, 2017).
The acceptable limit of Feand Mn in drinking water should be≤ 0.3 mg/L and 0.05 mg/L respectively(WHO, 2017). Precipitation of these metals produce dark sludge, which promote the growth of ferruginous and manganese bacteria on drainage system, thus enhance the corrosion of pipes. No doubt, Fe is important for human, but its existence in water more than normal amount makes it unfit because of metallic taste, odour, laundry stains and plumping fixings etc. Mn is harmful to the brain and cause different neurological disorder including Parkinson's disease. Malfunctioning of reproductive and immune systems along with harmful impacts on liver can be caused by this metal (Pejovic-Milic et al., 2009; Guilarte, 2013; Ansari & Hanief, 2015; Gebre, 2015; Admas, 2016; Singh & Issac, 2018; El-Gali, 2018; Begashaw and Tafesse, 2017; Ghosh, 2018; Muchun, Wenzhong, and Siqi, 2018).
During 2013, in Wonogiri District, Surakarta, a well-known herbal pharmaceutical company in spite of having well equipped laboratory and waste treatment plant (Indonesian: IPAL) was declared in red category by the Regulation of the Minister of Environment of the Republic of Indonesia by the Central Java Province Government. This declaration was because of violations of IPAL. Initial data showed that the concentrations of Fe and Mn were 1.684 and 0.993 ppm respectively.
Current study focused on evaluation of the effectiveness of EM-4 and allophanic andisol combination in-order to reduce the high Fe and Mn concentrations so that we can achieve the standard limit of 1.0 and 0.5 ppm of these metals. (Peraturan Menteri Lingkungan Hidup Republik Indonesia nomor 5, 2014).
In order to remove metals from waste water, various methods have been developed. Removal of heavy metals by using conventional technologies including precipitation of metals, electrochemical operation etc are quite expensive and also ineffective for low concentrations (Akl et al., 2013).So new technologies are in need that should be effective and practical from both economical and environmental point of view for both high and low concentrations. This idea leads to the use of combination of adsorption technology by allophanic andisol clay (AA)

with EM-4 biosorption. AA is able to reduce the high levels of heavy metals, cheap and found around the factory in Wonogiri (Pranoto, et al., 2013). While EM-4 is a commercial effective microorganisms that are cheap, easily available and are able to work with indigenous microorganisms to reduce heavy metals to minimum levels. The designed combination apparatus is called a hybrid bioreactor.

Adsorption is a physicochemical process in which a pollutant from aqueous phase attach to the surface of solid adsorbent through non-covalent and covalent interactions (Uddin, 2017; Wen, et al., 2018). Allophanic andisol was quite effective for heavy metals adsorption (Clark & McBride, 1984; Denaixet al, 1999; Abd-Elfatah& Wada, 2006; Iyoda et al., 2011).

Allophane is an amorphous clay mineral, available naturally in volcanic mountainous soils at altitude of 3000 m above the sea level, and wet tropical climate of Indonesia facilitate its formation. One unit of allophane made up of a hollow spherule having diameter of ~5 nm, and perforations with diameter ~0.3 nmin the wall with (HO)Al(OH2) and / or (HO)Si(OAl3) (Yuan & Wu, 2007; Iyoda et al., 2011). The capability of AA adsorption mainly depends on its specific surface and acidity, which can be enhanced by physical and chemical activation. Chemical activation by NaOH and physical activation done by heating up to 4000Ccleans impurities attached to the AA surfaces so that the acid sites emerge (Pranoto, et al., 2018). These mechanisms make AA acidity higher and specific surface wider.

Adsorption of heavy metals by using activated AA has been proved quite effective as Pranoto, et al., (2013) were successful with 99.9% Fe adsorption from 5 ppm and 88.8% Mn adsorption from 3 ppm.

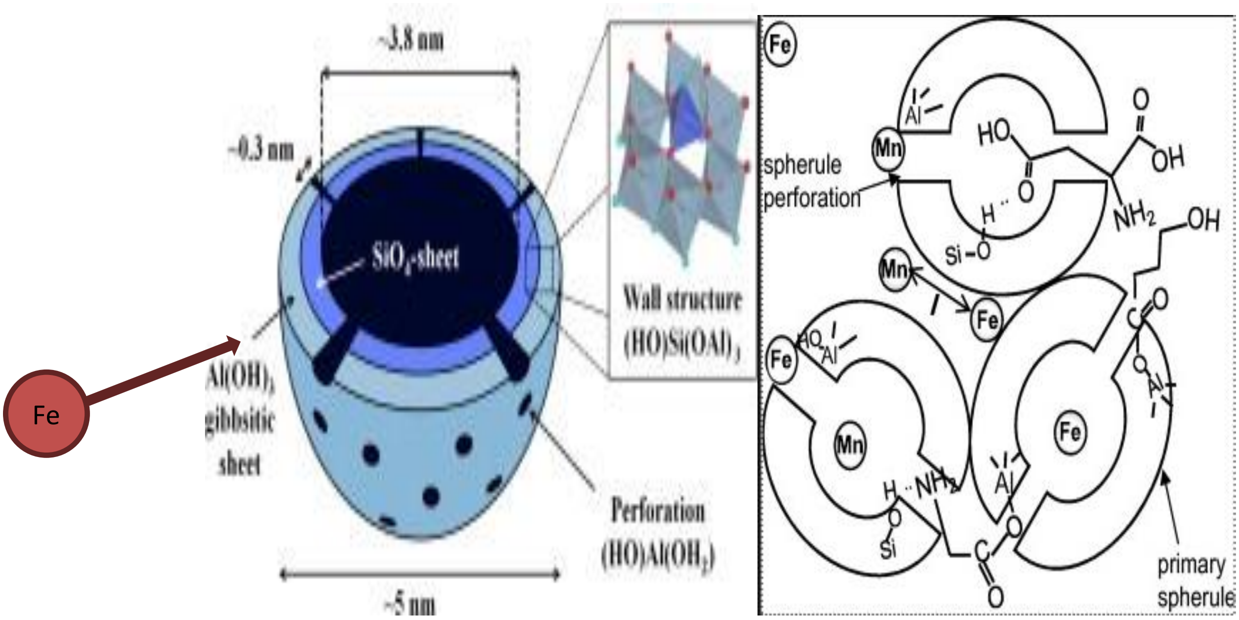

Figure 1. (A) Theoretical structure of allophane (adapted from Iyoda et al., 2011) and (B) Fe and Mn adsorption by allophane (adapted from Filimonova et al, 2016).

On the other hand, biosorption operation causes effective microorganisms to remove iron and manganese (Tobiason, 2016) through elimination, containment or transformation of the pollutants, into non-hazardous or comparatively less-hazardous forms in the environment through their metabolic activities.

The mechanism of removal by biosorption is using biomass mainly by surface adsorption (Garcia et al., 2016). This treatment is energy saving and eco-friendly and will result in bioor micro-remediation. The microorganisms may be already available to a contaminated site or may be isolated from another place and brought to the contaminated area (Okonko, *et al.*, 2007). Bioremediation is quite effective only if environmental conditions are conducive for microbial activity and growth (Vidali, 2001). Even though it is not possible to completely degrade or destroy toxic metals but still there are number of ways by which microorganisms can interact with these metals and convert make into their less toxic forms. Microorganisms can change oxidation level of these metals, and change their chemical properties, which results in acceleration of disposal of these metals by increasing their solubility, or making them immobilize by depositing them out of the soil solution (Cheung, 2013). Microorganisms have adopted various steps to respond the barriers developed by heavy metals through processes like transportation through cell membranes, biosorption by cell walls, trapping in extra cellular matrix, aggregation, chelation and redox reactions (Hassan et al., 2010). More advantages are the ability of microorganisms adapted to adverse environmental conditions with high toxicity or extreme pH values, they can also mutate easily during reproduction, even if most of them die due to high concentrations of contaminants, some will survive because they develop resistance and fast reproduction levels which can allow the entire population to counteract the contaminant's toxicity. Microorganisms have the ability to extract heavy metals from waste, even when their concentrations in waste is in range from less than 1 to about 20 mg/l. Moreover, microorganisms are quite flexible to handle a variety of chemical parameters in waste, and are useful to remove only the desired metal, and show cost effectiveness during biological metal cleaning techniques.

Therefore, the principles of bioremediation or microremediation involve complex interactions of biological, chemical and physical processes (Malik, 2004; Gavrilescu, 2004).The mechanismsare summarized in the following figure.

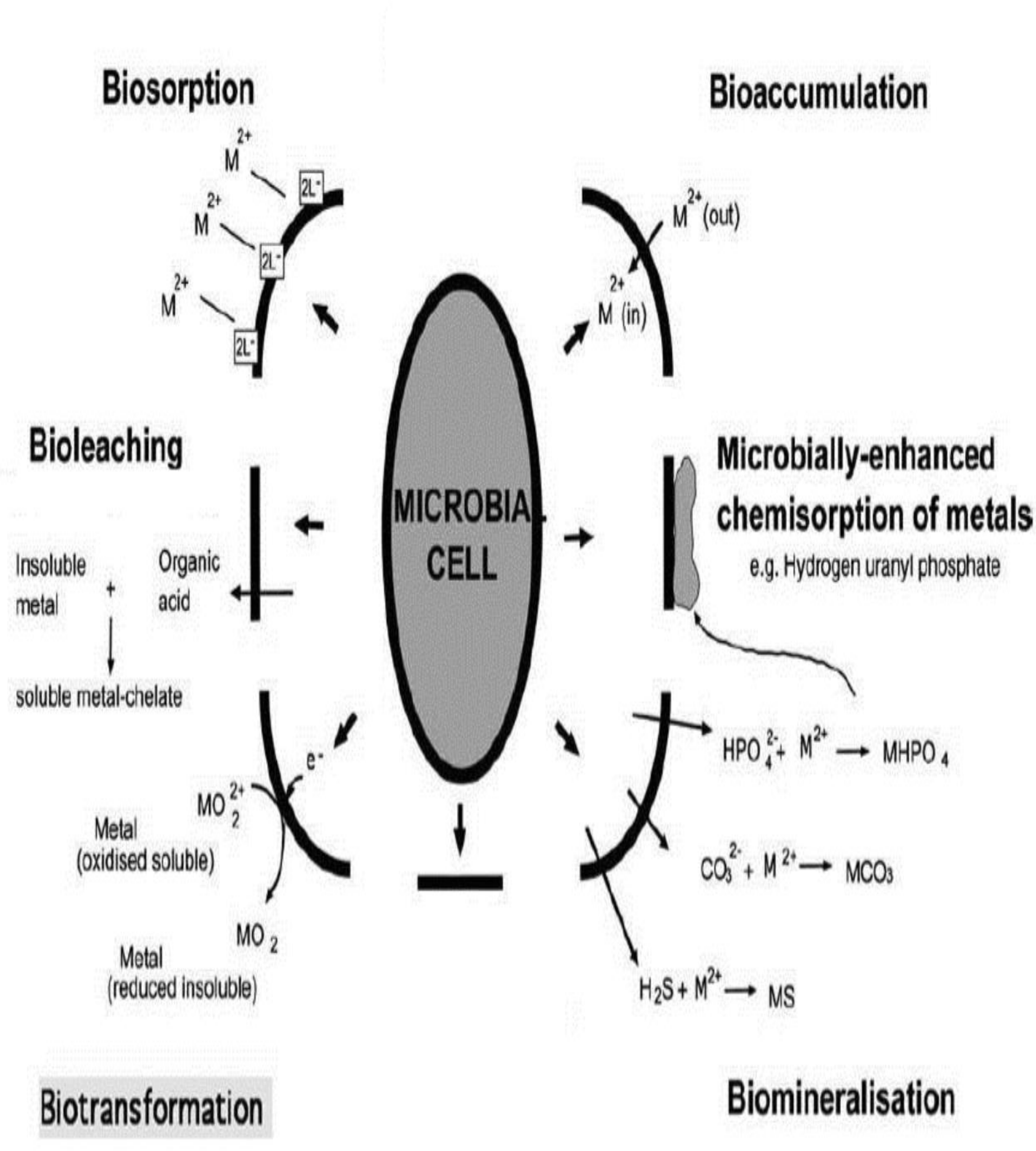

Figure 2. Metal uptake by biosorption (Luka, et al. 2018).

Effective Microorganisms (EM) are culture of useful organisms that live together that can be used for waste treatment (Namsivayam, 2011). EM consists of photosynthetic bacteria (e.g. *Rhodopseudomonas palustris*, *Rhodobacter sphaeroides*), lactobacilli (e.g. *Lactobacillus plantarum*, *L. casei*, and *Streptococcus lactis*), yeast (e.g. *Saccharomyces spp*.), and Actinomycetes (Olle, 2013).

EM-4 has also been shown to be beneficial for wastewater bioremediation (Szymanski and Patterson, 2003). EM-4 used in the experiment mainly consist of 90%

Lactobacillus spp. (Namsivayam, 2011; Maulin, 2017) that belong to lactic acid bacteria group, offer some advantages, including quick application, with-out requiring any expensive technology or infrastructure setup, are safe in application to human, and have ability of detoxification of heavy metals (Ahmed, et al., 2017). Lactobacillican can survive in an environment, where concentration of heavy metal are high, and hence helpful for their bio-remediation. The conventional remediation strategies are expensive and ineffective in case of low metal concentrations. Microbial assisted remediation has appeared cheap and easy alternative. The genera of *Lactobacillus* can perform bioremediation by using biosorption and bioaccumulation (Goyal, Belapurkar and Anand Kar, 2019).

L. bulgaricus and *L. delbrueckii* can make complex with iron through catechols and hydroxamic acids present on the cell wall of bacteria and form siderochrome or siderophore complexes which then transport into the cell. *L. plantarum* sequestrate$Mn^{2+}$and storage it in the cell (Boyaval, 1989; Elli, et al., 2000).Huet and Puchooa (2017) utilize lactic acid bacteria to reduce heavy metal and successfully reach 46.19 ± 7.651% reduction. Yeast can use cell surface to remove heavy metal ions. This removal is carried out by passive as well as active adsorption. Mixed cultures of five yeast strains, combination of yeast and photosynthetic bacteria and even yeast and micro algae enhance the removal of ions of heavy metal. Wang *et al*. (2018) removed a heavy metal ion from wastewater up to 94.71%. The capability of actinomycetes for removal of Fe and Mn can be credited to a large surface area, which is available for metal binding or to the production of some extracellular polymers that have metals affinity and facilitate the removal of these metals. Hozzein et al., (2012) succeeded removing 95.5% Fe and 90.9% Mn from the wastewater.

MATERIALS AND METHODS

Current investigation was carried out at the Sub-laboratory of Chemistry, Central Laboratory Sebelas Maret University, Surakarta, Indonesia.

2.1. Apparatus and materials

Allophane in andisol was used as main material during this study and was supplied from Lawu Volcanic Mount, Central Java, Indonesia. Other materials and instruments used in current research are: distilled water, digital pH meter (Eutech Instrument pH 700), UV-Vis Shimadzu (model UV-1601PC), digital thermometer, 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 bioball, EM4 solution for waste product and toilet produced by Songgolangit Persada Co. Ltd., Jakarta, Indonesia. The materials used for the analysis of iron and manganese such as standard solutions, nitric acids, H_2O_2, $(NH_4)2S_2O_8$, nessler tubes, isopropyl ether, etc. were provided.

2.2. Formation of allophane clay.

Sample of allophane clay was collected from andisol soil at Mount Lawu, rinsed with aquadest to remove impurities and then air-dried. Soil sample was grinded and filtered through 50-mesh size sieve. Soils passing through the sieve was dissolved in distill water and filtered again, and kept on drying for 4 hours at 105^0C (Pranoto et al., 2013; Pranoto et al, 2018).

In-order to increase sorption capabilities, allophane was treated with NaOH at 400^oC. This treatment resulted in the removal of all types of impurities, which have blocked pores of allophane. Once activation is completed, allophane was moulded into a tube having dimensions of 23 cm height, 6.5 cm outer diameter, 5.2 cm inner diameter.1.5 cm diameter of allophane pellets were also prepared.

2.3. Adsorption of EM4 on bioball.

To make homogenous solution, 2 ml of EM4 was added into 1 L of distilled water and stirred. This solution has pH 5.9. 18 bioballs were saturated into this solution and then incubated for 96 hours at 28^oC, followed by air-dried.

2.4. Collection of iron and manganese wastewater

Waste water of the herbal pharmaceutical industry in Wonogiri district, containing Fe and Mn were collected. These samples of waste water were preserved at 4 ^{o}C with regular monitoring of temperature and pH during batch and aerobic process.

2.5. Preparation of the system process

System process was prepared by using both batch and aerobic methods. Allophane pellets and bioballs were placed in allophane. Media bioballs were arranged at both end of tube covering with one third of the tube, whereas allophane pellets were placed in the middle. Both sides of tube were closed with gauze. In next step, this allophane tube was hanged into a glass container, having 10-liter sample solution, and an aerator. Iron and manganese concentrations were analyzed according to O'phenanthroline and Persulfate methods respectively for every 6 hours, at 28, 32, 37 and 46 ^{o}C. This arrangement of system process are mentioned below.

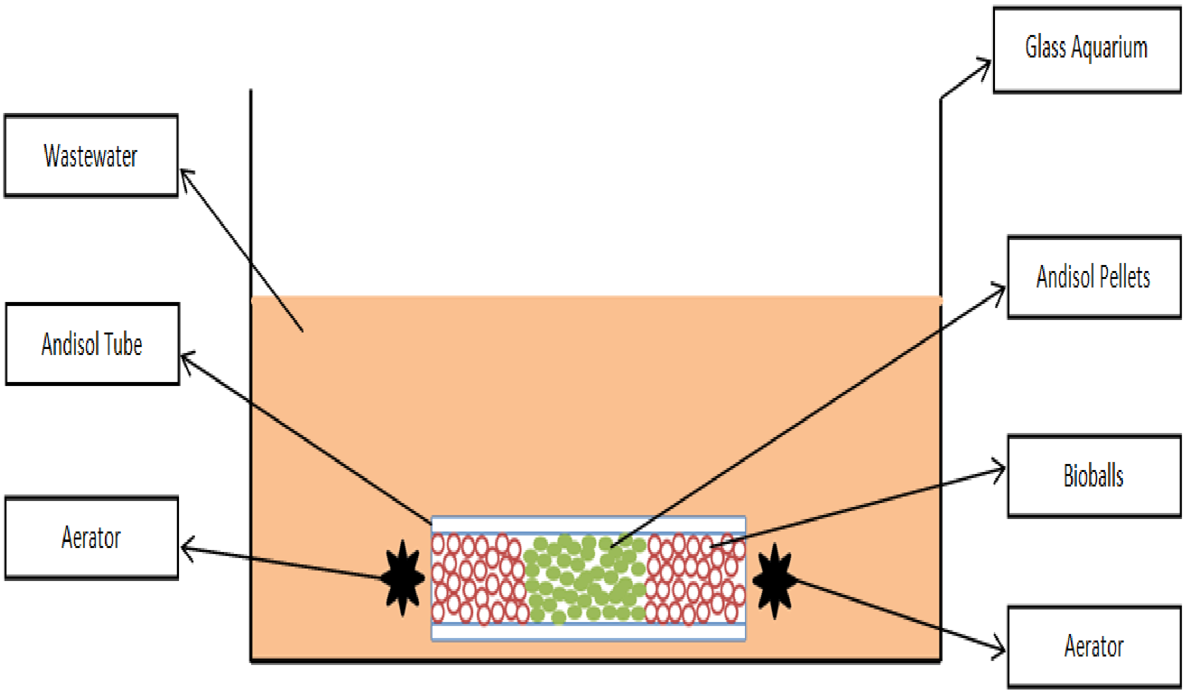

Figure 2. (A) Batch and aerobic system of the hybrid bioreactor in process. (B) Schematic hybrid bioreactor

RESULTS AND DISCUSSION

For the treatment of effluent drained from pharmaceutical unit, bioreactor system process was developed, which operated at various temperatures such as 28, 32, 37, and 46 ºC. Fe concentrations in this waste were tested using the O'phenanthroline method over the time duration of 0, 6, 12, 18 and 24 hours. Initially concentration of Fe was1.684 ppm, whereas pH of the waste was 5.8. It has been observed that the optimum parameters required for the maximum decrease (0.188 ppm, 88.8%, table-1) in the concentration of Fe in waste occurred at 37 °C, pH 6.1 with 24-hour contact time.

Table 1. Shows decrease of Fe concentrations

Fe concentration at 37 °C		
Contact Time (Hour)	pH	Fe Concentration (ppm)
0	5.8	1.684
6	5.8	1.121
12	5.9	0.642
18	6.0	0.302
24	6.1	0.188

Similarly, removal of manganese in the pharmaceutical wastewater carried out at various temperatures such as 28, 32, 37 and 46 °C over the period of 24 hours in the bioreactor system. Concentrations of manganese were tested using Persulfate method at duration of 0, 6, 12, 18 and 24 hours. Initially concentration of manganese was 0.993 ppm at pH 5.7. It is noticed from data interpretation that the optimum conditions required for the maximum removal of manganese is 37 °C temperature with contact time of 24 hours. At these optimum conditions, the Mn concentration was successfully reducedto 0.148 ppm with the efficiency of 85.1% (table2).

Table 2. The decrease in Mn concentrations

Mn concentration at 37 °C		
Contact Time (Hour)	pH	Mn Concentration
0	5.7	0.993
6	5.9	0.671
12	5.9	0.414
18	6.1	0.216
24	6.2	0.148

Successful decrease of Fe from 1.684 to 0.188 ppm (88.8% efficiency), and Mn from 0.993 to 0.148 ppm (85.1% efficiency), is the result of combination of adsorption and bio-filtration using both batch and aerobic methods. This reduction in Fe and Mn concentration meet the quality requirements of wastewater and allow its disposal into the fresh water bodies. Microorganisms have developed various ways to respond to the heavy-metal stress and have evolved capability to absorb heavy metals from aqueous waste, in the range from less than 1 to about 20 mg/l (Luka et al., 2018).

Iron and manganese from pharmaceutical waste were successfully removed by using adsorption and biological processes, which operated at the same time.

For effective biofiltration, EM4 microorganisms were immobilized on bio balls. These microorganism require continuous oxygen supply with optimal flow of 4 liter/minute.

A study about the adsorption of Fe by allophane collected from Mount Papandayan, West Java, Indonesia indicated a decrease in concentration of Fein distilled water by 99.9%, similarly allophane sampled from Mount Wilis, East Java, Indonesia used for the adsorption of Mn indicated reduction by 88.8% (Pranoto et al., 2013). Whereas by applying both adsorption and biological EM4 together for the treatment of pharmaceutical wastewater was resulted in lowering of Fe and Mn concentration with the efficiency of 88.8% and 85.1% respectively. Pranoto *et al.* (2013) used only allophane adsorption technique to remove Fe and Mn from distilled water.

Another investigation by Desica *et al.* (2016), studied the implication of zeolite adsorption and biological EM4 on effluent from Prambanan public hospital.But this research was not extended to the study ofFe and Mn removal. The biological system used for the removal of Fe from groundwater having concentration of Fe from 1 ppm to 5 ppm was succeeded with 93% to 95.25% removal. Similarly, for Mn, with same concentration in ground water, removal was 92.25% to 95% (Khedr et al., 2016). There is 88.8% removal for Fe and 85.1% removal for Mn in pharmaceutical wastewater by using allophane adsorption and biological EM4 system at same time. Main reason behind the difference of efficiency results of these two types of investigation is that for ground water only biological system was applied whereas for pharmaceutical waste water treatment, combination of two systems was used as this waste water contain many organic and inorganic pollutants in addition to Fe and Mn.

In 2015, McClellan*et al.* (2015) successfully achieved up to 98% removal of Fe and Mn at pH 9.0 and 90% removal of Mn at pH 6.5 in drinking water by using a biological system. The investigation was carried out by Tobiason *et al.* (2016) proved that pH made significant impact on biological systems, and also noted the pH fluctuation (5.7-6.2) by using hybrid system. Waste and drinking water require different pH and conditions for Fe and Mn removal, which cause the difference in removal efficiencies. Kasim *et al*. (2017) investigated that removal efficiencies of Fe and Mn are 52.33-97.18% and 12.5-60% respectively by using only biological process.

CONCLUSION

The combined system of adsorption and biosroption for pharmaceutical wastewater treatment was optimally operated at 37 °C temperature, 6.1 pH and 24 hours contact time for iron, and almost same conditions for manganese. This bioreactor, used both aerobic condition and batch method. This combined system has successfully discovered allophane as a new adsorbent, and its use in current investigation has proved that pH of wastewater in bioreactor has significant impact on the efficiency of Fe and Mn removal. Current study also compare this efficiency with biological system for the treatment of pharmaceutical wastewater. It is strongly suggested to continue the development of further sophistications in this hybrid system.

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