Removal of Iron and Manganese from Palm Oil Mill Effluent (POME) using Activated Clinoptilolite Zeolite

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Abstract. The adsorption capacity of activated clinoptilolite zeolite for the removal of heavy metal ions; iron Fe(III) and manganese Mn(II) from palm oil mill effluent (POME) was investigated in this batch sorption study. The physicochemical properties of both raw clinoptilolite zeolite and POME effluent were first characterized before the modification of the zeolite is made, chemically and physically. The raw filtered POME has an initial pH of 4.56 which was acidic, whereas the natural zeolite has a slightly alkaline pH at 7.52. The effects of pH (5, 7 and 9), sorbent dosage (15, 20 and 25 g in 125 ml of effluent), contact time (15, 30, 45, 60, 120, 150, 180 and 200 minutes) and agitation speed (120, 150, 180 and 200 rpm) on the sorption of heavy metal ions were evaluated. The concentration of heavy metals was analyzed using AAS. The concentration of heavy metal ions for each parameter has decreased significantly after batch study. The adsorption of heavy metal ions increased with the increasing of pH and adsorbent dosages. Optimum percentage of metal removal and the amount of metal ions adsorbed by the zeolite were determined at 85% of Fe(III) and almost 92% of Mn(II) in the experiments.

1. Introduction
Malaysia is one of the countries produces and exports palm oil in the world. Palm oil is usually used as the alternative for vegetable oil in daily life as it is extracted from the fruits of the oil palm. There are two types of wastes generated from the palm oil which are solid waste and liquid waste. A large volume of wastewater produced from milling process which is made up of used water and POME [1]. Raw palm oil mill effluent (POME) consisting of complex cellulosic matter mainly from processing of fresh fruit bunch (FFB) and normally presents as a brownish, colloidal slurry of water, oil and fine solids. About 2% of its suspended solids originated from palm fruit mesocarp [2]. Raw POME is an acidic effluent with a pH between 3.5 and 4.5 due to presence of complex organic acids, and possess a very high chemical oxygen demand (COD), biological oxygen demand (BOD), and total suspended solid (TSS) of 51 000 mg/L, 25 000 mg/L and 18 000 mg/L, respectively [3]. Apart of that, POME also contains assorted metals at critical levels such as iron (Fe), zinc (Zn) and manganese (Mn), which makes the discharge of the effluent into the waterways highly possible to cause public health threat and also interferes the food chain in the natural ecology [4].

Low pH and high concentration of metal ions are very toxic to living organisms and the environment. When the pH of wastewater is low, the chemical properties of soil are affected such as the nutrients supply for plant growth. While heavy metals pollutants are non-biodegradable, persistent and tend to accumulate in the bodies of living organisms. This will lead to acute diseases which can harm the body.
systems of human such as kidney, nervous system, gastrointestinal system and others [5]. Nowadays, various techniques have been explored to treat the heavy metal ions in POME but mostly are expensive or incomplete such as solvent extraction, electro-flotation, electro-dialysis, reverse osmosis, membrane separation, ion-exchange and chemical precipitation [6]. Therefore, adsorption as an economical approach has been widely advocated for the removal of heavy metal ions in wastewater using the natural, low cost and effective sorbent such as zeolite.

Clinoptilolite zeolite is a naturally microporous crystalline alumino-silicates mineral with three-dimensional structure, composed of SiO$_4$ and AlO$_4$ tetrahedral assemblies through the sharing of oxygen atoms in a honeycomb structure containing pores [7]. Its rigid anionic frameworks contain cavities holding exchangeable metal cations and can also host other molecules which makes them removable and replaceable. Because of its well-known adsorption properties, zeolites become among important inorganic cation exchangers and are extensively used in various industrial applications such as water and waste water treatment, catalysis, agriculture, animal feed additives, medicine and in biochemical applications.

Clinoptilolite zeolite can be found abundantly, proven to be safe, exhibited no toxicity and does not pollute the environment and has a great thermal stability [8]. Its unique and outstanding characteristics include high porosity, an inflexible structure, formed by paths able to encourage adsorption, ion exchange, selective diffusion and components separation from a mixture depending the molecular size and shape [9].

The important parameters to be determined in metals removal include pH, contact time, speed of agitation, and dosage of sorbent. The pH value should be increased after the treatment process compared to the initial pH value of raw POME [10]. The adsorption capacity of zeolite has a correlation with their microporous volume. The larger the micropore volume, the higher the adsorption capacity [11]. To determine the parameter limits of effluent are other than of standard A or B, the sixth schedule of Environmental Quality Act, 1974 can be referred, which is Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979 [Regulation 11 (5) (b)]. The parameter limit of effluent for iron is 5.0 mg/L, while for manganese is 1.0 mg/L.

In this study, the natural zeolite was first activated to be used as an adsorbent material for the removal of iron and manganese from raw POME under laboratory batch conditions, and the physiochemical properties of both zeolite and palm oil mill effluent (POME) wastewater were characterized. The effects of different contact times, agitation speeds, pH and sorbent dosages on the sorption of heavy metals in POME wastewater was later investigated. The optimum percentage of metal removal and the amount of metal ions adsorbed by the zeolite were determined as well.

2. Materials and methodology

Natural zeolite material used in this study was obtained from Messawa Village, Sumarorong District, Indonesia. It comes in granular forms and later pulverized using the Fritsch Pulverisette 9 vibrating cup mill at an optimum speed of 950 rpm for 60 seconds to become fine powder, and sieved through a 63µm sieve prior to experiments. Clinoptilolite has a highly structural similar to the heulandite but can easily be distinguished from heulandite by a higher silicon to aluminum ratio in favor to silicon, where Si/Al is more than 4 [12] and ranges between 4 to 5.5 [13]. During the ion-exchange process, clinoptilolite structure is remained intact even when there is H$^+$ ions displacement or swelling due to new cations absorption gives it an edge in terms of structural stability compared to other types of zeolites [14].

2.1. Activation of zeolite as sorbent and sample collection

To activate the zeolite, 300g of zeolite powder is washed thoroughly with distilled water and left in suspension for about 2 hours. Then, it was carefully filtered and oven-dried at 120 °C for about 4 hours. In the first stage, zeolite had undergone a chemical activation process using 1M hydrochloric acid (HCl). 83.5 mL of 37% HCl (concentrated grade) was diluted with distilled water and filled up in 1 L of volumetric flask. The zeolite sample is then carefully submerged in the hydrochloric acid solution for 2 hours and later rinsed with distilled water until the neutral pH is reached. The zeolite sample was oven-dried for the second time at 120 °C for 3 h, and later calcined in furnace at 600 °C for another 3 hours until it was completely dried. Dual modifications of clinoptilolite using HCl and high calcination was
intended to increase the effective diameter of channels and pores in the zeolite structure and remove the contaminants and organic wastes which block the zeolite’s cavity holes [15].

Sample of raw POME used in this study was collected from Malpom Industries Sdn Bhd in Nibong Tebal, Penang to be used as sorbate. The collected POME has been kept at temperature less than 4 °C in the chiller after reaching the laboratory to prevent solids biodegradation due to the action of microbial [16]. The characteristics of the POME sample are as summarized in Table 1. The data obtained was referred as typical values for comparison [17].

| Characteristics                  | Values   | Standard A | Standard B |
|----------------------------------|----------|------------|------------|
| Oil and grease (O&G)             | 15800 mg/L | 1.0 mg/L   | 10 mg/L    |
| Chemical Oxygen Demand (COD)     | 50500 mg/L | -          | -          |
| Biochemical Oxygen Demand (BOD₅) | 10197 mg/L | 20 mg/L    | 40 mg/L    |
| Total Solid (TS)                 | 31533 mg/L | -          | -          |
| Suspended Solid (SS)             | 4007 mg/L  | 50 mg/L    | 100 mg/L   |
| Dissolved Oxygen (DO)            | 0.47 mg/L | -          | -          |
| Ammonia Nitrogen (NTU)           | 613 mg/L   | 10 mg/L    | 20 mg/L    |
| Temperature                      | 54°C      | -          | -          |

2.2. **Characterizations of zeolite**

The determination of pH in zeolite was done in the ratio of distilled water: soil at 1:2.5 [18] using the pH meter (Hanna Instruments). The pH meter was first calibrated using the appropriate buffer solution (at pH 4.0 and 7). The reading is taken after the pH meter showed constant readings. The chemical compositions of the natural zeolite were determined by X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD).

2.3. **Batch sorption studies**

Batch sorption experiments were carried out in 500 mL beakers containing 125 mL of POME (a consistent volume used as sorbates), and the suspensions subjected to mix thoroughly in a conventional jar test apparatus at room temperature, in order to identify the effect of several process parameters such as the pH values (at 5, 7 and 9), dosages of zeolite (15, 20 and 25 g/125 mL), contact times (15, 30, 45, 60, 120, 150, 180 and 200 minutes), and different agitation speeds (120, 150, 180 and 200 rpm). The final concentration of metals was determined by atomic absorption spectrophotometer (AAS) using standard methods for examining water and wastewater [19]. The presented data are mean values of all assays carried out in triplicates.

For the effect of pH, 5g of zeolites were added to 125 mL of(filtered POME) and adjusted to pH 5, 7 and 9. The samples pH were adjusted by adding 0.1 N hydrochloric acid (HCl) and 0.1 N sodium hydroxide (NaOH). For adsorbent dosage test, different dosages (15 g, 20 g and 25 g) of zeolite have been added into 250 mL of filtered POME. Each dosage has been repeated twice for more accurate results. In contact time testing, 7 samples of 5 g of zeolites and 125 mL of filtered POME are stirred at different periods of time which are 15, 30, 45, 60, 120, 150, 180 and 200 minutes. For agitation speed test, 4 samples of 10 g zeolite added to 250 ml of filtered POME were mixed for 30 minutes through varying agitation speeds which are 120, 150, 180 and 200 rpm. After that, about 30 mL of each samples from every parameter testing has been pipetted out, diluted and sent for determination of final metal concentration by AAS.

The percentage of metal removal and the amount of metal ions adsorbed by the zeolite were calculated using the following equations:
% Removal = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}

Q_t = \frac{C_0 - C_f}{C_0} V \tag{2}

where \(C_o\) is the initial concentration of metal ions (mg/L), \(C_f\) is the final concentration of metal ion in solution (mg/L), \(Q_t\) is the amount of metal ions adsorbed on the time \(t\) (mg/g), \(V\) is the volume of solution (L), and \(w\) is the mass of natural zeolite.

3. Results and discussion

3.1. Chemical characteristics of zeolite

The pH of activated zeolite ranged between 7.20 - 7.52 which is considered as slightly alkaline. The moisture content found in the zeolite sample was 0.10 % and the organic matter found in the zeolite sample was 4.70 - 6.21 %, classified as low moisture and moderate respectively. Figure 1 showed the X-ray spectrum for clinoptilolite zeolite, as determined by XRD analysis. Table 2 showed the average chemical compositions in zeolite using XRF analysis.

![Figure 1. Spectrum for the development of clinoptilolite zeolite X-rays.](image)

Table 2. Average chemical composition of clinoptilolite zeolite.

| Main element (% weight) | Sample composition |
|-------------------------|--------------------|
| SiO₂                    | 63.00              |
| Al₂O₃                   | 12.30              |
| Fe₂O₃                   | 6.66               |
| CaO                     | 14.30              |
| K₂O                     | 2.18               |
| Na₂O                    | 1.16               |
| TiO₂                    | 0.58               |
| MnO                     | 0.16               |
| CuO                     | 0.053              |
| SrO                     | 0.181              |
| ZnO                     | 0.023              |
| ZrO₂                    | 0.042              |
| SiO₂/Al₂O₃ (ratio)      | 5.12               |
The results of X-ray Diffractometry (XRD) and X-Ray Fluorescence (XRF) of zeolite confirmed that clinoptilolite is the dominant mineral phase where Si / Al is 5.12. The final ratio Si / Al between 2 to 5 for zeolite is known as a middle molecular sieve [20] that enhances the ion exchange capacity and cation attractions lies inside the pores and channels [21].

3.2. Chemical characteristics of POME
The initial pH of raw filtered POME was 4.56 which is considered acidic. The raw filtered POME was diluted prior to test for the initial heavy metal ions concentration by using AAS. Iron and manganese concentrations were 1601.60 mg/L and 150.44 mg/L, respectively.

3.3. Effects of pH
The concentrations of Fe and Mn has significantly decreased against increasing of pH and after adsorption of zeolite, as clearly depicted in Figure 2 and 3. The optimum adsorption was found to occur at pH 9.0. Under the optimum condition, the removal efficiency was 90 % and 96 % for Fe and Mn, respectively as shown in Figure 4 and 5. The higher the pH, the better the removal efficiency achieved indicating that the metal sorption by zeolite is considerably depends on the pH. The removal efficiency of the selected metal ions increases with increasing the medium’s pH due to the deprotonation of oxygen functional groups favoured at moderate or higher pH values, consequently increased the active sites for heavy metal ions chelation that greatly enhances the zeolite’s adsorption capacity [22].

![Figure 2. Fe concentration against pH](image)

![Figure 3. Mn concentration against pH](image)

![Figure 4: Removal efficiency of Fe against pH](image)

![Figure 5: Removal efficiency of Mn against pH](image)

3.4. Effects of Adsorbent Dosage
Increasing dosage of adsorbent applied to the sorbate had showed the same trends as affected previously by pH, as can be seen in both Figure 6 and 7, as well as in the removal efficiency of Fe and Mn (Figure 8 and 9). The higher the adsorbent dosage, the better the adsorption efficiency. This is due to the better accessibility of superficial binding sites to chelate the toxic metals, which could be explained by growing of the available sites offered by the increasing amount of natural zeolite dosage. There is a little decrease of Fe adsorption capacity due to the incomplete utilization of the adsorptive capacity of adsorbent at a higher adsorbent dosage compared to lower adsorbent dosage. Meanwhile, the upsurge of the dosage might contribute to the agglomerations of adsorbent, hence decreased the available adsorption capacity due to the increase density.
3.5. Effects of Contact Time

Concentrations of Fe and Mn were steadily maintained after 15 minutes of contact time as seen in Figure 10 and 11. This shows that once adsorption reached the peak, times has no or little influence in the adsorption processes. This also dictated that at amount of 5 g, the presence of sorbent is too small in the sorbates, therefore it has been fully saturated. Elongating the contact time to over 200 min clearly gave no advancement in the adsorption capacity. But the percentages of Fe and Mn removal against contact time was bit fluctuated. Highest peak of removal by zeolites ranged about 87.50 % to 93.20 % for Fe and Mn, respectively (Figure 12 and 13). A rapid adsorption occurred at the beginning stage could be influenced by the higher availability of free sites for adsorption which then gradually engaged by the chelated ions over time [23].
3.6. Effects of Agitation Speed
Despite of decreased concentrations of Fe and Mn, the agitation speeds affecting variably as can be depicted in graphs of removal efficiency in Figure 16 and 17 below. The metal ions concentration analysed in Figure 14 and Figure 15, showed a significant drop after 120 rpm before it reached a constant state. This also shows that higher agitation speed has a little or not much contribution towards the decreasing concentrations of metal ions. However, as the stirring speed hastened to 120 rpm, the degree of sorption for both metals enhanced. Previous study has supported the results obtained by relating the increase of the coefficient of film transferred in the medium leads to the spike of sorption rate because of the reduced thickness of the horizon layer around the clinoptilolite particles [24]. The effects of agitation speed on adsorption ratio shows that almost 86 % and 92.50 % of Fe and Mn were adsorbed by zeolite at optimum speed of 200 rpm.

![Figure 14. Fe concentration against agitation speed](image)

![Figure 15. Mn concentration against agitation speed](image)

![Figure 16. Removal efficiency of Fe against agitation speed](image)

![Figure 17. Removal efficiency of Mn against agitation speed](image)

4. Conclusion
The removal of heavy metal ions from palm oil mill effluent (POME) using natural zeolite (clinoptilolite) has been examined in this work. In the early stage, the natural zeolite had been activated and the properties of both zeolite and POME wastewater had been characterized. The raw filtered POME has an initial pH of 4.56 which was acidic, contrasted with the pH of natural zeolite that is slightly alkaline (pH 7.52). The effects of pH, adsorbent dosage, contact time and agitation speed on the sorption of heavy metal ions in POME wastewater has been studied. The findings showed that the concentration of heavy metal ions has decreased significantly after adding the natural zeolite into the POME wastewater for the adsorption. The optimum percentage of metal removal and the amount of metal ions adsorbed by the zeolite for each parameter were also determined. The zeolite used as adsorbent for the metal removal in this work showed an effective reduction of iron and manganese ions from POME. The optimum pH has reached at 9, the optimum contact time happened after 60 minutes and the optimum agitation speed was indicated at 200 rpm. However, the optimum adsorbent dosage for metal removal was recorded at 25 g but the optimum adsorbent dosage for the amount of metal ions adsorbed by the clinoptilolite zeolite was at lower dosage, 15 g. In conclusion, natural zeolite showed great potential as a good adsorbent for the removal of heavy metal ions in high strength wastewater due to its fast adsorption-desorption properties.
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Acknowledgement

The authors would like to acknowledge the financial support from the Fundamental Research Grant Scheme RACER (FRGS-RACER) under a grant number of RACER/1/2019 (9027-00021) from the Ministry of Education Malaysia.