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Palm Oil Fuel Ash (POFA) as Adsorbent for Adsorption of Lead from Aqueous Solution

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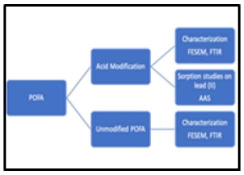
GRAPHICAL ABSTRACT



Flowchart of POFA preparation as adsorbents

ABSTRACT

Palm Oil Fuel Ash (POFA) is the by product from burning of empty fruit bunches, shells and palm oil fibers, as fuel in palm oil mill boilers. This research focuses on the preparation of modified POFA as an adsorbent for adsorption of lead from aqueous solution. The modified POFA was prepared by chemical activation using sulphuric acid, H_2SO_4. Characterizations of unmodified POFA and modified POFA, before and after adsorption were carried out using Fourier transformed infrared (FTIR) spectroscopy and field emission scanning electron microscopy-energy dispersive X-ray (FESEM-EDX). The surface of POFA is mainly composed of oxygen (40.9 %) and silicon (12.4 %). Micrographs of unmodified POFA and modified POFA indicate spherical and irregular shapes. However, it was found that the modified POFA has a more porous structure that indicates a better adsorptive capability. The adsorption behaviour of lead from aqueous solution onto modified POFA was investigated via batch adsorption study to examine the effect of process variables, namely, pH, adsorbent dosage and temperature. The optimum conditions for the adsorption of lead onto modified POFA were found at solution pH 9, with adsorbent dosage of 0.7 g/L and the temperature of 318 K with equilibrium less than 180 minute at agitation rate of 150 rpm. The study shows that POFA can be effectively used as a potential adsorbent for adsorption of lead from aqueous solution.

Keywords: palm oil fuel ash, modification of POFA, batch adsorption, heavy metals, lead

1. INTRODUCTION

Water is inevitably one of the most valuable natural resources existing on our planet that comprises more than 70% of the Earth's surface. However, the quality of water resources is decreasing due to the multiple contaminations from various sources [1]. In recent years, various toxic chemicals particularly heavy metals, aromatic molecules and dyes have been widely detected at dangerous levels in water in many parts of the world, posing a variety of serious health risks to human beings as well as aquatic living [2]. However, among the mentioned contaminants the most concerning contaminant of water is found to be heavy metals [3]. This is mainly because, unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products.

The presence of heavy metal ions is of major concern due to their toxicity to many life forms [4]. Due to their high degree of toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that plays a major role in public health deterrence. Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption, and co-precipitation and adsorption. Studies on the treatment of effluent bearing heavy metals have revealed adsorption to be a highly effective technique for the removal of heavy metals from storm water stream because of its convenience, ease of operation, and simplicity of design [5]. For adsorption, activated carbon has been widely used as an adsorbent [6]. Despite its extensive use in water and wastewater treatment industries, activated carbon remains an expensive material.

In that context, the palm oil industry in the Southeast Asian region produces vast quantities of solid by-products such as palm fiber and shell, which are used as boiler fuel by palm oil mills to produce steam for electricity generation and palm oil extraction [7]. Malaysia thus generates huge loads of palm ash each year. Hence, the utilization of such agriculture solid waste residues for wastewater treatment is most encouraged due to two main reasons. First, as wastes are available abundantly at no or very low cost and second, as POFA is disposed as waste in landfills, it causes environmental and other problems such as health related problems in Malaysia [8]. Therefore, the objective of this work is to study the utilization of palm ash as an adsorbent to remove heavy metals specifically lead in aqueous solution.

2. EXPERIMENTAL

The experimental procedure in this study was divided into three phases. First phase of the study focused on the preparation of adsorbent, POFA, preparation of adsorbate and characterization of POFA. In this study 0.5 M sulphuric acid (H_2SO_4) with the ratio of 3:1 of POFA-to-sulphuric acid, was used as the activating agent. As for the second phase of this study, it focused on characterization of POFA. The structural composition and morphological properties of the prepared adsorbent was characterized by Fourier transform infrared (FTIR) spectroscopy and field emission scanning electron microscope (FESEM), respectively. The third phase of the study was the removal of lead (II) in aqueous solution using the activated the POFA. The concentration of adsorbate, lead (II) was determined using atomic absorption spectroscopy (AAS). The adsorption behaviour of lead from aqueous solution onto modified POFA was investigated via batch adsorption study to examine the effect of process variables, namely, pH, adsorbent dosage and temperature.

2.1 Preparation of Palm Oil Fuel Ash (POFA) as an adsorbent

Preparation of Palm Oil Fuel Ash (POFA) includes several processes before being used for adsorption studies such as chemical activation, filtering, washing and lastly drying. Freshly obtained POFA was washed with distilled water to remove the dirt, dust and incompletely burned materials. The cleaned POFA was then oven dried at 110 °C for 48 hours to remove the moisture and was sieved through 45µm standard sieve. As for the modification step, 60 g of POFA was treated with 0.5 M sulphuric acid. For the removal of lead (II) from aqueous solution using POFA as an adsorbent, ratio of POFA to sulphuric acid that is 3 g: 1 mL of H2SO4 was used. The activated POFA was left for 12 hours after which it was oven dried for 24 hours at 110 °C. The dried sample was ieved using 45 -100 µm standard sieve and stored in an airtight container before proceeding with the adsorption studies.

2.2 Preparation of Adsorbate

Preparation of adsorbate involves the preparation of 1000 mg/L of lead stock solution and preparation of calibration curve before furthering the adsorption studies. 0.1 g of lead (II) nitrate was weighed accurately in a beaker by using analytical balance and was dissolved in a 1000 ml volumetric flask and dilute to the mark with deionized water to produce 100 ppm lead stock solution. The flask was then inverted a several times to ensure solution's homogeneity. The pH of the solution was adjusted using reagent grade dilute hydrochloric acid (0.1 mg/L) and sodium hydroxide (0.1 mg/L).

2.3 Adsorptive studies

Batch adsorption experimental procedure were performed to investigate the sorption of lead by POFA. The effect of various parameters such as pH, temperature, and adsorbent dosage were investigated. For each parameter the concentration of lead solution used was 5 mg/L.

3. RESULTS AND DISCUSSION

3.1 Field Emission Scanning Electron Microscopy with Energy Dispersive X-Ray (FESEM-EDX) Analysis

In this study, the morphology and elemental composition of unmodified POFA and the modified POFA (0.5 M H_2SO_4 in 24 hours) was analysed using FESEM-EDX. From Figure 1, it can be seen that POFA has very irregular and uneven shapes and the unmodified POFA particle is in spherical and irregular shape. The modified POFA has the same spherical shape as well; however, the modified POFA has more pores, cavities, hollow texture with irregular shapes due to the acid treatment. In short, modified POFA appeared to have a more porous surface which is a good adsorptive characteristic of an adsorbent.

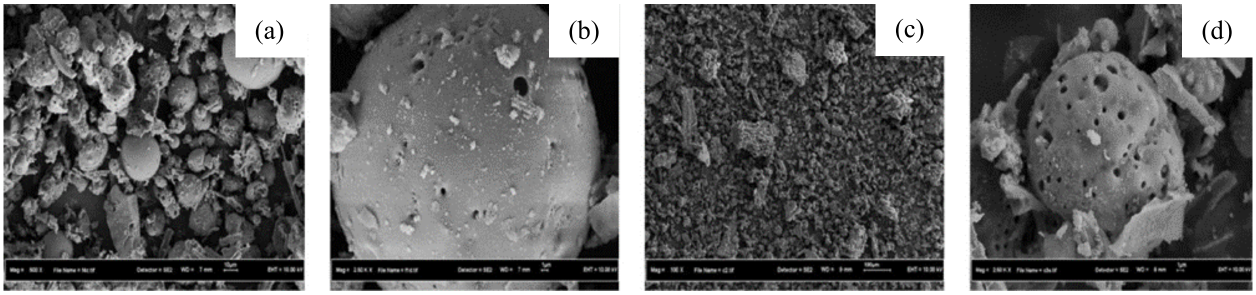


Figure 1 Surface morphology of unmodified POFA (a, b) and modified POFA (c, d) at low and high magnification under FESEM.

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was performed to investigate the functional groups of the modified POFA before and after the adsorption. As for the modified POFA that can be seen in Figure 2 the FT-IR peak located at 2923.85 cm^{-1} is indexed to CH2 stretching vibration. The vibration of C=O stretch bands at 1797.31 cm^{-1} showed the existence of carboxylic acids. For the spectrum of quartz, the main Si-O is located at 1023.00 cm^{-1}, with three relatively symmetric bands in the lower frequency region: 794.05, 688.81, and 463.75 cm^{-1} respectively. The band at 1023.00 cm^{-1} is also assigned to stretching of Al-O bonds. The band at 1429.10 cm^{-1} in the spectra of POFA is attributed to Si (Al)-O-Si asymmetric stretch. As can be seen in Figure 3 The change in intensity or shift in peak position gives information about the interaction adsorbate and adsorbent. The adsorption peaks at 3417.67 and 3433 cm^{-1} indicate the existence of phenolic and aliphatic OH group and after the adsorption as shown in Figure 3 band has broaden slightly to 3434.92 and 3443.67 cm^{-1} due to the presence in POFA after sorption with lead. The lower wavenumber of unmodified POFA at 562.03 cm^{-1} and for modified POFA at 563.50 cm^{-1} shows the attachment of either heavy metal (Pb^{2+}) to Si-O-Si (Al) therefore forming a Pb (Si)-O-(Si) Al or causing the replacement of Si-O due to the entry of weaker tetrahedral Al-O in IV-fold coordination into Si-O-Si bonds.

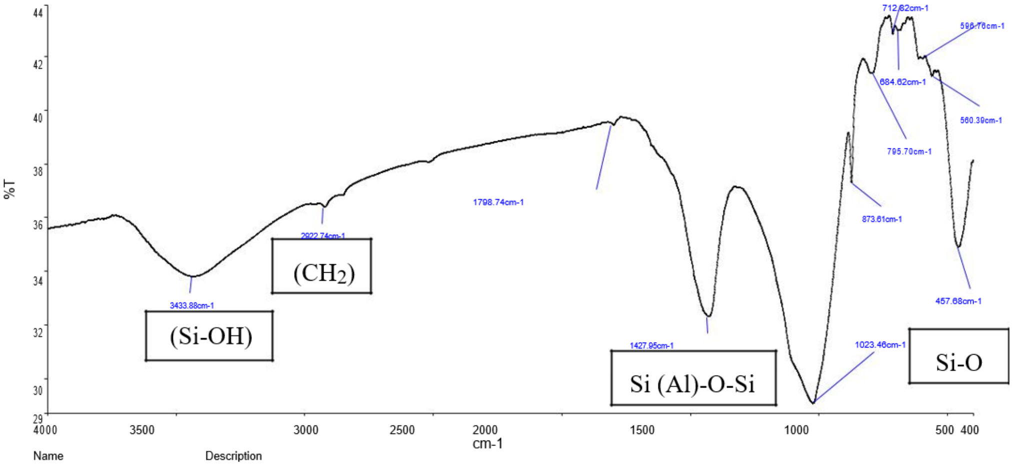


Figure 2 FTIR spectrum of modified POFA before adsorption.

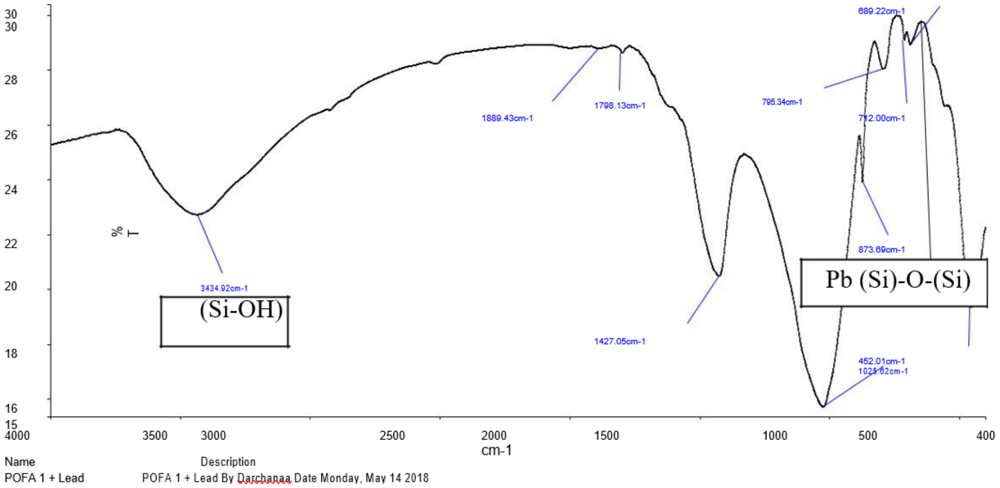


Figure 3 FTIR spectrum modified POFA after adsorption.

3.3 Adsorptive studies

The adsorption studies result shows the calibration curves of lead solution, the adsorption studies for the effect of adsorbent dosage, effect temperature and effect of pH. The calibration curve for lead was constructed from the data of the standard solution at five points 1 mg/L, 2 mg/L, 3 mg/L, 4 mg/L and 5 mg/L. Figure 4 displays the calibration curve for lead nitrate solution. The calibration curve was used to determine the concentration of lead solution after treating with the prepared modified POFA. Batch adsorption studies were carried out to find out the adsorption isotherms of lead elements on POFA.

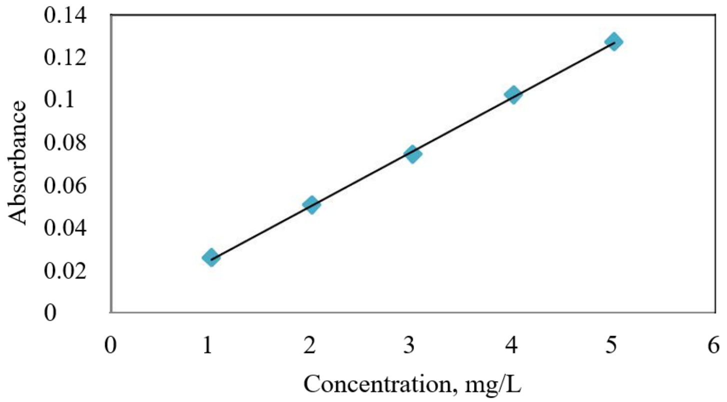


Figure 4 Calibration curve of lead (II).

3.4 Effect of adsorbent dosage

In this study, 5 mg/L of lead solution with varying amount of adsorbent from 0.1g to 1.5g of POFA is used to observe the effect of different amount of adsorbent on the adsorption of lead From the Figure 5, it can be seen that the percentage of removal of lead increases up to a certain limit and then it remains almost constant. The adsorption of lead was increasing as the as adsorbent dosage increases due to the effective surface and the availability of more adsorption sites. For the adsorbent dosage greater than 0.8 g, the incremental lead removal become very low and constant, as the surface lead concentration and the solution come to equilibrium with each other. Thus, the optimum dose observed in the present study is 0.7 gram per 50 mL of the solution

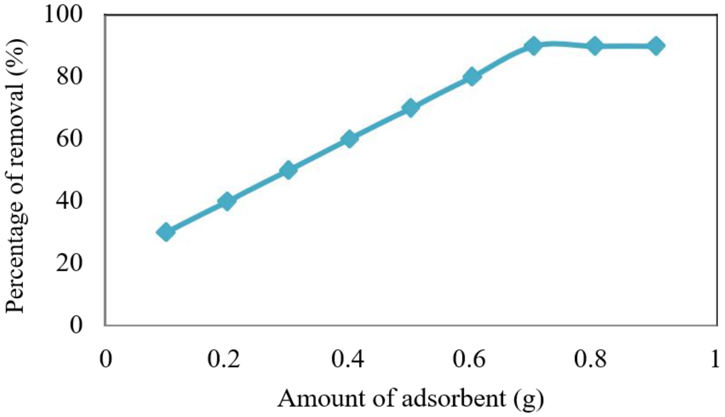


Figure 5 Effect of adsorbent dosage on the percentage removal of lead by modified POFA.

3.5 Effect of temperature

The effect of temperature on the adsorption isotherm was studied by carrying out a series of four different temperatures 25, 35, 45 and 55 °C with 0.7 g adsorbent in 50 mL of 5 mg/L of lead solution as shown in Figure 6. From the Figure 6 can be seen that when the temperature of lead solution increase starting from 25, 35, 45 and 55 °C, the percentage of lead removal increased as well. By increasing the temperature from 35 to 45 °C, the percentage of lead removal increased from 70 to 80%. Consequently, it is clear that the adsorption equilibrium is a temperature dependent process. The increase of adsorption capacity with the temperature indicated that the adsorption process in this finding is endothermic in nature.

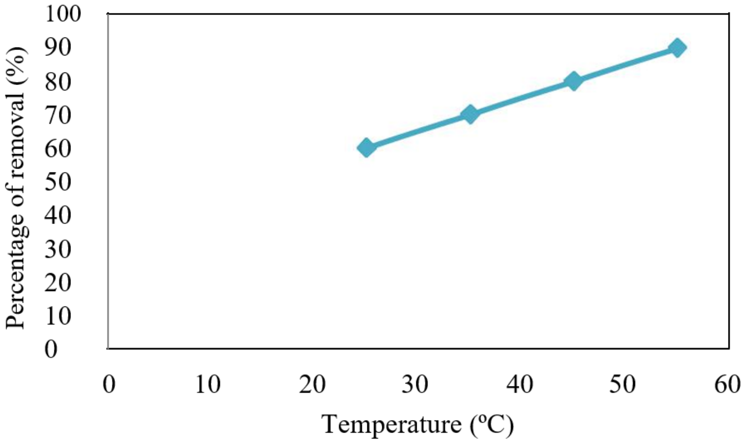


Figure 6 Effect of temperature on the percentage removal of lead by modified POFA.

3.6 Effect of pH

In this study, the effect of solution's pH on the adsorption of lead was carried out at 25ºC, with 0.7 g/L adsorbent in 5 mg/L of lead solution with varying pH from 2 to 12 as shown in Figure 7. It shows the effect of pH on the adsorption of Pb (II) ions using POFA. The adsorption capacity of POFA increased slowly from pH 5 and achieved its optimum rate at pH value of 9. The result shows mainly the adsorption of Pb (II) ions were low at acidic condition. This is attributed to the acidity medium which affect the metal uptake of the adsorbent due to higher presence of H+ which resulted in a positive surface charge. Based on the observation, it can be stated that the optimum pH for the removal of Pb (II) ions using POFA was obtained at pH 9 and was used in the following experiments in order to obtain optimum removal efficiency

4. CONCLUSION

The objective of this study is to modify Palm Oil Fuel Ash (POFA) and characterize as well as utilize POFA as an adsorbent for lead removal from an aqueous solution. The modified POFA was prepared by chemical activation using the sulphuric acid, H_2SO_4. Characterization of POFA and modified POFA after the adsorption of Pb (II) ion was carried out by using Fourier transformed infrared (FTIR) spectroscopy and field emission scanning electron microscope–energy dispersive X-ray (FESEM-EDX). Micrographs of raw POFA, unmodified POFA and modified POFA indicate spherical and irregular shapes. Modified POFA has a more porous surface with more cavities. The adsorption of lead (II) ion from aqueous solution by modified POFA was investigated under the different experimental conditions such as adsorbent dosage, temperature and pH in batch process. The optimum condition for the adsorption of Pb (II) was found to be at pH 9, with 0.7 g/L adsorbent dosage at 318K in 5 ppm of lead solution, agitation rate of 150 rpm, within the equilibrium time of less than 180 minute.

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