Preparation and Characterization of Activated Cow Bone Powder for the Adsorption of Cadmium from Palm Oil Mill Effluent

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Abstract: Several studies have been conducted on the removal of heavy metals from palm oil mill effluent. In this study, cow bones were developed as an adsorbent for the removal of cadmium II from POME. A batch experiment was conducted to investigate the effectiveness of the prepared activated cow bone powder for the sorption of cadmium II from raw POME. The experiment was carried out under fixed conditions using 100mg/L raw POME combined with different adsorbent dosage of CBP of 184.471 Ra(nm) surface roughness. The equilibrium adsorption capacity of the hydrophobic CBP of average contact angle 890 was determined from the relationship between the initial and equilibrium liquid phase concentrations of POME. The optimum adsorption of cadmium II on CBP was at 10g adsorbent dosage for sample 1 and 2 at 97.8% and 96.93% respectively. The least uptake was at 30g adsorbent weight for both samples at average of 95.1% for both samples. The effective removal of cadmium ion showed that CBP has a great potential for the treatment of heavy metal in POME.

Keywords: POME, cow bone, adsorption.

1. Introduction
Most Wastewater containing heavy metals is of utmost importance globally because of their potential treat to both aquatic ecosystem and the soil environment. According to World Health Organization, heavy metal is hazardous even at low concentration and causes various forms of diseases [1,2]. The presence of cadmium in water is very toxic for the aquatic ecosystem [3] the effect of the water consumption containing cadmium has been linked to cancerous growth, hormonal disorder, renal failure etc. Therefore, effective treatment of cadmium is essential for the preservation of aquatic ecosystem. Several technologies based research has been documented for the removal of heavy metals from aqueous solution.

Some of the methods are coagulation and flocculation [4], photocatalyst [5], membrane filtration process [6]. In the treatment of palm oil mill effluent (POME), researches have been conducted by Harsono et al. [7] using anaerobic treatment. Hazlan [8] also reported that evaporation process can be used for the treatment of POME and also electrocoagulation to reduce the pollutants [9]. However, the above treatment methods can only be applicable for high concentration of POME and also very expensive to operate.

In recent studies, there is growing interest in the removal of heavy metals by adsorption method. Using locally sourced natural materials prepared as adsorbent. Some of the materials include chitosan-clay composite, walnut shell [10], kaolinite and montmorillonite [11] and palm kernel shell charcoal [12]. The method of adsorption among researchers for the removal of heavy metals is due to the cost effectiveness, availability of the naturally sourced materials and efficiency in the treatment of high strength industrial wastewater with quality effluent [13,14]. The reversible nature of adsorption process implies that regeneration of absorbents is possible through desorption processes [15]. The ability to reuse spent by regeneration suggests that adsorption technology is well suited for the preservation of the climate by reducing the necessity of burning and discharging of spent adsorbent media.

The use of adsorption for the treatment of high strength industrial wastewater such as POME has rarely been reported in literature. Hence, its inclusion will enhance the adsorption technology and will provide an alternative treatment of heavy of cadmium in POME. The production of POME especially in
Malaysia known to be one of the largest producers of palm oil recorded to have national production rate of 0.67 cubic meters per tonne of fresh fruit bunch (FFB) processed by mill is a major challenge to researchers [16]. Effective treatment of heavy metals such as cadmium from POME which has been proven by [3] to be very toxic to aquatic environment requires very efficient technology in facing the current challenges. The method of adsorption using prepared cow bones was adopted for this research to investigate the treatment efficiency of activated cow bone powder for the removal of cadmium from POME. Bone powder is obtained from ignition process of crushed bones initially formed as bone char, the process is achieved by heating at 500-700°C. Bone char is produced through the carbonization process of cattle bones, it contains 10% carbon and 90% of hydroxyapatite [17]. The bone charcoal also have the composition of tricalcium phosphate (70-76 wt %) and calcium carbonate (7-9wt %) [18]. Use of bone char has been applied in the study of [17] for the removal of flouoride from water solution. The uses of bone powder have also been applied in the study of [18] for the removal of lead in aqueous solution. However, the application of cow bone powder for the treatment of high strength industrial wastewater has rarely been reported in literature.

This study will provide an alternative treatment technology for agro based industrial wastewater especially Malaysia which is known to be the largest producer of palm oil in the world after Indonesia [5]. The main objective of our present study is to investigate the treatment efficiency of prepared activated carbon produced from cow bones at different adsorbent dosage of cow bone powder (CBP) for the adsorption of cadmium from POME.

2. Materials and Methods

2.1 Preparation and Characterization of Adsorbent
Fresh femur of cow bones was obtained at Bazaar Kedai Rakyat Johor. The bones were carefully washed with water severally, cleaned from meat and later washed again repeatedly to remove impurities on the surfaces. The bones were rinsed with de-ionized water and transferred to the oven at 80 °C to dry. The dried bones were crushed and ignited at 700°C for 5 hours. The loss of ignition (LOI) was evaluated by weighing the sample before and after ignition. The bone char produced were further reduced using the ceramic ball mill grinder. The solubility of the surface of the prepared media in contact with deionized water is illustrated in Figure 1 and was achieved using VCA optima.

Finally the average particle size of less than 150µm was used for the study and was obtained using the 150µm sieve size. The field emission scanning microscopy JEOL JSM-7600F was used to determine the surface morphology and the average particle sizes used for the study. The samples were coated with electric conductive gold film prior to the investigation. The X-ray fluourescence (XRF) S4 pioneer model was used to determine the chemical composition of the media.

2.2 Adsorbate
The POME sample used for the study was obtained from Kilang Sawit PPNJ Kahang Johor. The sample was stored in a 30 L plastic container, transported and stored in the laboratory according to standard methods for the preservation and storage of wastewater [19]. The characterization of the raw POME was achieved before preservation and storage. The result of the characterization is represented in Table 2.

2.3 Batch Study
The batch adsorption study was carried out at 30°C in a 250 ml conical flask containing 100 ml of the raw POME. The agitation of the mixture was performed at 200rpm and a predetermined period of 105 minutes contact time for all analysis. The pH 7 was adopted for the study, the adjustment was conducted using solution of 30%diluted sodium hydroxide and dilute sulphuric acid. The rate of adsorption of cadmium II on CBP was achieved at different adsorbent dosage to obtain the optimum dosage for the uptake of the heavy metal. A set of replicate was prepared for each of the adsorbent mixture. For both sample and replicate, the conical flasks were removed from the orbital shaker and filtered at the end of the contact time, the filtration of the sample was performed with 0.45µm glass fibre membrane and was analysed using inductively coupled plasma (ICP) mass spectrometer Elan 9000. The result presented as averages of three measurements. Relative standard deviation (RSDs) of less than 5% was obtained for the samples and replicates. The pattern of adsorption is presented in Figure 2. The rate of adsorption of cadmium on CBP was calculated as:

\[
\% \text{ removal} = \frac{C_o - C_e}{C_o} \times 100
\]  

(1)
Where:

\[
\begin{align*}
\text{Co} & = \text{The initial liquid face concentration (mg/L)} \\
\text{Ce} & = \text{The equilibrium liquid-phase concentrations (mg/L)}
\end{align*}
\]

3. Result and Discussions

The behaviour of the adsorbent media in de-ionized water as observed through VCA optima as illustrated in Figure 1.

![Figure 1](image)

**Figure 1.** Microphotographs of sample with (a) 90.8° and (b) 87.6° contact angles using the water drop penetration time test.

According to Leelamanie [20], hydrophobic media using water drop penetration time have contact angles within the range of 88-93°C. The effectiveness of CBP for the removal of Cd by varying the weight of the media showed the adsorptive capacity of CBP at different dosage for the uptake of Cd²⁺ from raw POME. The percentage removal by weight of adsorbent after treatment is illustrated in Figure 3. The results of the ICP mass spectrometer Elan 9000 test for the adsorbent signified the effectiveness of the prepared media, the results are presented for the sample and the replicate. The optimum removal was observed at 10 g dosage with 97.8% uptake for sample 1 and 96.3% uptake for the replicate. Further dosage showed a decrease in the rate of adsorption for both samples. The lowest removal of cadmium (II) was 0.819 µg/L (94.5%) and 0.65 µg/L (95.6%) at dosage of 30g for both samples. The rate of adsorption was partly constant for 20 and 30g dosage.

The adsorptive behaviour of CBP depends on the pore size arrangement of the particles, the hydrophobic surface and the chemical composition of the media. The high removal rate of cadmium (II) is reasonably possible as a result of the availability of active sites and larger pore spaces. The macro pores and meso pores provided readily available sites for the cadmium ions to react with the surfaces internally and externally. The active sites were responsible for >90% removal of Cd(II). The hydrophobic surface provided electrostatic interaction between sorption sites and the metal ions. Also, the significance of calcium in the chemical composition makes high capacity for exchangeable ions at neutral pH possible, this cause very strong electrostatic interaction between the positively charged sites of CaO and the anionic sites of POME [21], the carbon surfaces influenced sorption and the hydroxyapatite arrangement of the phosphate ions provided sites for the attraction of cadmium ions. The surface morphology and the particle distribution as shown in Figure 2. The atomic force microscope AFM XE-100 park system was used to determine the surface roughness of the adsorbent media. The sample was stored at room temperature without any noticeable form of bacterial contamination throughout the period of the study.
Figure 2. Particle size distribution of CBP.

Table 1. The result of the XRF analysis.

| Formula | Concentration(%) |
|---------|------------------|
| Orig-g  | 8                |
| Added-g | 2                |
| CaO     | 49.80            |
| P_2O_5  | 32.90            |
| C       | 1.00             |
| Na_2O   | 0.96             |
| SiO_2   | 0.89             |
| MgO     | 0.78             |
| Al_2O_3 | 0.44             |
| Cl      | 0.11             |
| K       | 0<LLD            |
| Fe      | 0<LLD            |
| LOI     | 13.13            |

Table 2. The characteristics of the CBP and raw POME.

| Parameter                  | CBP Value | Raw POME Value |
|----------------------------|-----------|----------------|
| Bulk density(g/ml)         | 0.81      | pH             |
| Solid density (g/ml)       | 3.24      | 10,333.3       |
| Porosity                  | 73.9%     | 2233.3         |
| Length(µm)                | 0.777     | 937            |
| Roughness Ra(nm)          | 184.471   | COD (mg/L)     |
|                           |           | 53,374         |
|                           |           | Cadmium at pH |
|                           |           | 15.6 µg/L      |
4. Conclusion
The purpose of this study was to investigate the adsorption efficiency of CBP used as alternative to activated carbon for cadmium removal from POME. The performance of the CBP was analysed in the batch study conducted using different adsorbent dosage of the media. The investigation showed that the prepared activated CBP offers an effective non-toxic alternative treatment for the uptake of cadmium ion from raw POME. The rate of adsorption is a function of the effectiveness of the adsorbent media and the concentration of the adsorbate. The results showed that CBP achieved >90% removal of cadmium ion throughout the study. Therefore it can be widely applied as an effective media for the treatment of cadmium ion in raw POME.

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