



## BATCH ADSORPTION OF MANGANESE FROM PALM OIL MILL EFFLUENT ONTO ACTIVATED COW BONE POWDER

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### ABSTRACT

Several studies have been conducted for the removal of heavy metals in literature using natural adsorbent. The study of the removal of heavy metals from raw palm oil mill effluent considered as one of the major high strength wastewater has rarely been reported. In this study, Cow bones were developed as effective carbon adsorbent. The investigation of the effectiveness of the prepared activated cowbone powder was studied for the removal of manganese ion from raw POME. The surface roughness of the prepared activated CBP was 184.471 Ra (nm) of length 0.777  $\mu\text{m}$  observed through atomic forced microscope. The experiment were carried out with 100ml of raw POME under different adsorbent dosage and other fixed conditions. The equilibrium adsorption capacity of the activated CBP was determined from the relationship between the initial and equilibrium liquid phase concentrations of POME. The result of the investigation showed optimum adsorption of the manganese ions onto the adsorbent media at 15 g adsorbent dosage for sample 1 and 2 with 98.3 and 98.4 % removal efficiency respectively. The lowest adsorption capacity of the media was at 5g for both samples at average of 95.34%. The result showed activated CBP can be a very effective alternative to activated carbon for the removal of manganese from raw POME.

**Keywords:** activated cow bone powder, palm oil mill effluent, manganese, adsorption.

### INTRODUCTION

Adsorption technology is the most widely used treatment method of organic and inorganic toxic wastes (Tongpoothorn *et al.* 2011, Li *et al.* 2013, Monsalvo *et al.* 2012). The study of adsorption for the treatment of wastewater has been proven to be less expensive, effective for wastewater treatment depending on the type of adsorbent used. Heavy metals is hazardous, contribute to various diseases and affect the ecosystem. They are toxic even at low level bioaccumulation in water according to world health organisation (Lourie E, 2010, Beesley, 2014). For this reason, the removal of heavy metal ions from wastewater have become major source of concern to water quality managers and is given extensive research attention. Many research areas have focussed on removal of heavy metals using chemical precipitation and the use of physical treatments such as ion exchange, solvent extraction and the method of adsorption. Adsorption treatment method is considered as the most effective method of treating high strength industrial wastewater and heavy metals in water (Rizzo, 2015, Darael, 2015). The use of locally sourced adsorbents such as chestnut, bark, sawdust, pine-nut cone, pine-needle have been used for cationic removal (Kim, 2014, Vecino, 2014), others include the use of industrial materials (Hua, 2015), bentonite (Anna, 2015), date stones (Bouhammed, 2015), cassava peel (Simate, 2014), forest biowaste (Kim, 2015), Kaoline (Zhao, 2014), moringa pods (Mattouqi, 2015) and is capable of generating very high-quality treated effluents. Adsorbents can serve as alternative to activated carbon which are commercially very expensive and very sophisticated due to its design for various applications. Due to the reversible process of adsorption

method, adsorbents can be reused through regeneration by desorption processes (Tresintsi, 2014).

This research reports the investigation of the removal of Manganese onto activated cow bone powder at different dosage from palm oil mill effluent (POME). Bone powder is obtained through the process of carbonization of crushed bones by heating at 500-700°C in a furnace. After the heating process, the crushed bones become bone charcoal which is composed of tricalcium phosphate (70-76 wt %), carbon content (9-11%) and calcium carbonate (7 - 9 wt %) (Cheung, 2001). Bone powder has been used as adsorbent in the study of Cha (2011) for the removal of lead in aqueous solution. The use of bone powder has been reported by many researchers for wastewater treatment but the use of activated cowbone powder for the treatment of high strength waste water such as POME has rarely been reported in literature.

This study is important because Malaysia is the second largest producer of palm oil in the world, for instance in 2012 only, palm oil industry produced 43 million tonnes of biomass (Chang, 2014). The total land available for oil palm has increased from 55,000 ha in 1960 to 5.23 million ha in 2013 which is equivalent to 16% of the total available land area in the country (MPOB, 2013). The objective of the present study is to investigate the effectiveness of the prepared activated carbon using different adsorbent dosage of cow bone powder (CBP) for the removal of manganese from POME.



## EXPERIMENTAL

### Preparation and Characterization of Adsorbent

The femur of cow bones were purchased at Agro Bazaar Kedai Rakyat in Parit Raja, Johor. The bones were washed, cleaned from meat, then washed again several times to remove fats and impurities. The bones were rinsed with tap water and were put in the oven at 80 °C to dry. The dried bones were crushed and then put in the crucibles and transferred to the furnace for ignition at 700 °C for 5 hours. The weight of each sample was measured before and after ignition and the weight loss was used to determine the loss of ignition (LOI). The samples were further reduced using the rotor mill and finally the working particle size was obtained using the 150 µm sieve

size. The surface morphology and particle size distribution was achieved using the Field emission scanning microscopy JEOL JSM-7600F, prior to the investigation, the surface of the samples were coated with thin film of electric conductive gold film. The particle size distribution is illustrated in Figure-1. The chemical composition of the adsorbent is determined using X-ray fluorescence S4 pioneer model, the result is shown in Table-1. The surface roughness was evaluated using atomic force microscope AFM XE-100 park systems. The surface characteristics of the CBP is shown in Table-2. The CBP was stored at room temperature without any noticeable form of bacterial contamination throughout the period of the study.

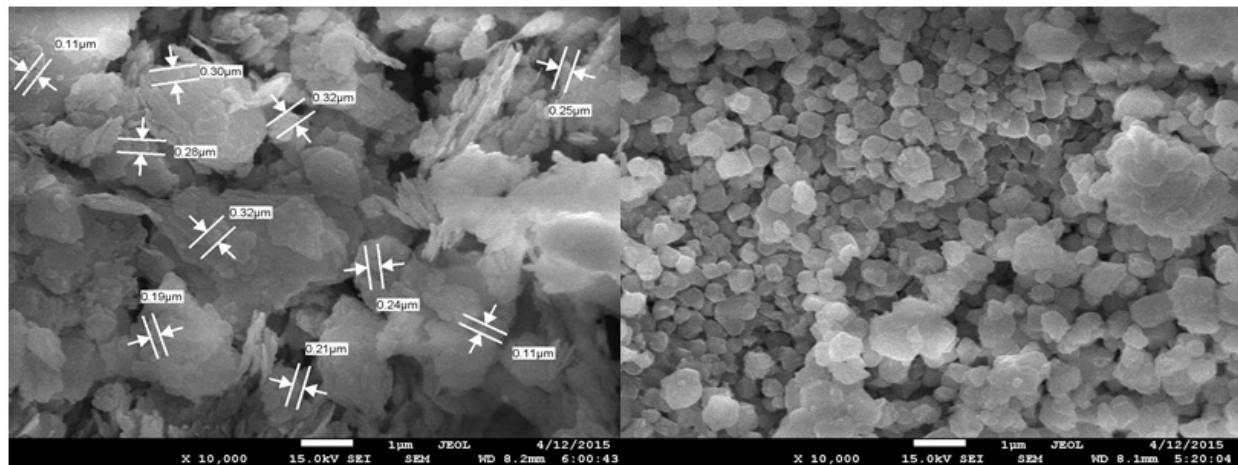


Figure-1. Particle size distribution of CBP.

Table-1. Chemical composition of CBP.

Formula	Concentration(%)
Orig-g	8
Added-g	2
CaO	49.80
P <sub>2</sub> O <sub>5</sub>	32.90
C	1.00
Na <sub>2</sub> O	0.96
SiO <sub>2</sub>	0.89
MgO	0.78
Al <sub>2</sub> O <sub>3</sub>	0.44
Cl	0.11
K	0<LLD
Fe	0<LLD
LOI	13.13

Table-2. Characteristics of the CBP and raw POME.

CBP		Raw POME	
Parameter	Value	Parameter	Value
Bulk density(g/ml)	0.81	pH	4.5
Solid density (g/ml)	3.24	Suspended solids (SS) mg/L	10,333.3
Porosity	73.9%	Oil and grease (mg/L)	2233.3
length(µm)	0.777	Ammonia Nitrogen (mg/L)	937
Roughness Ra(nm)	184.471	COD (mg/L)	53,374
		Manganese at pH 4.5	5.497
		Manganese at pH 7	4.783



### The Adsorbate

The raw POME samples were obtained at Kilang Sawit PPNJ Kahang, Kluang Johor, stored in a 30 L plastic container. The 30 L containing raw POME was transported and stored in the laboratory cold room according to the standard method for the preservation and storage of wastewater (APHA *et al.* 2005). Prior to the preservation and storage, characterization of the raw POME sample was achieved.

### Methods

The batch adsorption isotherm study were carried out in a 250 ml conical flask at 30°C containing 100 ml of the POME sample. The pH of the raw POME was adjusted using NaOH and H<sub>2</sub>SO<sub>4</sub> to pH 7 and the agitation of the mixture was performed at pre-determined period of 105 minutes contact time for each of the analysis at 200 rpm shaking speed. The adsorptive uptake of Mn<sup>2+</sup> onto CBP was achieved using different dosage of the CBP (5, 10, 15, 20, 25, 30) for the six 250 ml conical flasks. A replicate sample was prepared for each of the adsorbent dosage. After the end of the contact time, the conical flasks were removed and filtered. The filtered solution obtained using 0.45 µm glass fibre membrane was analysed using atomic absorption spectrometer (AAS), AAnalyst 800. The data are presented as averages of three measurements. A relative standard deviations (RSDs) of less than 5% was achieved for the samples and the replicates. The concentration of manganese adsorbed onto CBP was calculated as:

$$\% \text{ removed} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

C<sub>0</sub> = the initial liquid face concentration (mg/L)

C<sub>e</sub> = the equilibrium liquid-phase concentrations (mg/L)

V = the volume of the solution

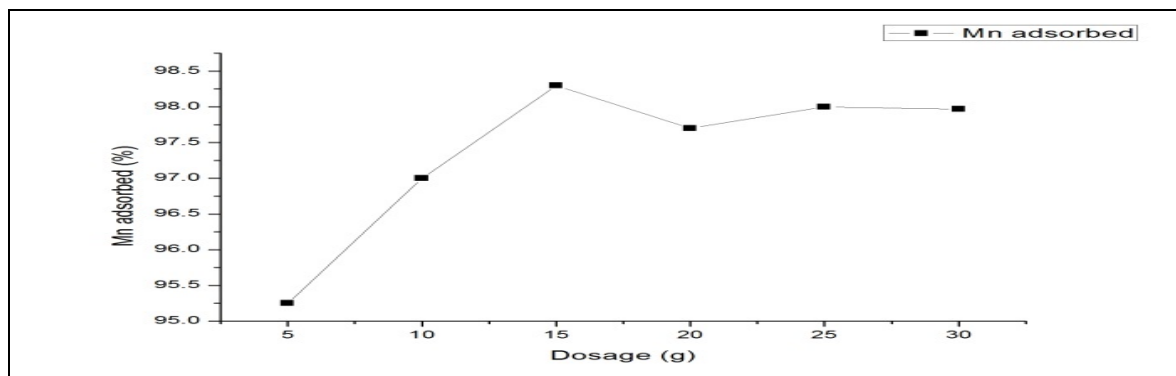
W = the weight of carbon used (g)

### RESULTS AND DISCUSSION

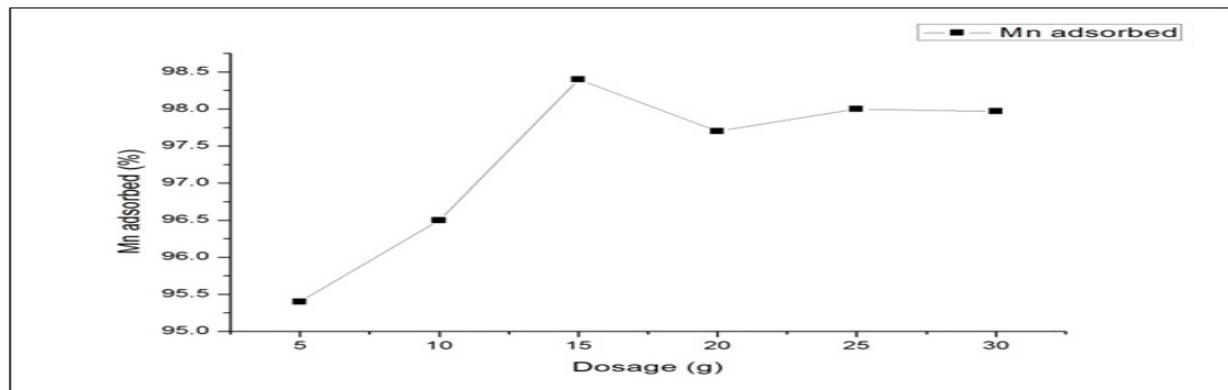
The effect of adsorbent mass in the removal of Mn<sup>2+</sup> onto CBP showed the adsorptive capacity of CBP for the removal of manganese from raw POME for the two

samples each prepared for the adsorption. The adsorptive uptake is illustrated in Figure-2. The results of the Analyst test for the adsorbent dosages showed effectiveness of the prepared activated carbon. It was observed that the percentage removal increase with increasing dosage of adsorbent until peak adsorption was obtained at adsorbent quantity of 15 g for both samples, immediately there was decrease in adsorption and almost constant adsorption was observed as the dosage increases. It can be observed that effective adsorption sites increase but decrease at further adsorbent dosage after adsorbent quantity of 15 g was used, 98.3% adsorption efficiency was achieved for sample 1 and 98.4% for sample 2. The manganese content at 5 g adsorbent dosage was reduced to 0.227 mg/L (95.3%) for sample 1 and 0.222 mg/L constituting 95.4% adsorption efficiency for sample 2.

These were the lowest rate of adsorption of the activated cow bone on manganese. The optimum dosage from the adsorbent of the sample and replicate efficiency was obtained at 15g dosage. The rate of adsorption was partly constant after the optimum dosage and decline at 30 g adsorbent dosage. All dosage used recorded more than 90 % adsorption efficiency. The high adsorption efficiency for each dosage is due to the availability of active sites and larger pore spaces of CBP particles which by implication means the internal structure is mainly macropores and mesopores. In the absence of micro pore spaces, there is readily available site for the manganese ions to react with the surfaces, internal and external sites. The active sites and the surfaces of CBP can best explain its effectiveness in the sorption of manganese. The pore spaces of CBP provides effective sites for ion exchange and sorption. The abundance of calcium ions has very high capacity for exchangeable ions, at a neutral pH, there is a very strong electrostatic attraction between the positively charged sites of CaO and the anionic composition of the POME. (Debnath, 2014), the presence of component of carbon surfaces contribute the process of sorption and the phosphate ions with hydroxyapatite lattice arrangement is capable of providing empty sites for the attraction of manganese ions which aids the sorption process.



Sample 1



Sample 2

**Figure-2.** Effect of adsorbent dosage on the removal of manganese from POME.

## CONCLUSIONS

The result of the treatment of manganese from raw POME using CBP shows that activated cow bone powder provides very active surfaces for the adsorption of manganese. The adsorption process is a function of the adsorbent media and the concentration of the adsorbate. The results showed that all the the adsorbent dosage used for the treatment achieved more than 95% removal efficiency of manganese with the optimum adsorption achieved at 15 g adsorbent dosage with average of 98.4% adsorption efficiency. Therefore CBP can be considered as a very effective media for the treatment of high strength wastewater containing manganese.

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