Removal of Zinc from Simulated Wastewater using Chitosan Coated Coconut Shell Charcoal

Sanusi S. N. A[1], Noh N[2], Bakri N. S[1], Mohd Redzuan N. N[1], Muhamad Faizul Tan F. A. T[1]

[1] *Faculty of Chemical Engineering, UiTM Pasir Gudang*

[2]*Faculty of Civil Engineering, UiTM Pasir Gudang*

Universiti Teknologi MARA, Johor Branch, Pasir Gudang Kampus, Jalan Purnama, Bandar Seri Alam, 81750, Masai, Johor Darul Ta'zim.

Abstract

An efficient adsorbent was prepared using coconut shell charcoal to remove zinc and the study was made. Modified coconut shell charcoal with coated of chitosan and/or oxidizing agent which is sulphuric acid are used as the adsorbent as the study was undertaken to produce a low cost yet effective biosorbent. The adsorption process was determined and the efficiency was evaluated by measuring the extent of adsorption of zinc in simulated wastewater. Each of the adsorbent was analyzed based on the percentage of removal efficiency, pH and adsorbent dosage. The result was characterized with inductively coupled plasma optical emission spectroscopy (ICP-OES). The maximum adsorption of Zinc (99.914%) was observed at 59.11 mg/L of $ZnCl_2$ and adsorbent dose of 5 g for chitosan acid treated coconut shell charcoal (CACSC). It is beneficial that the use of coconut shell and chitosan to produce activated carbon potentially leads to the production of a highly effective adsorbent generated from less expensive raw materials that are from renewable resources.

Keywords: Adsorption; Coconut shell; Chitosan-coated carbons; Simulated wastewater; Zinc

---

1. Introduction

Coconut palm tree is grown in more than 90 countries in an area of 14.231 million hectare with a total production in terms of copra equivalent of 11.04 million tons. Indonesia, the Philippines and India are among major coconut producing countries in the world. However, only coconut oil and its husk are used in production processes while coconut shells are being thrown. Coconut shell is one of the solid disposal that gives a serious problem for local environment as it represents more than 60% of the domestic waste volume (Alif Syazani et al., 2016). Therefore, coconut shell is used in certain production especially in adsorption process as it brings many advantages. The usage of coconut shell is much cheaper compared to other because it comes from agricultural waste. It can create a greener environment.

There are many natural materials for instant fibers, wood and limestone that are available in a large quantity that may have potential to be used as low cost adsorbents because of its unused resources and environmental friendly. Some researchers have reported synthesis novel TiO_2 and coconut shells powder with sufficient amount for the treatment of pharmaceutical and personal care products (Khraisheh et al., 2014). The sorption properties of coconut shell are due to the presence of some functional group contain in it such as carboxylic, hydroxyl and lactone which have the affinity for metal ions (Islam et al., 2017). The development of surface in recent years modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity. The use of coconut shell with surface modification can help to reduce the cost of waste disposal, provide a potential inexpensive alternative to existing commercial activated carbon and most importantly improve its metal removal performance (Amuda et al., 2007).

Chitosan has the highest sorption capacity for several metal ions compare to other low cost adsorbents. Chitin (2-acetamido-2-deoxy-ß-D-glucose-(N-accetylglucan)) is the main structural of molluscs, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps (Saifuddin & Palanisamy, 2005). While chitosan (2-acetamido-2-deoxy-ß-D-glucose-(N-accetyl glucosamine)) is partially deacetylated polymer of chitin and is usually prepared from chitin by deacetylation with a strong alkaline solution as shown in Figure 1. The researcher reported that chitosan can chelate five times greater amounts of metals compared to chitin. They further claimed that this property are due to the free amino groups contain in chitosan affect from the deacetylation of chitin. This material, chitosan, is slightly soluble at low pHs and sometimes possesses problems for developing commercial applications such as the active binding sites of chitosan are not readily available for sorption. It is an important role in process design in order to transport of metal contaminants to the binding sites. Therefore, to provide physical support and the increasing of the accessibility of the metal binding, it is necessary yet important for process applications.

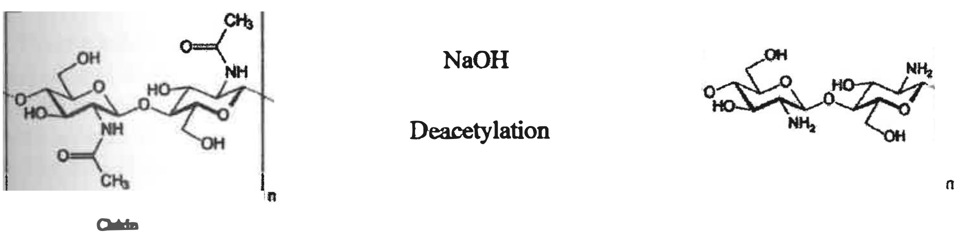

Figure.1 Conversion of chitin to chitosan by deacetylation.

This adsorbent will then use to treat heavy metal in wastewater that obtained from industrial. Heavy metal such as zinc is a classified chemical element which tremendously dangerous to the environment especially to the people. It contain toxicity and give bad effect not on to aquatic ecosystems, but also to human body such as the nervous system, gastrointestinal system, cardiovascular system, blood production, kidneys and reproductive system (Tran et al., 2017). The physical and chemical characteristics of heavy metal need to be treated with caution, as the metals involved are not always consistently defined. It tends to be less reactive than lighter metals, relatively dense as well as contain less soluble sulfides and hydroxide. Thus, it is essential to remove heavy metal that contain in the wastewater before it is transport and cycling to the natural environment. This treatment process of reassuring heavy metal from those industrial wastewater include precipitation, membrane filtration, ion exchange, adsorption and co-precipitation (Cristian et al., 2015). The important process usually used in removing heavy metal is adsorption.

The objective of this work were to coat the surface of coconut shell charcoal with chitosan and/or oxidizing such as sulfuric acid to measure the percentage removal of zinc in wastewater by varying the pH of solution and dosage of adsorbent using suitable parameters.

2. Methodology

2.1 Preparation of Simulated Wastewater

The stock solution for simulated wastewater (1000 mg/L) which is zinc chloride were prepared by dissolving 2.08 g of the respective powder in distilled water (1 L). The required solutions were prepared by diluting the stock solution with distilled water. The wastewaters were diluted until 59.11 ppm. The determination of zinc in sample were calculated using ICP-OES (PERKIN ELMER, PINAACLE 900T) (Al-Musharafi et al., 2013).

2.2 Preparation of chitosan gel.

A 25 g of chitosan was slowly added to 0.5 L of 20 wt% acetic acid (with constant stirring). The mixture was heated to 40-50 °C using hotplate stirrer. The chitosan was allowed to cool at room temperature to obtain the whitish viscous chitosan gel.

2.3 Preparation of Adsorbents

There are four adsorbents to be obtained from the experiments. The use of the adsorbents is to remove zinc. All the adsorbents used coconut shell charcoal as the main material. The first adsorbent, only used coconut shell charcoal. The second adsorbent, used coconut shell charcoal coating with chitosan only. The third adsorbent, used acid-treated coconut shell charcoal only. The fourth adsorbent, used acid- treated coconut shell charcoal coating with chitosan. The overall process is shown in Figure 2.

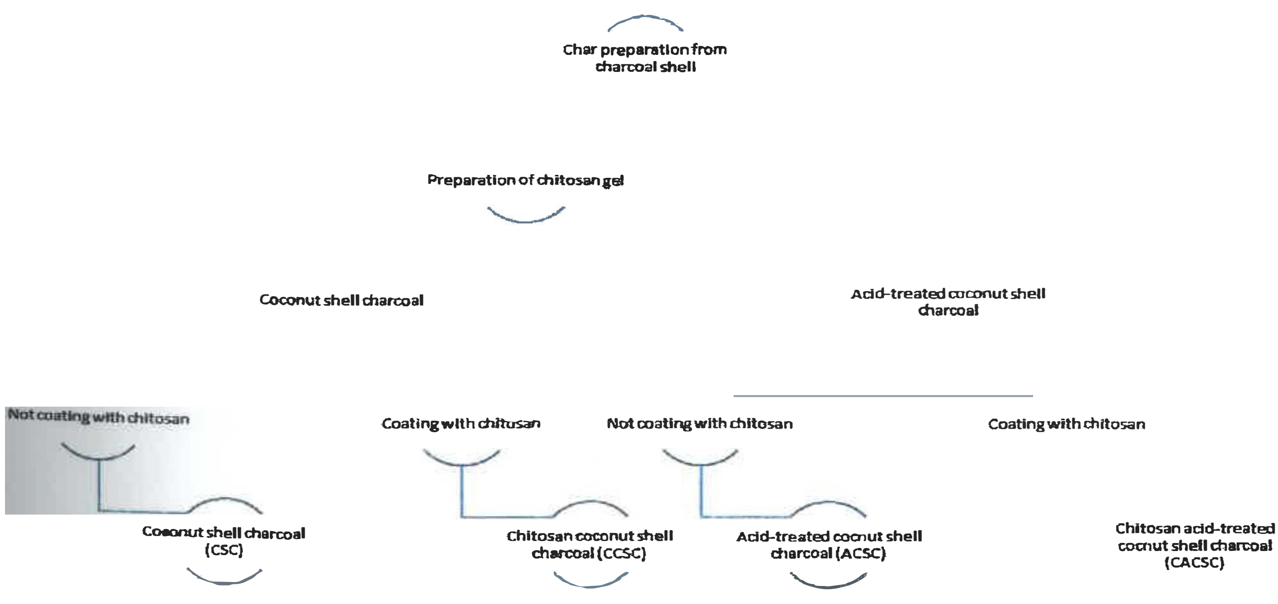

Figure.2 The process flow of adsorbents used in the experiments.

2.3.1 Preparation of charcoal from coconut shell.

Coconut shell was obtained at local stall in Bandar Seri Alam area. Preparation of char from coconut shell was carried as previously described with slightly adaptation based on Figure 2.1 below (Babel & Kurniawan, 2004) The coconut shell was first dried at the open space in UiTM Pasir Gudang for 24 hours to reduce the excess water in the coconut shell. Then, the coconut shell is being separated from the husk. The dried shell was place at the crucible and burn at 500 ℃ for 20 min using muffle furnace (NUVE, MF 106). The weight loss of the sample was determined by the difference in the weight of the sample before and after calcination. The calcination sample was crushed and sieved into the range of 0.5 to 1mm size particles using a sieve. The total weight powder formed is about 1000 g.

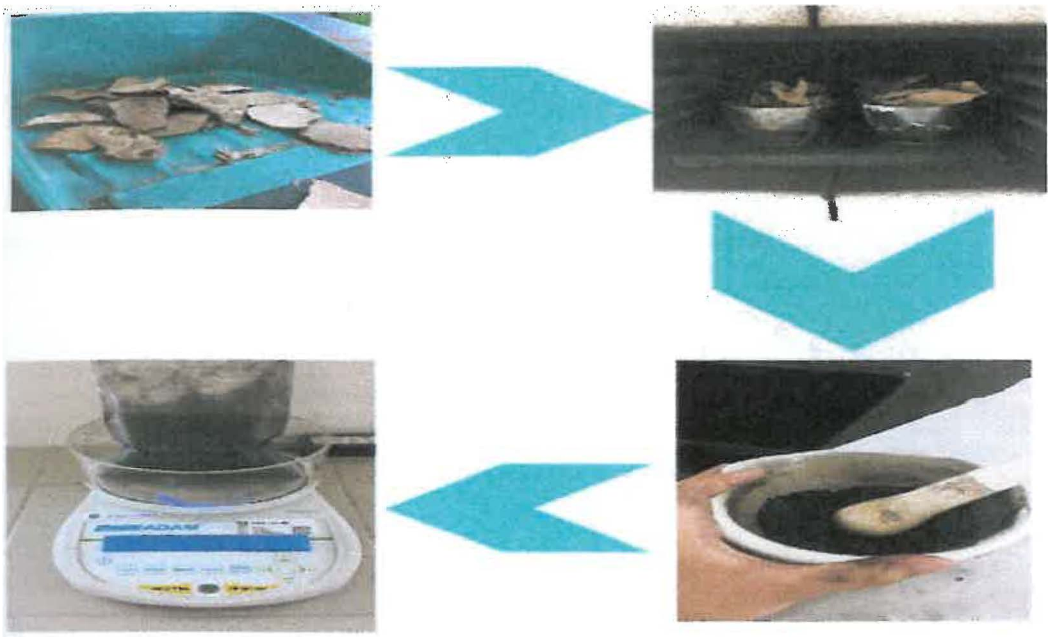

Figure. 2.1 The char preparation from coconut shell.

2.3.2 Preparation of acid-treated coconut shell charcoal (ACSC).

The coconut shell charcoal was washed with deionized water until any leachable impurities due to free acid and adherent powder were removed. The sample were then treated with 1% of sulphuric acid, H_2SO_4 (v/v) in an incubator at 110 ℃ for 24 hours and soaked with deionized water again until the pH value of the solution is 3-4. Then, the adsorbent was soaked in 1% of sodium bicarbonate, $NaHCO_3$ (w/v) until any residual acid left was removed. Finally, the samples (acid-treated coconut shell charcoal) were dried overnight in an oven at 110 ℃, cooled at room temperature, and stored in a desiccator for further use (Amuda et al., 2007).

2.3.3 Surface modification of acid-treated coconut shell charcoal (ACSC) and coconut shell charcoal (CSC) with chitosan.

ACSC and CSC (250g) was slowly added to dilute chitosan gel (chitosan gel-water, v/v heated to 50℃) and mixing was carried out at 150rpm for 24 hours, respectively. The chitosan coated ACSC (CACSC) was then washed with deionized water and dried at 102°C for 2 hours before use (Saifuddin & Palanisamy, 2005).

The CACSC and CCSC were then soaked in 0.25% NaOH solution until any residual acid was removed. These rinsed extensively with deionized water and dried in an oven at 102°C for 2 hours, cooled at room temperature and stored in desiccators.

2.4 Determination of zinc removal efficiency.

The experiment were conduct at ambient temperature using the optimum conditions of factors that influence adsorption such as pH of wastewater (pH value of 7) and adsorbent dosage (5 g, 10 g, 15g, 20 g) (Amuda et al., 2007). Simulated wastewater (50 mL) containing zinc was placed in a 250 mL Erlenmeyer flask and 5 g adsorbent was added. The mixture was mechanically agitated at 200 rpm on reciprocate shaker. The same process was applied by different dosage which is 10 g, 15 g and 20 g. The zinc concentration of the treated wastewater was analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Amuda et al., 2007).

The removal efficiency (E) of adsorbent on zinc was calculated by using Equation (1)

$$E\,(\%) = \frac{C_f - C_i}{C_i} \times 100 \quad \text{.......... Equation (1).}$$

where C_i and C_f are initial and final equilibrium concentration of zinc (mg/L) in wastewater.

2.5 Determination of pH.

A 50 mL of 0.01 M NaCl solution was placed in a closed Erlenmeyer flask. The pH was adjusted to a value of 3, 5, 7 and 9 by adding HCl 0.1 M or NaOH 0.1 M solutions. Then, 0.15 g of CSC sample were added into the solution and the final pH measured after 21 hours under agitation at room temperature. The pH for each sample were then measured using pH meter.

3. Results and Discussions.

3.1 Effects of different adsorbents dosage (g)

Zinc chloride was used as the source of zinc in the simulated wastewater. The simulated wastewater have a concentration of 59.11 ppm. To investigate the highest zinc removal by the adsorbent, batch experiments were conducted by varied the dose of the adsorbents which between 5 g, 10 g, 15 g and 20 g. The agitation time at 3 hours, the agitation speed at 200rpm and the temperature at 25°C were kept constant (Saifuddin M & Kumaran, 2005).