Efficiency of zinc ions (II) adsorption using activated carbon from palm kernel shell

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Abstract. The adsorption of wastewater from various industrial sources is important and one of the dangerous challenges the environment. This study focuses on the investigation of the efficiency of zinc ions adsorption by using activated carbon in synthetic wastewater. Activated carbon was prepared from palm kernel shells that were obtained from Songkhla province, Thailand. Activated carbon was prepared from palm kernel shells containing sodium chloride as a catalyst at the ratio 1:0, 1:1 and 1:2 (w/w), respectively. Activated carbon was calcined at 700 °C for 2 h. Next, it was washed with hot distillate water until pH = 7. After that, it was dried at 105 °C for 24 h. Iodine number was analyzed by using CHNS/O analyzer. The concentration of solution was examined by using atomic absorption spectrophotometer (AAS). The prepared activated carbon was characterized by thermogravimetric analysis (TGA), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), X-ray fluorescence spectrophotometer (XRF), X-ray diffractometry (XRD) and Fourier-transform infrared spectroscopy (FTIR). For the pure activated carbon, it was noteworthy that the major components were O (37.25%), N (30.95%) and C (26.54%), whilst a minor content was H (2.23%), C (1.73%) and Si (0.76%). This result was strongly consistent with the XRF analysis. The ratio of activated carbon to sodium chloride 1:2 (w/w) exhibited the highest iodine number (180.95±10.82 mg/g). The factors of adsorption including initial concentration (20-150 ppm) and adsorption time (2-10 h.) The result showed that the optimum conditions of adsorption containing concentration were 65 ppm and adsorption time was 10 h. The efficiency of adsorption was 69.73 %.

Keywords: Activated carbon, Adsorption, Palm kernel shell, Zinc ions

1. Introduction
Heavy metal cations such as Cu^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} are common metals found in many industrial wastewaters [1]. Activated carbon (AC) is the most widely used adsorbent for metals removal due to
Its high surface areas resulted from porosity, size of pores larger than adsorbate molecules. Conventionally, AC is synthesized using agricultural wastes, such as coconut shell, rice husk, almond shell, cashew nut shell, tomato, and palm kernel shell (PKS) [2–6]. The potential of using PKS which are cheaper and easily available to produce AC, it can change lignocellulose to carbon become an interesting material for adsorbents. The purpose of this research study was to develop AC from PKS in preliminary test for zinc (II) ion removal from synthesis wastewater. The effect of the amount of sodium chloride loading on AC preparation, zinc concentration and contact time on AC adsorption was studied. In addition, the AC were characterized by TGA, SEM-EDS, XRF, XRD and FTIR.

2. Experimental
2.1. Materials
AC was prepared from PKS that were obtained from Songkhla province, Thailand. The sodium chloride (NaCl; Merck) was used as chemical activation. The analytical reagent grade zinc nitrate (Zn(NO₃)₂; Merck) was used as stock zinc solution for all experimental studied.

2.2. Preparation of adsorbent
PKS were collected thoroughly washed with distilled water to remove the adsorbed organic leftover materials and impurities. The PKS were dried in an oven at 105 °C for 24 h. Subsequently, the dried PSK were ground into powdered to obtain size of smaller than 90 µm. The PKS were pyrolyzed into biochar. The AC were prepared through the chemical activation by using biochar mixed with sodium chloride at the ratio 1:0, 1:1 and 1:2 (w/w), respectively. In the typical process, to prepare AC 1:1 (w/w) sodium chloride loaded, 1 g of sodium chloride was added with distillate water, followed by the addition of 1 g of dried biochar. The mixture was stirred at 500 rpm for 3 h. Then, the mixture was dried overnight followed by calcination at 700 °C for 2 h. The mixture was washed with warm deionize water and dried at 105 °C overnight and then stored in a desiccator for further experimentation.

2.3. Adsorbent characterization
Iodine number of AC was analyzed by using CHNS/O analyser. The thermal decomposition of the AC, as obtained from PKS, and the AC 1:0 was determined by TGA using a Perkin-Elmer TGA7 thermal gravimetric analyzer. 20.60 mg of AC was placed in an aluminium pan and heated under nitrogen (N2) atmosphere from 50 °C to 1000 °C at a heating rate 20 °C/min. The surface morphology of the AC 1:0, AC 1:1 and AC 1:2 were investigated by using SEM-EDS analysis (Oxford Aztec model) at 10,000x magnification with an accelerating voltage of 10.0 kV. The actual surface elemental composition of AC was evaluated by XRF analysis using a Philips, power 2400 model. The chemical functional groups of the activated carbon were characterized by FT-IR analysis using a Thermo Nicolet Nexus 670 FTIR spectrometer. The solid sample and potassium bromide powder were placed on the monolithic diamond crystal plate and the spectrum was collected on a Perkin-Elmer spectrometer. The IR spectrum was operated at frequency range of 4000–400 cm⁻¹. The composition of the crystalline phases of the AC 1:0, AC 1:1 and AC 1:2 were evaluated by XRD. Samples were run in a continuous scan mode at a 2θ range of 10 – 90°. The iodine numbers were also determined for all AC.

2.4. Adsorption experiments
Different zinc concentration (20–150 ppm) in aqueous solutions is prepared by dissolving zinc nitrate in distillate water. The actual initial and final zinc (II) ion concentration was determined using atomic absorption spectrometer (AAS), Varian Model SpectraAA 30 equipped with a GTA 110 graphite furnace, a deuterium lamp as background correction system was used. The concentration of gas-phase atoms was measured by absorption light of atomic absorption spectrometer (AAS). 50 mL of zinc aqueous solution of known actual concentration and AC dose were taken in 100 ml of reagent bottom and the solution mixture was agitated in the shaker at 220 rpm. The effects of contact time in the range of 2–10 h, initial concentration of zinc solution in the range of 20–150 ppm were studied in batch
process at room temperature condition. The spent AC was filtered after the completely processes by using filter paper. The percentage removals of zinc (II) ion were calculated by the following equation
\[
\% \text{ removal} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100
\]
Where \(C_0\) and \(C_e\) are the initial and equilibrium Zn(II) ion concentration (mg/L) respectively.

3. Results and discussion
3.1. Characterization of AC
3.1.1. TGA analysis. Fig. 1 is shown the thermal decomposition of the AC 1:0, showing its decomposition behaviour in the form of a TGA thermogram over a heating range of 50–1000 °C. A total mass loss of 95.10% was detected in two stages. The first weight loss step accounted in the temperature range between 200–350 °C and was corresponds to the evaporation of free moisture, whilst the second weight loss step accounted in the temperature range between 350–710 °C and corresponded to the decomposition of lignin, cellulose and hemicellulose and the organic matter [3]. After 710 °C no weight loss observed.

3.1.2. XRD analysis. Powder XRD profiles of the AC are illustrated in Fig. 2. The AC patterns exhibited peak at a 2θ of 10°–30° and 40°–50° that corresponded to the amorphous carbon (0 0 2) and C (1 0 1) that’s contains of aromatic carbon sheets [7].

![Figure 1. Representative TGA profile of the AC 1:0.](image1.png)

![Figure 2. Representative XRD patterns of the AC 1:0, AC 1:1 and AC 1:2 phase.](image2.png)

3.1.3. FTIR analysis. The FT-IR patterns of the AC over the range of 650–4000 cm\(^{-1}\) is shown in Fig. 3. The peak in the region between 3000 and 3500 cm\(^{-1}\) corresponded to the OH bonding peak, which
was attributed to the absorption of water on the AC surface. The spectrum peak at 1713 cm\(^{-1}\) was assigned to the asymmetric stretching of the C=O group. The asymmetric stretching of the C=C and C=\text{-}C aromatics bonds was clearly exhibited near 1647 cm\(^{-1}\) corresponded to the asymmetric carboxylate stretch [3].

Figure 3. Representative FTIR spectrum of the (a) AC 1:0 (b) AC 1:1 and (c) AC 1:2.

3.1.4. SEM-EDS and XRF analysis. The morphologies of the AC were determined by SEM analysis (Fig. 4), revealed that the AC:1:0 had a porous surface, but after activation with sodium chloride a highly smooth textured was detected. The elemental composition of the AC was evaluated by SEM-EDS and XRF, with the quantitative results summarized in Table 1 and Table 2, respectively. Three typical points were chosen to examine the element analysis. It is evident that the AC 1:0 mainly consisted of carbon (C) and oxygen (O), with the C element ranged from 78.84 wt.% to 79.65 wt.% and O element ranged from 20.35 wt.% to 21.16 wt.%. After different sodium chloride was activated on AC, the element was changed.

Table 1. EDS analysis of the surface of the AC 1:0, AC 1:1 and AC 1:2.

| Image | Text point | C     | O     | Na      | Cl      | Other |
|-------|------------|-------|-------|---------|---------|-------|
| Fig. 2a | A          | 78.84 | 21.16 | -       | -       | -     |
|       | B          | 79.08 | 20.92 | -       | -       | -     |
|       | C          | 79.65 | 20.35 | -       | -       | -     |
| Fig. 2b | A          | 20.30 | 34.74 | 9.39    | 12.45   | 23.12 |
|       | B          | 20.01 | 34.82 | 9.56    | 12.24   | 23.37 |
|       | C          | 19.97 | 34.78 | 8.57    | 12.36   | 24.32 |
| Fig. 2c | A          | 77.40 | 13.89 | 3.02    | 2.49    | 3.20  |
|       | B          | 77.32 | 13.78 | 3.11    | 2.44    | 3.35  |
|       | C          | 77.73 | 13.55 | 3.03    | 2.57    | 3.12  |

Table 2. Elemental composition of the AC 1:0.

| Element | Concentration, % | Element | Concentration, % |
|---------|------------------|---------|------------------|
| O       | 37.25            | K       | 0.14             |
| N       | 30.95            | Al      | 0.10             |
| C       | 26.54            | Mg      | 0.10             |
| H       | 2.23             | Fe      | 0.07             |
| Ca      | 1.73             | P       | 0.04             |
| Si      | 0.76             | Na      | 0.03             |
3.1.5. Iodine number. The adsorption capacity of activated carbons was determined by iodine number. It can be seen from Table 3 that iodine adsorption of AC prepared with sodium chloride and activation at 700 °C. The iodine number of AC1:0 prepared with activation temperature of 700 °C is lower than that of AC prepared with different impregnation sodium chloride at the ratio 1:1 and 1:2 (w/w). The iodine number at the activation temperature of 700 °C was highest for AC1:2. This is attributed to more extensive reaction between NaCl and surface AC. Therefore, AC1:2 were considered for further study.

Table 3. Iodine number of adsorbent.

| Activated carbon (w/w) | Iodine number (mg/g) |
|------------------------|----------------------|
| 1:0                    | 85.82±1.13           |
| 1:1                    | 134.48±7.17          |
| 1:2                    | 180.95±10.82         |

3.2 Zn (II) adsorption
Table 4 shows the effect of initial Zn (II) concentration (20–150 ppm) of AC1:2 on the 2 h of contact time and adsorbent dosage of 0.5 g. The actual concentration was measured by AAS technique. Zn (II) adsorption capacity of PKS based AC increased from 38.42% to 40.26% with increased zinc concentration from 20 ppm to 150 ppm. This result can be attributed to the higher initial Zn (II) concentration providing a higher driving force to overcome mass transfer resistance on the adsorbent phase through the use of high concentration of zinc solution. After that, Zn (II) adsorption gradually decreased. Therefore, 65 ppm of zinc concentration was selected for further study.
The relation between contact time and %adsorption is shown in Figure 5. In this experiment, the Zn (II) solution is 65 ppm, adsorbent dosage of 0.5 g, and agitation in the shaker at 220 rpm. Zn (II) adsorption increased (40.26–69.73%) with 2–10 h of contact time.

Table 4. Effect of initial zinc concentration with range of 20–150 ppm on AC adsorption (AC 1:2, 2 h of contact time, agitation in the shaker at 220 rpm)

| Expected zinc concentration (ppm) | Actual zinc concentration (ppm)* | Actual zinc concentration after adsorbed (ppm)* | % Adsorption |
|----------------------------------|--------------------------------|-----------------------------------------------|-------------|
| 20                               | 19.65                         | 12.10                                         | 38.42       |
| 65                               | 67.18                         | 40.13                                         | 40.26       |
| 150                              | 149.15                        | 97.42                                         | 34.68       |

* Concentration, measured by atomic absorption spectrometer (AAS).

Figure 5. Effect of contact time on AC adsorption (AC 1:2, 65 ppm of initial zinc concentration, agitation in the shaker at 220 rpm)

4. Conclusions
PKS could be used for AC preparation. The adsorption of AC prepared by carbonization at 700 °C and impregnation of sodium chloride at the ratio 1:0, 1:1 and 1:2 (w/w), respectively. It is an alternative adsorbent for the removal of Zn (II) from synthesis wastewater based on its high removal capacity of zinc. The best condition for the Zn (II) adsorption process is the 65 ppm of initial zinc concentration, 10 h of contact time, and 0.5 g of AC dosage. Under these conditions, the maximum percentage Zn (II) removal of 69.73% was obtained.

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