Corn cob based activated carbon preparation using microwave assisted potassium hydroxide activation for sea water purification

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Abstract. Corn cob based activated carbons have been made through processes of pre-carbonization and microwave assisted chemical activation. In this study, potassium hydroxides (KOH) are used as an activating agent, which by 5% potassium hydroxides in weight of self-adhesive carbon grain of corn cob are soaked in 150 ml distilled water. Samples are then irradiated using microwave with power of 360, 450, and 720 watt for 15 minutes. The activated carbons are applied for water purification of sea water. Physical and chemical properties of the activated carbon are characterized, including microstructure, surface morphology, heavy metal adsorptions, and pH, temperature and colour of sea water. Analysis of microstructure show that the activated carbons have amorphous structure marked by two ramp peaks at the 2θ around of 22 and 44°, respectively. The morphological surface shows that AC720 has more porous rather than AC360, and AC450. The porous activated carbon of AC720 has the highest heavy metal adsorption of 85.20%, 89.80%, and 70.41% for Ni, Pb, and Zn, respectively corresponding to colour level of 126 PtCo, salinity of 25.6% and pH of 7.41.

Keywords: Corn cob, microwave irradiation, activated carbon, physical properties, heavy metal adsorption.

1. Introduction
Indonesia approximately has 17,504 large and small islands with a coastline of 95,151 km. Because of archipelago territory, many people live in the coastal areas having difficulty of clean water for their daily needs. Efforts to find clean water in coastal areas are by utilizing sea water instead. The sea water must be treated before being utilized.

Water treatment methods have been developed by researchers both physically (filtration, sedimentation and adsorption), chemistry (coagulation and aeration), or microbiologically. The adsorption process is a physical water treatment method that has been developed. Adsorption is a process of absorbing impurities in water, hence the water turn out to be clean. Substances are used in the adsorption process namely adsorbents. Activated carbon is one of the most widely used as adsorbents. Activated carbon is very suitable to be used as an adsorbent because it has a large specific surface area, good pore size distribution so that activated carbon is widely applied to control air pollution and water purification [1].
The use of natural ingredients or biomass from agricultural waste is very effective to be used as a raw material of activated carbon production. The usage of biomass from agricultural and industrial waste as an adsorbent has low cost and environment friendly. The biomass has been proven to be precursors material for activated carbon production, including green coke [2] and lingocellulose-containing materials such as rubber wood [3], almond shell [4], tobacco [5], argan shell (*Argania spinosa*) [6], oil palm empty fruit bunches [7,8], pineapple peel [9] and Terminalia catappa fruit shells [10].

Corn (*Zea mays*) is one of the staple foods of carbohydrate source substitute for rice. The need for corn which has recently increased which causes environmental problems because merely the seeds are used as food and industrial raw materials while corn cobs and cornstalk waste are discarded and burned. The effort of the corn waste is by applying the corn cobs waste as economic material for making activated carbon.

The structural component content of corn cob i.e. cellulose (41%), hemicellulose (36%) and lignin (6%) indicating corn cob is potentially and effectively used as a precursor for activated carbon production, besides that the ash content contained in corn cobs is also quite low at 1.50% [11]. The carbon content of corn cobs is 80.50% and low of ash content is also an advantage of corn cobs from the other biomass for activated carbon production because of the greater carbon content compared to the ash content.

Activated carbon is indentified as surface area increment and high absorb impurities. Water treatment using activated carbon is more economical because it is made from natural ingredients or biomass. Chemical activation is used 5% KOH as an activation agent and heated by microwave irradiation with various output power of 360 watts, 450 watts, and 720 watts. Thus, the aims of the present study are to determine the effect of variations of microwave irradiation power on microstructure, surface morphology, surface area, and absorption capacity of activated carbon on heavy metals as well as physical and chemical properties of seawater such as color, pH, temperature and salinity.

2. Materials and Methods
The activated carbons are specifically prepared from corn cob using KOH as an activation agent in chemical activation. The pre-carbonization, chemical activation and microwave irradiation are three main processes in activated carbon production. The initial process of activated carbon production is cleaning the corn cobs from sticking dirt and then cut it 5 mm pieces. The pieces of corn cob are pre-carbonized at 200°C for 4 hours in an electric oven. The pre-carbonized of corn cob are then mashed using mortal and sieved to obtain the self-adhesive carbon grain (sacg) with grain size fewer than 100 Mesh. The chemical activation is processed using KOH to the tune of 5% of the mass of the sacg in 150 ml distilled water. The slurry is stirred at 400 rpm for 25 hours at room temperature. The samples are then irradiated using microwave for 15 minutes at various output power of 360 Watt, 450 Watt, and 720 Watt. The activated carbon obtained is washed for several times using distilled water. After the pH of solution reaches neutral, the activated carbon is dried at the temperature of 105°C for 24 hours.

The physical properties of activated carbon, i.e. microstructure, surface morphology and element content are characterized using X-ray diffraction, scanning electron microscopy and energy dispersive X-ray, respectively. Color level, salinity and pH of sea water after treatment using activated carbon are determined using spectrophotometer, salinometer and pH meter, respectively. The adsorption of heavy metal (specifically Pb, Zn and Ni) from sea water treated by activated carbon is conducted using atomic absorption spectroscopy.

3. Results and Discussion
The resulting X-ray diffraction pattern confirms that all of activated carbons have amorphous structure which is indicated by the presence of plane (002) and (100) at 2θ angles around 21° and 43° as shown in Figure 1. The XRD peak plane of (002) and (100) is shifted to higher of the angle 20 which cause
interlayer spacing decreased with increasing of output power of microwave. The shifted of peak plane of (002) and (100) are caused by rearrangement of carbon atom to the actual position in the activated carbon structure.

![X-ray diffraction pattern for AC360, AC450 and AC720](image)

Figure 1. X-ray diffraction pattern for AC360, AC450 and AC720

The interlayer spacing ($d_{002}$ and $d_{100}$) and microcrystalline dimension (stack height, $L_c$ and stack diameter, $L_a$) are calculated from X-ray diffraction data using Bragg equation and Scherer equation, respectively. Numbers of layers ($N_p$) are calculated by the ratio of $L_c/d_{002}$. In the calculation of interlayer spacing and microcrystalline dimension, the XRD data is firstly fitted using Microcal origin. Table 1 shows the data of interlayer spacing and microcrystalline dimension after irradiating with microwave at output power of 360 Watt, 450 Watt and 720 Watt. It is well known that the broader peak resulted in smaller microcrystallite size [12].

| Sample | 2θ (002) | 2θ (100) | $d_{002}$ | $d_{100}$ | $L_c$ | $L_a$ | $N_p$ |
|--------|----------|----------|-----------|-----------|-------|-------|------|
| AC360  | 22,118   | 43,143   | 4.014     | 2.094     | 6.459 | 25.907| 1,609|
| AC450  | 22,682   | 44,808   | 3.915     | 2.020     | 6.675 | 23.538| 1,705|
| AC720  | 22,981   | 44,875   | 3.865     | 2.017     | 6.959 | 22.926| 1,801|

Table 1 shows the $L_c$ of AC720 is higher than of $L_c$ of AC360 and AC450 that is equal to 6.959 Å. The higher in $L_c$ shows that surface area of activated carbon is higher and pores of activated carbon increased [13][14]. Interlayer spacing of activated carbon does not significantly affect to the output power of microwave irradiation. The change in output power of microwave irradiation has effect it to the microcrystalline dimension of activated carbon, on contrary to the microstructure which is slightly change.

Figure 2 shows the surface morphology of activated carbon prepared from corn cob with different of output power of microwave irradiation. The surface morphology of the AC360 (Figure 2(a)) shows that the pores produced are hardly and covered by impurities. The increment in output power of microwave irradiation cause the diameter pores becomes wider and the pore becomes wide opened as well shown seen in Figure 2(a) and 2(b) for AC450 and AC720 respectively. The more pores fashioned cause the higher the surface area of activated carbon. Overall, the pores produced on activated carbon with various output power of microwave irradiation are macropores, while micro and mesopores are not visible because of limited magnification.
Energy dispersive X-ray (EDS) analyzed shows the presence of elements of carbon, oxygen and potassium. The oxygen content and non-carbon materials are decreased with increasing of the output power of microwave irradiation. The higher in output power of microwave irradiation affects the temperature of activated carbon increased which causes oxygen and other non-carbon material evaporate and the carbon content increased as shown in Table 2.

### Table 2. Elemental composition of activated carbon

| Sample | Carbon (wt%) | Oxygen (wt%) | Potassium (wt%) |
|--------|--------------|--------------|-----------------|
| AC360  | 75.19        | 24.28        | 0.53            |
| AC450  | 70.07        | 26.05        | 3.89            |
| AC720  | 78.46        | 20.20        | 1.34            |

The sea water is taken from shore of Dumai, Indonesia. Initial concentration of heavy metals in sea water is found 1.250 ppm, 1.530 ppm and 0.551 ppm for Ni, Pb and Zn respectively. The high chemical content of heavy metals found in Dumai sea water is caused by the human and industries activities such as petroleum refining, oil palm refining, dockyard, port and ship activities and household waste. The amount of adsorption of activated carbon from corn cob on Ni, Pb and Zn heavy metals are listed in Table 3.

### Table 3. Absorbability of activated carbon on heavy metal in sea water of Dumai

| Sample | Heavy metal | Initial concentration (ppm) | Final concentration (ppm) | Removal percentage (%) |
|--------|-------------|-----------------------------|---------------------------|------------------------|
| AC360  | Ni          | 1.250                       | 0.264                     | 78.88                  |
| AC450  | Ni          | 1.250                       | 0.286                     | 77.12                  |
| AC720  | Ni          | 1.250                       | 0.185                     | 85.20                  |
| AC360  | Pb          | 1.530                       | 0.206                     | 86.53                  |
| AC450  | Pb          | 1.530                       | 0.186                     | 87.84                  |
| AC720  | Pb          | 1.530                       | 0.156                     | 89.90                  |
| AC360  | Zn          | 0.551                       | 0.189                     | 65.69                  |
| AC450  | Zn          | 0.551                       | 0.142                     | 74.22                  |
| AC720  | Zn          | 0.551                       | 0.153                     | 70.41                  |

The percentages of heavy metal removed by activated carbons are not significant for any changes in output power of microwave irradiation. The absorbability data as listed in Table 4 shows the AC720 has a highest adsorbed as predicted by the Lc and SEM image. The increasing in output power of microwave irradiation is produced when the temperature increase. The temperature increased generates the growth of pores, pores become wider and pores cavity opened, and resulted higher surface area.
Figure 3 shows the color of Dumai sea water before and after purification process using activated carbon. Figure 3(a) confirm that the sea water is cloudy and yellowish, on contrary in Figure 3(b), (c) and (d), the sea water becomes clearer after purification process, which is purity of sea water treated by AC720 is clearer than sea water treated by AC360 and AC450 which indicates the output power of microwave irradiation affects to purification process and heavy metal absorbability. The purity level of sea water is not enough to state that the sea water clear or cloudy sight and more convincing, the purity level of sea water are tested using Spectro Hach. The clarity level of untreated sea water is 147 PtCo and the purity of the treated sea water is shown in Figure 4. The treated sea water by AC720 has a lower purity level i.e. 126 PtC0 than treated by AC360 and AC450.

![Figure 3. Purity of sea water (a) before purified, (b) purified by AC360 (c) AC450 and (d) AC720](image)

The pH of Dumai sea water is measured using pH meter. The untreated of sea water is 7.62 indicates alkaline. The treated sea water by AC360 and AC450 has a similar pH level of 7.42 and 7.41 for treated sea water by AC720.

![Figure 4. Color Test of Seawater After Activated Carbon](image)

The chemical compound of salinity based on total salts concentration are fresh water (< 0.5‰), brackish (0.5‰ - 30‰), saline (30‰ – 50‰) and brine (> 40‰). The salinity of purified sea water by AC360, AC450 and AC720 are not significantly different. The treatment of Dumai sea water using activated carbon does not affect to the salinity. The salinity of unpurified Dumai sea water is 25.7‰ and the salinity of purified sea water by AC360, AC450 and AC720 are 25.7‰, 25.7‰, and 25.6‰ respectively.

4. Conclusion
The X-ray diffraction pattern of all activated carbon prepared from corn cob shows an amorphous structure which is marked by two broader peaks at 20 around 21° and 44° corresponding to plane (002) and (100), respectively. Dumai sea water is treated by AC720 having a better chemical properties than by AC360 and AC450, with higher adsorption to the heavy metal (Ni 85.20%, Pb
89.80 and Zn 70.41), lower color level of 126 PtCo, pH at 7.41 and salinity of 25.6‰. The best condition of AC720 was associated to higher stack height $L_c$ and lower stack diameter $L_a$.

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