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UTILIZATION OF COAL ACTIVATED CARBON AS ADSORBENT AMMONIUM WITH THE HIGH CONCENTRATION

PERCOBAAN PEMANFAATAN KARBON AKTIF BATUBARA SEBAGAI PENYERAP AMONIUM DENGAN KADAR TINGGI

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ABSTRACT

Ammonium adsorption process carried out by batch system, with making 208-233 mg/L concentration of ammonium solution. In the adsorption batch systems, particle size of activated carbon -8 + 12 mesh and -16 + 20 mesh was added into 200 ml ammonium solution with the weight of 20, 40, 60 and 80 g, and a contact time respectively 30, 60, 120, 180 and 1440 minutes (24 hours). During the adsorption, stirring to optimize adsorption is conducted regularly. The activated carbon used in this research consist of two types are coal based activated carbon and coconut shell activated carbon. Coal activated carbon has a surface area 196.7 m^2/g and 643.0 m^2/g. While coconut shell activated carbon has a surface area of 59.6 m^2/g and 985.9 m^2/g. Results of the adsorption process showed that coal activated carbon with a surface area of 643, 0 m2/g have the same capability ammonium adsorption with coconut shell activated carbon with a surface area of 985.9 m2/g. These results showed that a both types of activated carbon can be used optimally for the removal ammonium with percentage of adsorption reaches more than 90%.

Keywords: activated carbon, ammonium, adsorption

ABSTRAK

Penurunan kadar amonium dengan cara adsopsi oleh karbon aktif batubara dilakukan dengan sistim batch, dengan membuat larutan amonium yang berkadar 208-233 mg/L. Pada adsorpsi sistim batch, karbon aktif yang berukuran -8+12 mesh dan -16+20 mesh ditambahkan ke dalam 200 ml larutan amonium dengan berat 20, 40, 60 dan 80 g, dengan waktu kontak masing-masing 30, 60, 120, 180 dan 1440 menit (24 jam). Selama adsorpsi berlangsung, dilakukan pengadukan secara berkala untuk mengoptimalkan penyerapan. Karbon aktif yang digunakan dalam penelitian ini terdiri atas dua jenis yaitu karbon aktif yang terbuat dari batubara dan karbon aktif yang terbuat dari tempurung kelapa sebagai pembanding. Karbon aktif batubara memiliki luas permukaan196,7 m^2/g dan 643, 0 m^2/g. Sedangkan karbon aktif tempurung kelapa memiliki luas permukaan 59,6 m^2/g dan 985,9 m2/g. Hasil proses adsorpsi menunjukkan bahwa karbon aktif batubara dengan luas permukaan 643,0 m2/g memiliki kemampuan adsorpsi amonium yang sama dengan karbon aktif tempurung kelapa dengan luas permukaan 985,9 m2/g. Hasil ini menunjukkan bahwa kedua jenis karbon aktif ini dapat digunakan secara optimal untuk penurunan amonium dengan persentase penyerapan mencapai lebih dari 90%.

Kata kunci: karbon aktif, amonium, adsorpsi

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INTRODUCTION

Activated carbon is a useful adsorbent used widely in industries such as food processing, pharmaceuticals, chemical, petroleum, mining, nuclear, and automobile, to purity, decolorize, deodorize, dechlorinate, detoxicate, filter, and as a catalysts. Manufacture of activated carbon consists of two main processes is carbonization and activation. During carbonization majority of the non-carbon elements, such as hydrogen, oxygen is the first lost as gases and develop internal pores. After the carbonization, the next process is conducted by means of chemical and physical activation. The activated carbon consist of various size of pores is clasified as a micro pores micro (<2 nm or 20Å), meso pores (2-5 nm or 20-50 Å), and macro pores (> 5 nm or 50Å). The sizes and volumes of pores is determining a large of surface area. The larger a number of micro pores, a surface area and adsorption capacity is increased. However the characteristics of pores such as size, morphology, and the surface properties of pores, for example, the presence of surface functional groups also can be influence to the adsorption capacity (Tamai, et al., 2004). The adsorption capacity also is affected by factors such as contact time, amount of adsorbat, properties of surface such as acidic, basic or neutral behavior. The properties of surface is affected by the presence of heteroatoms, generally in the form of organic functional groups, such as oxygen, nitrogen and hydrogen is bound to a molecule of carbon atom (Yehya and Teresa, 2003). Oxygen is the most dominant, forming oxides of functional groups, such as carbonyl, carboxyl, hydroxyl, lactones, quinones, and others, is formed as a results of chemical adsorption between carbon surface and oxygen that are around (Bochm, 2002). Oxygen functional groups is containing proton donors have been very well known for a removal of heavy metals from water, because metal ions have a tendency to form metal complexes with the negatively charged of acidic groups (Halim, et al., 2013).

Some of the studies for an ammonia or ammonium removal have been conducted by using activated carbon. However studies does not mention a types of raw material of the activated carbon. However, in Indonesia generally of the use of activated carbon are made from coconut shell. This is because generally of the activated carbon production are made from coconut shells, which are used for the several of utilization on the various types of industries. While, although there are industries that the used coal activated carbon, can ascertained be was obtained through imports from the other countries like as China and America (Anonymous, 2012). As well as coconut shell activated carbon, coal activated carbon can be made through steam activation process by using a rotary kiln. The steam activation of the coconut shell charcoal can produce a surface area more than of 1000 m^2/g. However, the steam activation to coal charcoal can result a surface area less than 700 m^2/g. Usually, the large surface area was indicated that the higher of the adsorption of active carbon and the price is more expensive.

Ammonium is a ammonia compounds, nitrogen organic compounds, nitrate and nitric is soluble in water. Ammonia is important gas because it is toxic and threatening the health if inhaled in large quantities (rate of respiratory between 50-100 ppm) while in the lower levels can cause irritation of the eyes, throat and nose. Mainly the ammonia emissions is resulting from the fertilizer industry, manufactures of coke, burning fossil fuels, livestock, and process cooling material. Among of all these sources, 90% of ammonia emissions resulting from livestock waste and fertilizer production (Gonçalves, et al., 2011). While industries are resulting a effluent with the ammonium high content is the factory paint, rubber processing, palm oil, fertilizer industry and others. The ammonium content is very various with the range from 10 mg/L up to 30 mg/L in surface water or more in the effluent (Titiresmi and Sopiah, 2006). The ammonium high content of the effluent was contained in the fertilizer reaches more than 2000 mg/L. While the ammonium content with the range concentration between 200-600 mg/L are in addition to the manufacture of shrimp waste also in the rubber processing industry (Nindrasari et al., 2011). Ammonium at the specific content can be harmful of aquatic life, encourage the occur of eutrophication, corrotion at specific metals, even can cause poisoned which resulted in lung damage and death. The ammonium high content caused decreasing oxygen soluble and toxic behavior on methanogenesis bacteria which is decompose organic matter in anaerobic conditions. Therefore, in environmental management to eliminate ammonium was received as considerable concern because it is damaging aquatic ecosystems (Uygur and Kargi, 2004).

A lot of technics have been conducted for NH_3 or NH^{4+} removal in industries effluent such as reaction with the gases, ion exchange, used by polymer of recines, membrane separation, thermal treatment, catalitic decomposition, and adsorption by porous material (Blonigen, et al., 2005). Li and Liu (2009), at the present, some ways were conducted for ammonium content of effluent processing, among others by biological treatment using microbe, air stripping, breack-point chlorination, and ion exchange. However, that ways of mention had limited, in addition to need a big cost, also can not reduce amount of ammonium on least levels. Beside that, any conventional process such as aerasi system, electrolysis or addition of chlorine. This method is used to decrease high levels of ammonium less than or more than 200 mg/L. While for the ammonium removal with the concentration above of 2.000 mg/L using SHARON technology (Single High Activity Removal Over Nitrite) -Anaerobic Ammonium Oxidation which is a new technology (Pasaribu, et al., 2005).

Base on that conditions are conducted an experiments by ammonium solution with range concentration of 208-233 mg/L, nearly ammonium concentration on conventional processes. The experiment is conducted as first step for studying adsorption capacity of activated carbon in decreasing ammonium high content. With the result that application of field directly, efectifities of contact time, particle sizes, and usesd number of activated carbon can be find out. Beside that, use of two types of activated carbon also to study how coal activated carbon as an alternative adsorben to change coconut activate carbon.

METHODOLOGY

Activated carbon is prepared by carbonization and physical activation. Carbonization process is conducted on 500-600°C with particle size ± 1 cm of coal feed. Rate of feed is 100 kg/hour, is necessary contact time inside of rotary kiln of ± 2 hours. Next step, activation process on charcoal was resulted of carbonization. In the activation process, a number and dimention of pores is increasing until internal surface area to be larger (Niraj, et al., 2012). In the physical activation, raw was used as oxydator behavior to react with carbon for forming gases, and (Campbell, et al., 2012).

The activation on 900°C, particle size of charcoal feed +6 mesh, and rate of feed 35 kg/hour, are need contact in rotary kiln is ± 4-5 hours. While rate of steam in activation is 150 kg/hour. The examinatin charactrization of activated carbon carbon is determined with iodine analysis in ASTM 4607-94 Standard Test Method for Determination of Iodine Number of Activated Carbon. While of determination of surface area by methode of Brunauer, Emmett, and Teller (BET) isotherms adsorption N_2 on monolayer adsorbat (Krista and Randall, 2007), base on gas volume was adsorbed. Figure 1 show a flow chart manufactured of activated carbon.

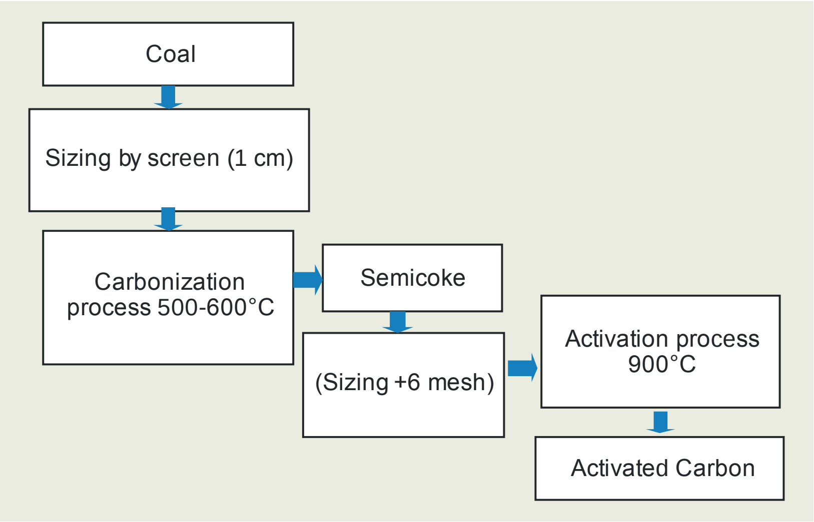

Figure 1. Flow chart process of activated carbon production

The activated carbon was resulted from the activation process is crushed to particles size of -8+12 mesh and -16+20 mesh as a consideration. In to beaker glass with 200 ml ammonium solution of 208-233 mg/L is added 20, 40,60 and 80 g of activated carbon. On each mixtures is offered contact times with the variety of 30,60, 120, 180 and 1440 minutes (24 hours) is stirring manually every 10 minutes for 30 seconds. Exceptly sample with the contact times of 24 hours the stirrer is stopped afetr 180 minutes. After that a mixtures is filtered and filtrate is storage place in bottle. Futhermore, for detecting a ammonium removal, is conducted filtrate analysis.by using spectrophotometry. Determination of optimal parameter is carried out by calculation of efficiency percentages of highest ammonium removal by using the equation :

$$\%E = \frac{C_0 - C_1}{C_0} x100\%$$

where is;
% E = Removal efficiency
Co = Ammonium concentration before adsorpsi (ppm)
Ce = Ammonium concentration after adsorpsi (ppm)

RESULTS AND DISCUSSION

Table 1 shows a results of analyisis of activated carbon sample. CAC 197 and CAC 643 are coal activated carbon. While CSAC 60 and CSAC 986 are coconut activated carbon. CSAC 60 is activated carbon was obtained from market to purity of aquarium fish.

Results of analysis was indicated that increase of surface area versus increase of Iodine number is directly (Table 1).The measurement of surface area is showing a pores dimension is micro type with the radius of < 20 Å. The greater it is surface area, a volume of pores are larger. Conversely, the lower of surface area, a volume pores is lower. In addition to surface area, value of Iodine number showed that activated carbon has high adsorption. Iodine number is capacity of each gram activated carbon to adsorp each miligram anorganic matter (I_2).

Figure 2 is showed that lower surface area, value of Iodine number of coal activated carbon and coconut shell activated carbon are higher. However for large surface area, value of Iodine number both types of activated carbon is lower. Determination to difference of surface area and Iodine number have purpose to study effectivity of ammnonium adsorption by low surface area and high surface area.

Ammonium Adsorption

Figure 3 shows that coal activated carbon (CAC 643) and coconut shell activated carbon (CSAC 986) particle size -16+20 mesh is tended with the similar adsorption capacity. The time contact is longer, ammonium removal is greater, at the 24 hours seen that adsorpstion is not saturated. A similar pattern was shown by CAC 197, with the ammonium removal is lower. At the 30 minutes, CAC 197 and CSAC 986 have a similar adsorption capacity. In Figure 3 also looks that CSAC 60 m^2/g shows fluctuating adsorption with the percentage of less than 40%. Different with use of activated carbon -8 + 12 mesh size (Figure 4) is showing a ammonium removal decrease at the 24 hours by CAC 643 and 986 CSAC.

Figure 5 shows that four type of activated carbon have a similar adsorption pattern, exceptly at the 24 hours CSAC 60 was saturated. Eficiency of highest ammonium removal was achieved by the CAC 643 which a surface area less than CSAC 986. This is caused CAC 643 from coal has macro pores over than CSAC 986 from coconut. Macro

Table 1. Characteristic of coal activated carbon and coconut activated carbon

Sample names	Iodine number mg/g	Surface area m^2/g	Total volume pores (cc/g)	Radius pores (Å)
CAC 197	238	196.7	0.1340	11.10
CSCAC 60	154	59.6	0.0382	13.26
CAC 643	605	643.0	0.3569	11.10
CSAC 986	790	985.9	0.5264	10.68

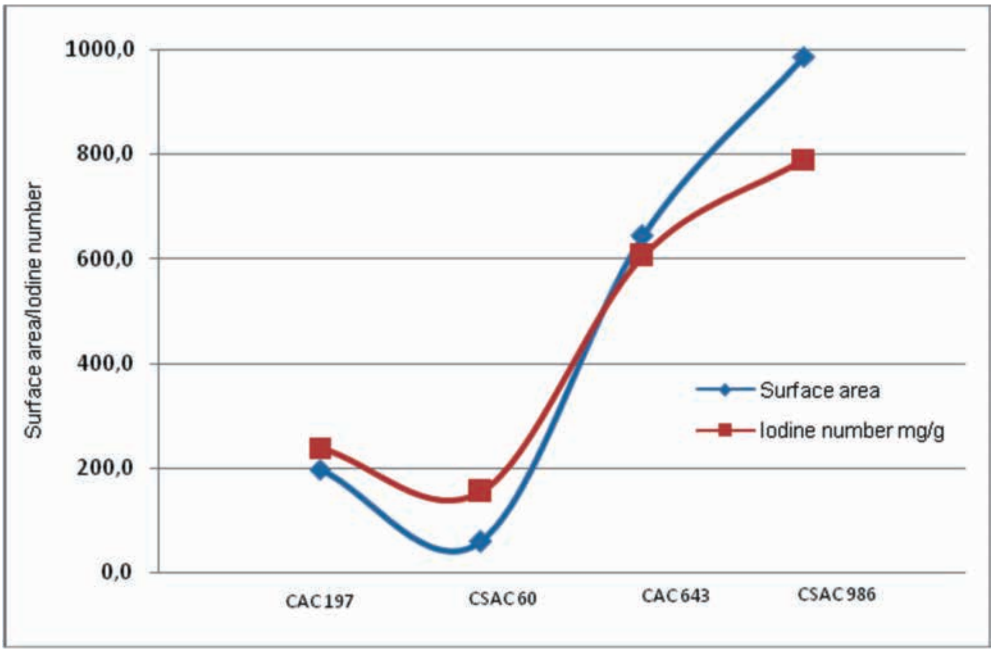

Figure 2. Surface area and Iodine number of activated carbon

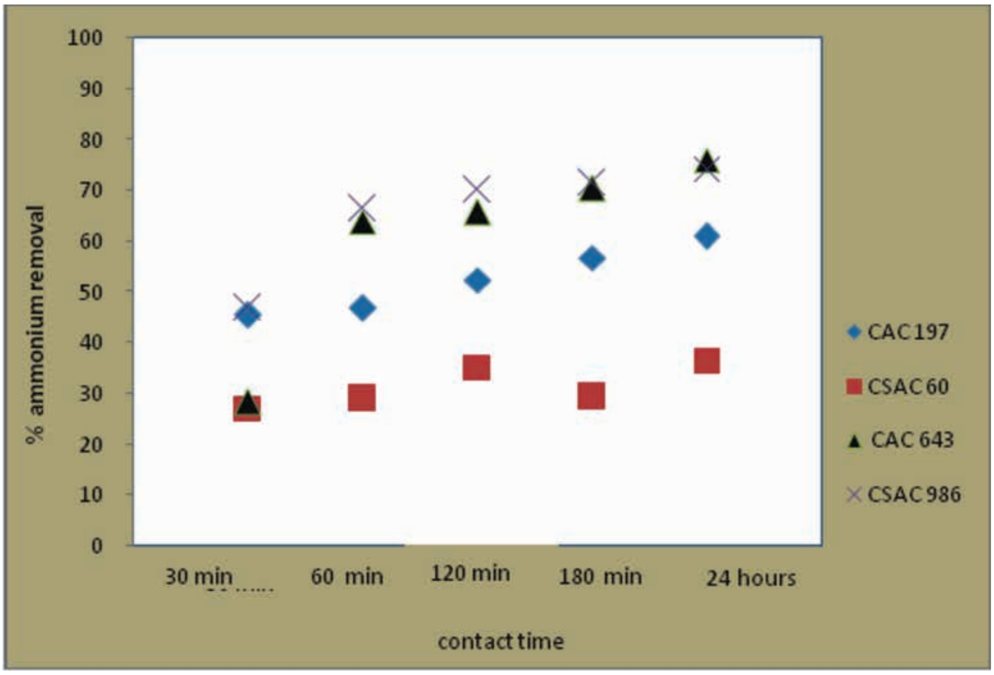

Figure 3. Effect of contact time on ammonium removal by activated carbon 20 g of particle size -16+20 mesh

pores as the entrance to meso pores and micro pores. So that, any substance will be inserted into macro pores. Therefore, in some conditions the adsorption of CAC 643 is better than CSAC 986. This conditions also looks adsorption pattern of CAC 197 has capacity to decrease of ammonium with the level adsorption is better than CSAC 986 at the 30 minutes. Different with the Figure 5, Figure 6 shows that the adsorption CSAC 60 is similar to CAC 643. While CSAC 986 shows rate

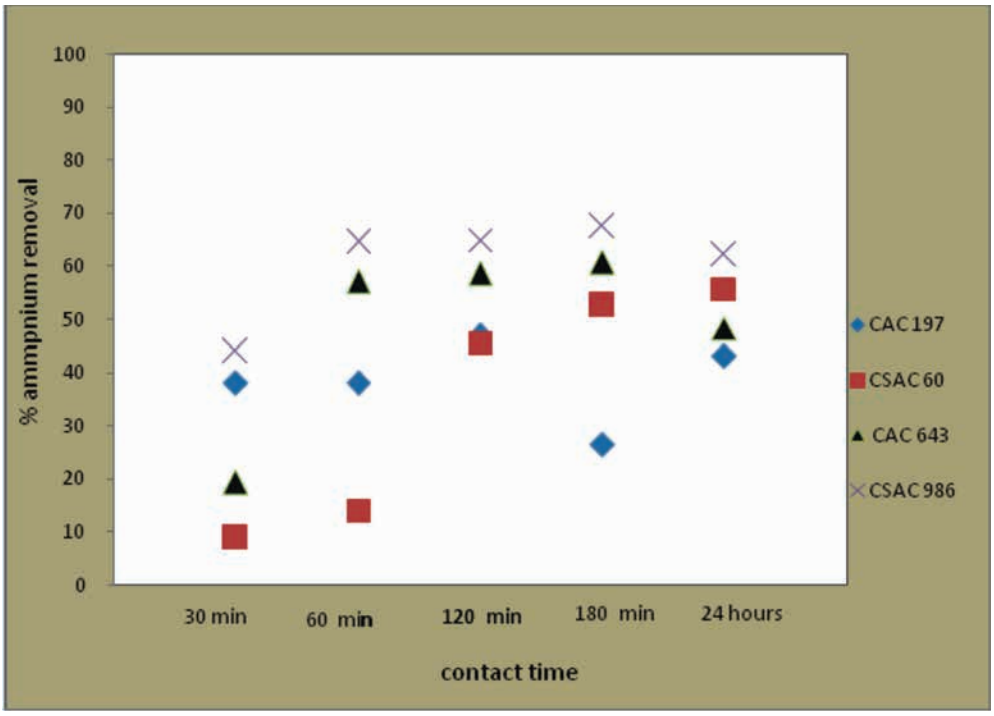

Figure 4. Effect of contact time on ammonium removal by activated carbon 20 g of particle size -8+12 mesh

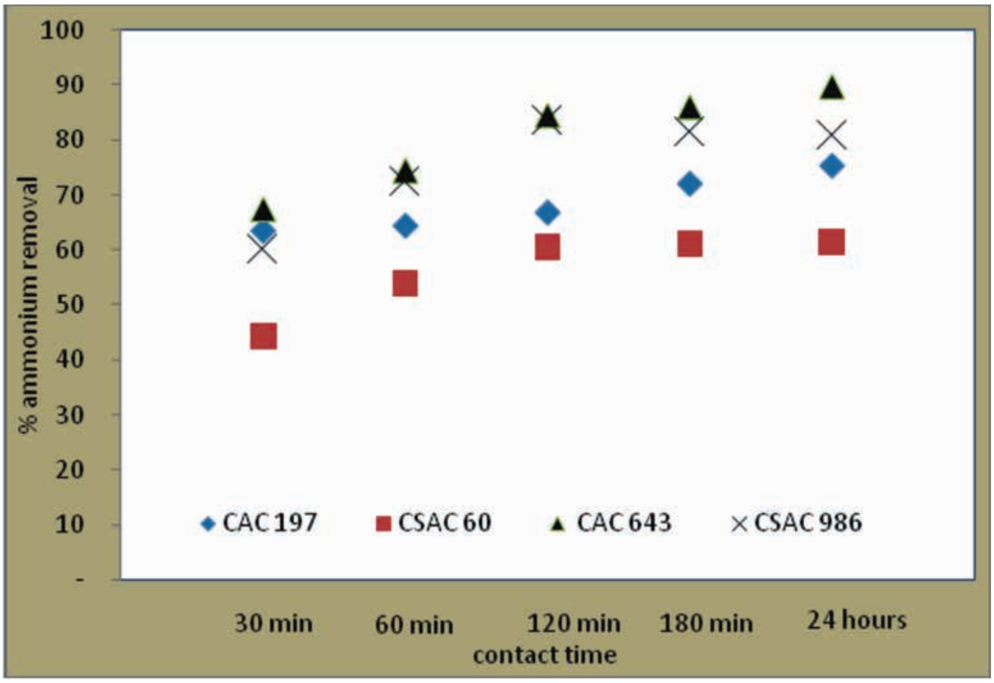

Figure 5. Effect of contact time on ammonium removal by activated carbon 40 g of particle size -16+20 mesh

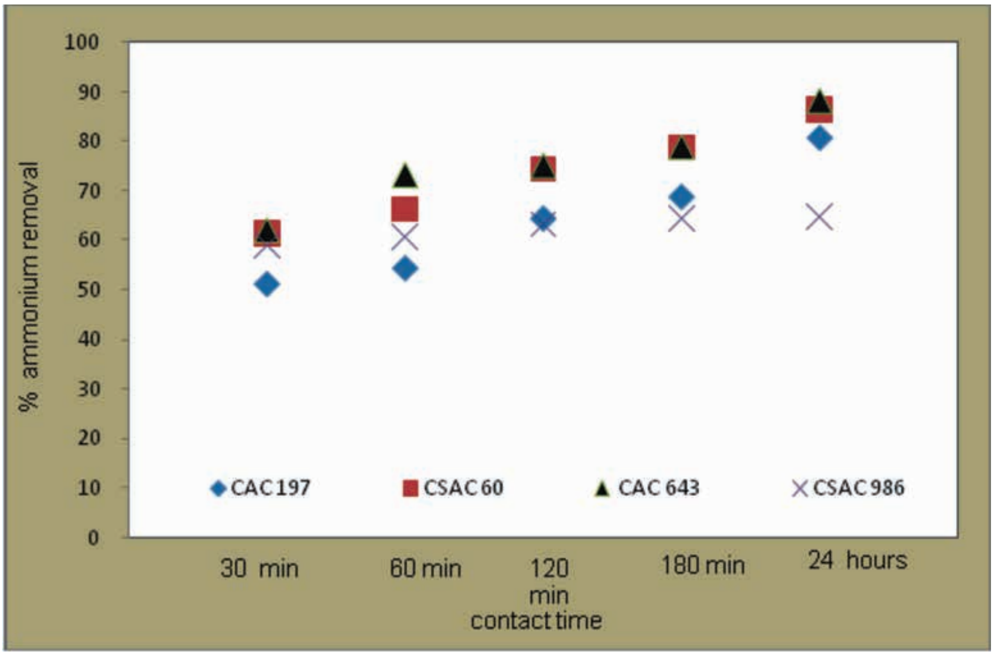

Figure 6. Effect of contact time on ammonium removal by activated carbon 40 g of particle size -8+12 mesh

of least adsorption. In such conditions, the use of activated carbon 40 g of particle size -8 + 12 mesh is very affects adsorption of activated carbon CSAC 986 which has a large surface area.

Effect of contact time with the use of activated carbon 60 g (Figure7), shows four types of activated carbon has a level of adsorption with a similar pattern, and relatively stable. This shows that the use of activated carbon 60 g of particle size -16 + 20 mesh does not significant to decrease of ammonium. While in Figure 8 the highest adsorption was achieved with percentage more than 90%. It means that amount of activated carbon 60 g of particle size -8 + 12 mesh, and a contact time at 24 hours, almost 100% ammonium can be removed. These results show that the optimal parameters for ammonium adsorption process is used of coal activated carbon and coconut shell activated carbon of particle size -8 + 12 mesh with each surface area 643 and 986 m^2/g (Monika, et al., 2014). This condition also showed after a period of use at 24 hours, the activated carbon was not saturated.

Figures 9 and 10, the adsorption by using activated carbon amount of 80 g shows the results are not optimal. It was shown by adsorption percentage obtained less than 60% of particle size -16 + 20 mesh and less than 70% by activated carbon of particle size -8 + 12 mesh. This is caused to the use of activated carbon weight 80 g in 200 ml ammonium solution (40%) is excessive so that the space of contact time between ammonium with a granular of activated carbon is inhibited. This condition also caused the adsorption process was saturated, it looks at a contact time of 24 hours rate adsortption was decreased.

In the adsorption process the contact time between adsorbent and adsorbate, amount addition of activated carbon surface area affects to removal of ammonium process. Although after 24 hours some condition processes showed a tendency to increase adsorption, however at a specific time will have saturated and activated carbon is not effective to use. The saturation point is also influenced by particle size of the use of activated. The use lot of activated carbon cause a contact between activated carbon and ammonium are not optimal because the substance is adsorbed only attached to the surface of solids and do not enter into solids, hampered by too many of solids or adsorbent (Setiawan, 2000) As a result, in some conditions (like as Figures 9 and 10), a large surface area can not adsorb ammonium optimally. Therefore, the appropriate parameters for the process of adsorption must be known.

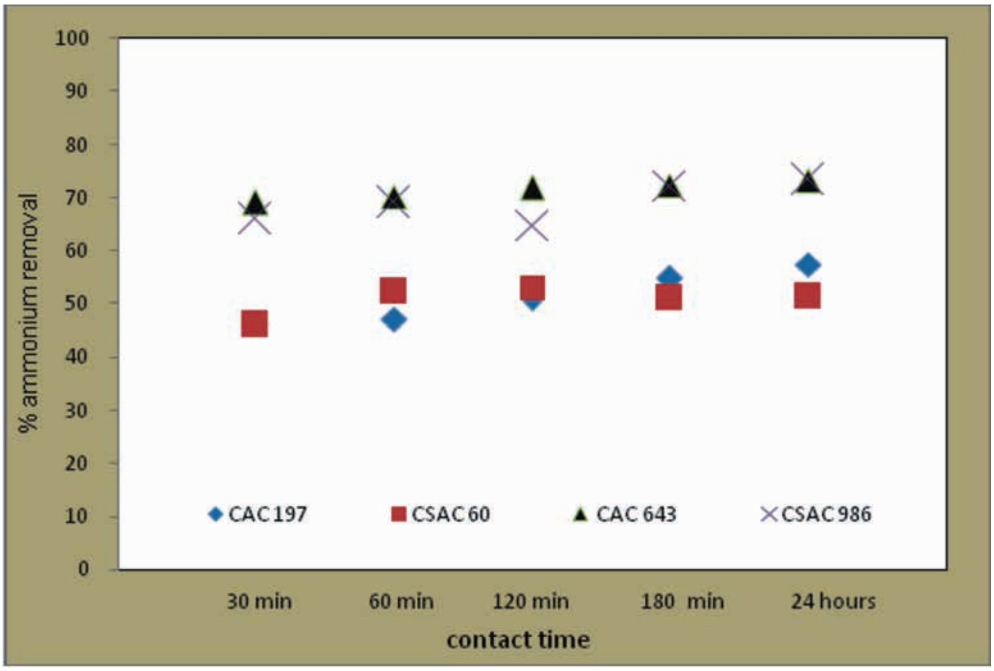

Figure 7. Effect of contact time on ammonium removal by activated carbon 60 g of particle size -16+20 mesh

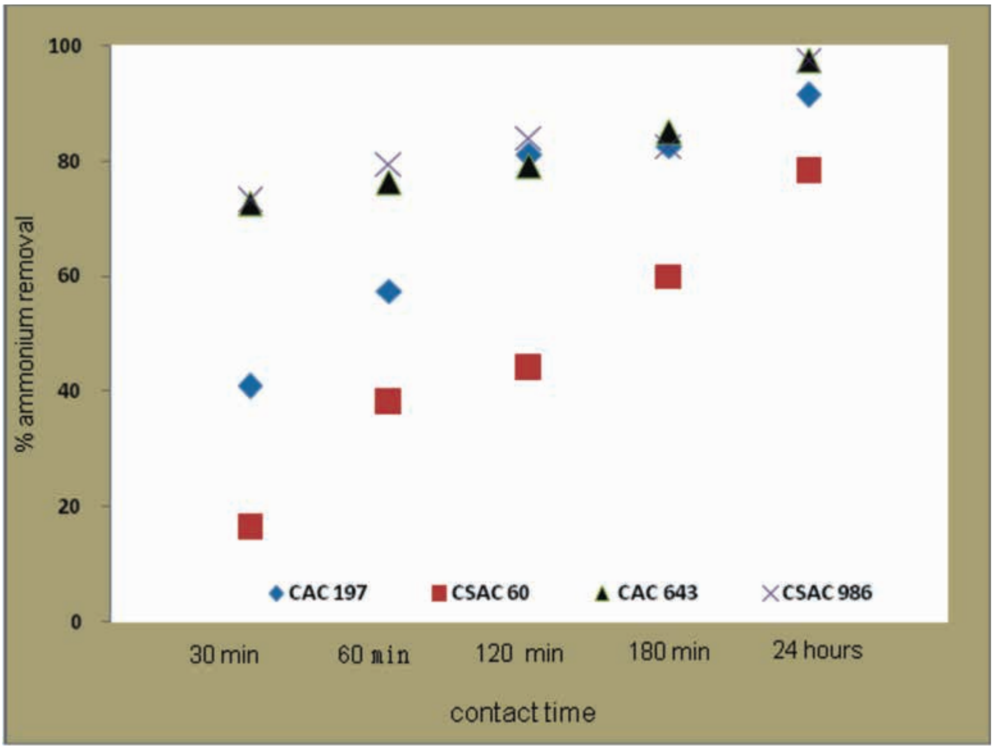

Figure 8. Effect of contact time on ammonium removal by activated carbon 60 g of particle size -8+12 mesh

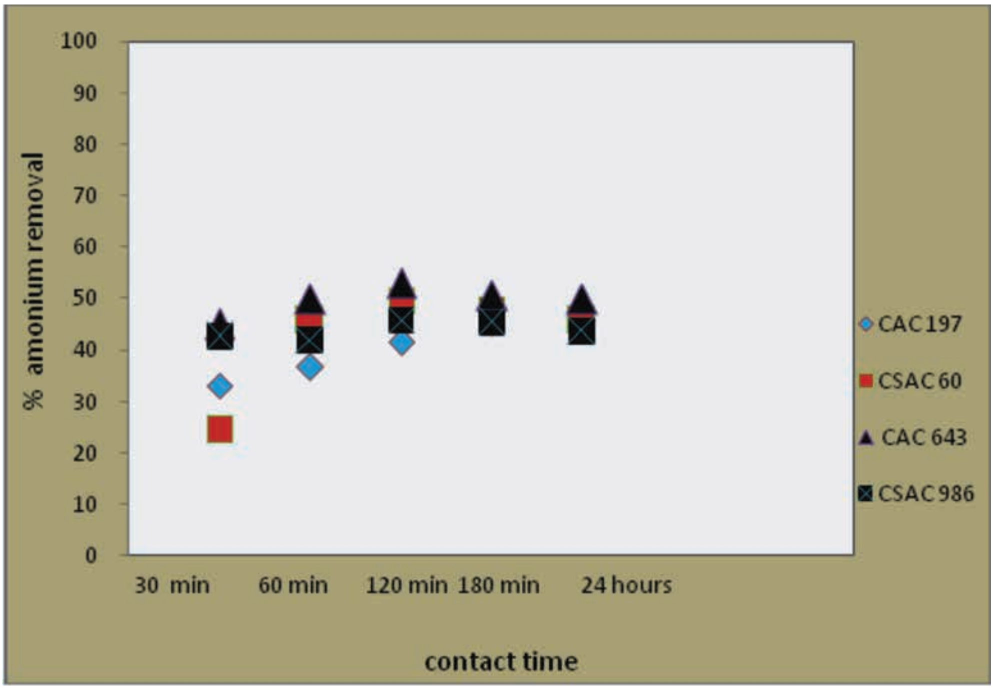

Figure 9. Effect of contact time on ammonium removal by activated carbon 80 g of particle size -16+20 mesh

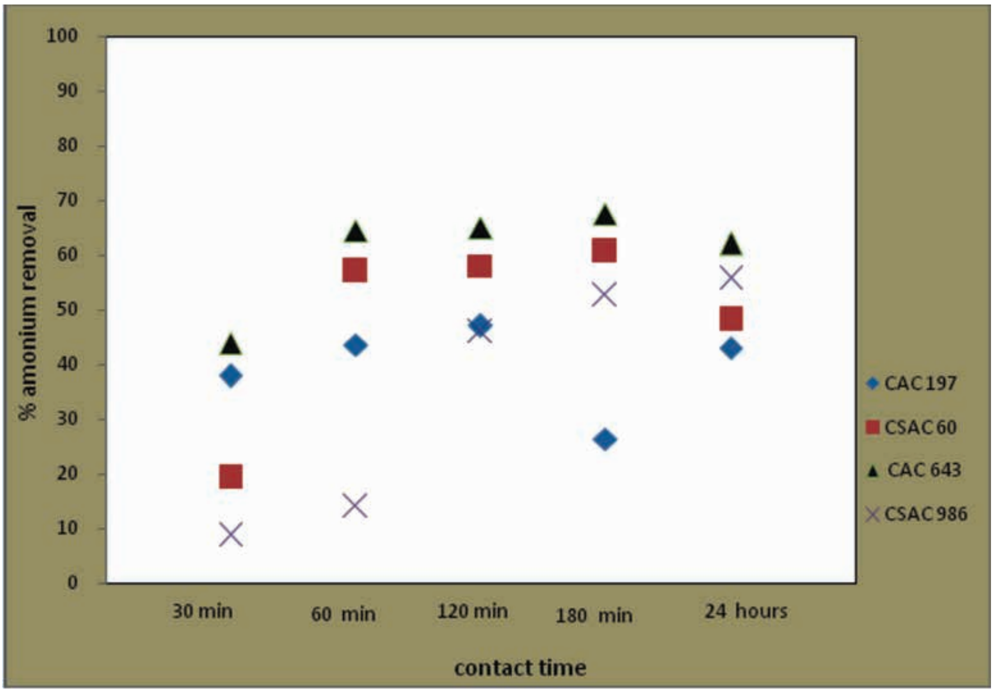

Figure 10. Effect of contact time on ammonium removal by activated carbon 80 g of particle size -8+12 mesh

CONCLUSION

- Based on the results of experiments by using activated carbon coal and coconut shells was obtained the results as following. Data of the research indicated a trend that the adsorption capacity is increased with the increasing of surface area and contact time.The optimum conditions is reached at the use of particle size of activated carbon -8+12 mesh amount of 60 g with the ammpnium adsorption almost achieved 100% at contact time for 24 hours. These results is indicated after that 24 hours the activated karbon is not saturated.
- The use of activated carbon -16+20 mesh with the large of surface area is indicated that the optimum adsorption is occured at the contact time of 24 hours with the use amount of activated carbon of 40 g
- The duration longer of the contact time and rate of decreased adsorption shows that the activated carbon is not saturated and can be used on more than 24 hours.
- The use of too many activated carbon can be cause the transfer of substance into solids is hampered.
- Both of particle size can used for a removal ammonium, however weight of activated carbon and contact time is different
- Necessary to further research for determine the lifetime of the activated carbon by adding contact time more than 24 hours

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