ADSORPTION OF AMMONIA AND METHYLENE BLUE USING COMBINATION OF COST-EFFECTIVE COCONUT HUSK ACTIVATED CARBON AND SILICA (SiO₂) AS AN ADSORBENT

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ABSTRACT

Ammonia and methylene blue are hazardous industrial wastes which are dangerous to health and the environment. Adsorption is one of several separation processes that can be employed to reduce these contaminants in water. Activated carbon is the most commonly used adsorbent for this process due to its high adsorption effectivity. However, adsorbents with one type of activated carbon generally have lower adsorption efficiency hence modification such as treatment and combination was proposed. This study aims to explore the potential of the combination of silica and coconut husk activated carbon for the removal of ammonia and methylene blue in industrial liquid waste. Several types of adsorbent were used in this research namely pure silica (activated and nonactivated), coconut husk (activated and nonactivated) and the combined pure silica-coconut husk (with combination ratio of 70:30). The results showed that the coconut husk-pure silica combined adsorbent showed the best adsorption performance in terms of removal efficiency and adsorption capacity for both methylene blue and ammonia. The removal efficiency of ammonia and methylene blue was 99.49% and 83 %, respectively. Whereas, the adsorption capacities of this combined adsorbent were 0.017 mg/g and 1.3913 mg/g for methylene blue and ammonia, respectively.

Keywords: Silica, Coconut Husk, Activated Carbon, Adsorbent, Ammonia, Methylene Blue.

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INTRODUCTION

Over the past decades, the contamination of water by industrial-source wastes has become a global problem and requires serious attention.^{1,2} Most industries produce hazardous wastes and are often disposed of directly into water bodies. Such wastes are synthetic dyes from the textile (e.g. batik-manufacturing) industry like methylene blue.³ The presence of methylene blue in the water bodies at high doses is risky for human health as well as aquatic habitats. Also, the contamination of water bodies decreases environmental aesthetic values.^{3,4} Besides dyes, there is also chemicals contaminant such as ammonia generated from the liquid waste of tofu-making industry.⁵ The high ammonia content in tofu liquid-waste is from the breakdown of protein and fat in soybeans by microorganisms. Ammonia is the toxic end-product of the metabolism reaction of nitrogen. Thus, liquid waste containing high concentrations of ammonia, especially free ammonia is very toxic to aquatic biota.⁵ It was reported that ammonia content in water bodies with a concentration of over 1 mg/l is lethal to fish.^{5,6} It is specified by Indonesian national regulation that the permitted disposal level of methylene blue to the environment is not more than 0.5 mg/L.⁷ For that reason, treatment is needed to lower or even remove the content of these contaminants.

Many methods have been reported to solve this problem such as extraction, membrane separation, ion exchange and adsorption. The adsorption method is the most widely used and preferred.⁸ Adsorption is a process that occurs when a fluid (liquid or gas) is caught by a solid and formed as a thin film on the surface of the solid material or commonly named adsorbent.⁹ As it is cost-effective, easy and safe of operation and

does not hurt the environment, adsorption has been popularly preferred and applied in many removal processes.⁹⁻¹² Conventionally, activated carbon and zeolite are the most frequently used adsorbents, however, the adsorption capacity of these two adsorbents is quite low in removing dyes due to their microporous characteristic.¹³

Recently, it has been reported that silica is an adsorbent material showing a fairly high adsorption performance against heavy metals, dyes, phenolic compounds, pesticides and so forth in the water. This is because silica is a nontoxic mesoporous material having large pore volume and surface area as well as outstanding stability.¹³ However, it should be noted that with increasing consumption for applications in the industrial field, the economical value of commercial silica also increases. Hence, the production of silica from more affordable sources is highly considered. One of the most promising sources comes from agricultural biomass wastes. All of these natural materials have the potential to be used as adsorbents due to high lignocellulose content.¹⁴ These waste biomaterials are suitable to be selected as an alternative source for adsorbent materials because, in addition to having renewable sources, inexpensive and available in large quantities, the preparation of adsorbents from these materials also helps in reducing production costs because the processing generally only involves washing, drying, and size reduction.¹³

Amongst many potential biomass-waste sources that were used widely as adsorbents, we chose coconut husk (CH) to be studied. Besides content high lignin, hemicellulose, and cellulose,¹⁴ silica-containing ash can be produced from CH through thermal treatment with the controlled condition, the produced amorphous silica is highly promising to be used as an adsorbent.¹⁵

A few numbers of literature reported the utilization of CH as an adsorbent for the removal of wastewater contaminants. Hasany et al studied the performance of CH adsorbent in the removal of Cd (II), Cr (III) and Hg (II) metals.¹⁶ Jain et al used CH adsorbent for removal of tropaeoline dye and it was disclosed that the activated CH sorbent showcased performance that is as good as that of commercial activated carbon.¹⁷ However, pure adsorbent tends to have low adsorption capacity, hence various treatments and modifications are developed to enhance their performance. The modification can be done chemically like alkaline treatment, acid treatment, the bleaching treatment and by combining the adsorbent with another material.¹⁸ Manju et al¹⁹ impregnated CH adsorbent with copper and successfully improved the adsorption capacity to arsenic. Modification can also be carried out physically as conducted by Foo et al in which they activated CH-based adsorbent by microwave irradiation.²⁰

In this study, we investigated the performance of the CH-sourced and pure commercial silica adsorbents. The study aims to compare whether the performance of low-cost based natural adsorbents can match that of commercial silica. Also, these two types of silica-based adsorbents are combined to obtain an adsorbent with better performance. The preparation of the adsorbents was reported in our previous work⁷, therefore, in this paper, the continuation of research is reported only in terms of performance evaluation of prepared CH and silica adsorbents for removal of ammonia from tofu-making liquid waste and methylene blue as representative waste from batik-manufacturing industry.

EXPERIMENTAL

Materials

Coconut husk collected from the area of Neuheun, Aceh Besar was used as biomass-source to produce adsorbent. The pure commercial silica was purchased from Merck and also used as an adsorbent. H₂SO₄ with the purity of 98% (Merck) with a concentration of 0.1 M, ammonia, methylene blue and distilled water were also involved during the preparation, activation and performance test of adsorbents.

Preparation and Activation of Adsorbent

The preparation of adsorbent from CH was carried out as reported in our earlier work.⁷ The raw CH with a total weight of 10 kg was heated to form carbon in a muffle furnace. The obtained CH carbon and pure silica were mixed while stirring for 2 hours. The sorbent mixture was dried overnight in the oven to remove the water content. After that, the sorbent was soaked in H₂SO₄ solution in a 500 ml flask for 24 hours then drained and filtered. It was then followed by pH neutralization using rinsing using water. Subsequently, the sorbent was calcined for 2 hours at a temperature of 800°C.²¹ Finally, silica as much as 10 grams was dispersed in distilled water with a silica-to-water ratio of 10:1, followed by drying and carbonation. At last, the activated sorbent was sieved to 100 mesh size.

Adsorbent Adsorption of Ammonia and Methylene Blue

The adsorption experiment was conducted as follows. 100 ml of methylene blue dan 100 ml of ammonia was separately put into the 200 ml flasks. The adsorbent was added into each flask with a dosage of 0.2 gram for methylene blue-containing flasks and 0.5 gram for ammonia-containing flasks. The mixture was stirred for 2 hours then filtered and followed by an analysis of ammonia and methylene blue concentrations by using UV-Visible Spectrophotometer (Pharmaspec-1700, Shimadzu).

RESULTS AND DISCUSSION

Efficiency and Capacity of Methylene Blue Adsorption

Several parameters such as the sorbent dosage, the concentration and pH of feed solution greatly influence the efficiency or removal process by adsorption.²² In this experiment, the initial concentration of methylene blue is 0.04 ppm and five types of adsorbents are used i.e. non-activated coconut husk (NCH), activated coconut husk (ACH), non-activated pure silica (NSi), activated pure silica (ASi), and activated combined coconut husk-pure silica (CHSi). From the results of the experiment, it is revealed that the efficiency of methylene blue removal is highly affected by the difference in adsorbent types, activation process, and contact time, as shown in Fig.-1.

Fig.-1: The Removal Efficiency (%) of Methylene Blue

Figure-1 shows that the removal efficiency slightly differs for each adsorbent with the CHSi adsorbent resulting in the highest value of 89.16% at 120 minutes of adsorption time and the lowest efficiency was obtained at adsorption using non-activated CH (NCH) adsorbent (70.41%). Meanwhile, the adsorption capacity using ACH and Si adsorbents achieved removal efficiency of 81.77%, and 85.20%, respectively. The dismissal of methylene blue from the solution occurs due to the reaction between methylene blue and silica in the prepared adsorbents, the reaction is as follows:

The negatively charged oxygen atom in the silica oxide compound binds the positively charged N atom in the methylene blue compound which facilitates the adsorption of methylene blue by the active SiO_2 .²³ The CHSi adsorbent gives the highest efficiency in removing methylene blue due to the presence of more silica content with the addition of pure silica as confirmed by the XRD analysis, where the CHSi adsorbent has 83% silica, meanwhile the silica content in NCH, ACH and NSi adsorbents is 62, 75, and 63.2%, respectively. The capacity of adsorption indicates the quantity of adsorbent that can be adsorbed by the adsorbent.²² Figure-2 showed the effect of several types of adsorbents on the capacity of methylene blue adsorption.

The results in Fig.-2 revealed that the adsorption capacity improved with prolonged adsorption duration. The highest value was achieved at 120 minutes of adsorption time for all types of the adsorbent. The respective adsorption capacity for CHSi, ACH, NCH, and ASi adsorbents were 0.0178 mg/g, 0.0163 mg/g, 0.0140 mg/g, and 0.0175 mg/g. Similar to results of removal efficiency, the high adsorption capacity of

combined coconut husk and pure silica (CHSi) adsorbent is due to the higher composition of SiO_2 in comparison to the other adsorbent types.^{7,24} Also, the chemical activation also plays part in enhancing the adsorption performance of the adsorbents, as seen from the results, the activated adsorbents (ACH) has better adsorption capacity and efficiency than the non-activated adsorbent (NCH).

Fig.-2: The Adsorption Capacity (mg/g) of Methylene Blue

Efficiency and Capacity of Ammonia Adsorption

For this experiment, 6 ppm artificial ammonia was used for the adsorption process using 2 types of adsorbents namely CHSi and ACH adsorbents with a dosage of 0.5 gram. It is revealed that the types of adsorbents, the contact time and activation treatment on the adsorbents affect the removal efficiency of ammonia. The results are presented in Fig.-3.

Fig.-3: The Removal Efficiency (%) of Ammonia

Figure-3 shows that the combined CHSi adsorbent achieved the highest removal efficiency of 99.45% after the adsorption process for 120 minutes. This is due to the higher silica content in the coconut husk adsorbent combined with pure silica (CHSi) rather than in the coconut husk adsorbent only (ACH). According to XRD analysis reported elsewhere, the CHSi adsorbent prepared with CH-to-silica combination ratio of 70:30 contains 83% silica.⁷

Figure-4 shows that at an adsorption time of 120 minutes, the CHSi adsorbed 1.3924 mg/g of ammonia, meanwhile the ACH adsorbed lower ammonia as much as 1.391 mg/g. It can be concluded that the combined adsorbent has a slightly better adsorption capacity compared to coconut husk adsorbent only. This is due to the higher content of SiO_2 and higher surface area as well as pore volume of CHSi compared to the ACH adsorbent.⁷

As reported in our earlier work,⁷ the composition of SiO_2 in the 70:30 CHSi is higher than that of ASi and ACH. The high content of SiO_2 is advantageous for an adsorbent as it promotes the reactivity of sorbent

which means 70:30 CHSi has better reactivity compared to the other two adsorbents (ASi and ACH).²⁴ It is reported that with a higher level of silica, makes the adsorbent to have better adsorption and ion exchange performance.²⁵

Fig.-4: The Adsorption Capacity (mg/g) of Coconut Husk-based Adsorbents

The Effects of Adsorbent Variables on the Adsorption Performance

For this study, only CHSi adsorbent is used as it showcases the best performance amongst the other prepared adsorbents in previous experiments. Meanwhile, the adsorption time and mass of the adsorbent are varied. For the adsorption experiment on ammonia, the adsorbent used is 0.5 gram, whereas 0.2 gram of adsorbent is used for adsorption in the removal test of methylene blue. The influences of these variables on the removal efficiency of both ammonia and methylene blue are presented in Fig.-5.

Fig.-5: The Removal Efficiency of Ammonia and Methylene Blue

The results in Fig.-5 confirm that using a higher amount of adsorbent leads to higher removal efficiency. As observed from Fig.-5, the ammonia removal efficiency is higher than that of methylene at the same adsorption time and adsorbent type. For the methylene blue sample, the adsorption was conducted by using 0.2 gram CHSi adsorbents, whereas, for ammonia, the removal process was carried out with the addition of 0.5 gram CHSi as adsorbent. This is because, with the increasing amount of the adsorbent, more particles and surface area are available to reactively adsorb the adsorbate in the sample.⁷ Moreover, the lower removal efficiency of methylene blue adsorption is because dyes such as methylene blue are very complex compounds so that methylene blue is more difficult to decompose or eliminate compared to an organic component like ammonia.²⁷

CONCLUSION

A low-cost natural material of coconut husk has been prepared with various activation treatment and combination with pure commercial silica. Also, the adsorption performances on the ammonia and

methylene blue removal were evaluated in this report. The activated coconut husk adsorbent showed an excellent performance in removing ammonia and methylene blue in liquid waste. The combining the coconut husk adsorbent with pure silica further improved the removal efficiency and adsorption capacity for both ammonia and methylene blue samples due to increasing content of silica and pore volume as well as surface area properties. The best adsorption performance was achieved when using the adsorbent amount of 0.5 gram and the adsorption process contact time of 120 minutes.

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