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Immobilization of activated carbon on alginate beads as decolorization agent and its characterization for black Liquor wastewater

Ajeng Arum Sari[1] *, Andreas[2], Fathmasari Fitrianingsih[3], Muhammad Nurdin[3] and Adelia Anju Asmara[4]*

[1]Research Unit for Clean Technology, Indonesian Institute of Sciences, Komplek LIPI Gedung 50, Jalan Sangkuriang, Bandung, Indonesia
[2]Research Center for Chemistry, Indonesian Institute of Sciences, Kawasan Puspiptek Serpong, Tangerang Selatan, Indonesia
[3]Faculty of Mathematic and Sciences, University of Haluoleo, Kampus Hijau Bumi Tridharma, Kendari, Indonesia
[4]Department of Environmental Engineering, Faculty of Civil Engineering and Planning, Universitas Islam Indonesia, Jalan Kaliurang Km. 14,5, Yogyakarta, Indonesia

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ABSTRACT

The production process of bioethanol made from oil palm empty bunches produced black liquor which was massive and potential to become a source of water pollution in the environment as it was untreated first. Therefore, conversion of black liquor sludge becomes activated carbon immobilized with alginate is a promising alternative method to modify the structure and improve the capacity of decolorization agents. The aim of this study was the utilization of activated carbon (AC)-alginate beads for repeatedly decolorization agent and identification of its characteristics in black liquor wastewater. The decolorization of black liquor wastewater by using AC-alginate beads reached 93.77% in the optimum of contact time 4 h, 2 g of activated carbon mass inside AC-alginate beads. Moreover, the capacity adsorption reached up to 344.827 $mg.g^{-1}$ and fulfilled the Freundlich isotherm with thermodynamic parameters of ÄG° = - 0,589983 $kJ.mol^{-1}$. By delusion process utilizing methanol, AC-alginate beads were able to reuse repeatedly as much as 3 times with a maximum percentage of decolorization from the 1st to the 3rd application, which was 93.77, 77.84, and 61.91%, respectively. According to FTIR analysis, AC-alginate beads had the functional groups C-O-O, O-H, C-H, and -C-CH_3 which played a role in reducing the color of black liquor.

Key words: *Activated carbon, Alginate beads, Black liquor sludge, Decolorization*

Introduction

Bioethanol derived from biomass was developed as one of renewable energy diversification methods to provide environment friendly fuel (Hossain *et al.*, 2019). Numerous, Oil Palm Empty Fruit Bunches (OPFEB) waste is well recognized as the greatest quantities biomass in Indonesia that potentially promised raw material was converted to bioethanol and not interfering food stock like sugars and vegetable (Pradana and Budiman, 2015). During bioethanol pretreatment process, it produced wastewater called black liquor. With regard to bioethanol pilot plant production, once process resulted 74.46

kg of bioethanol with around 3,000 L of black liquor (Sari *et al.*, 2017). Black liquor was identified as harmful wastewater having high turbidity and Chemical Oxygen Demand (COD). As explained by Barlianti *et al.*, (2016), black liquor had pH of 13.09, COD reached 145,000 mg/L, and Total Suspended Solid (TSS) up to 36,550 mg/L.

Black liquor characteristics contained 78% of organic matters and 22% of inorganic compounds that lignin composition in organic composite reached 37.5% out of dried mass and generated blackish brown color of black liquor sludge (Bajpai, 2017). Lignin known as complex aromatic polymer which had hydrophobic and a rigid structure so that difficult to be decomposed (Patil *et al.*, 2016). Black liquor that was not handled properly caused polluted water and affected to aquatic ecosystem and its organisms. Therefore, the study is required importantly to reduce the generation of one hazardous substance in second generation bioethanol production.

Several studies had been done to treat black liquor wastewater for instance green process optimization used Response Surface Methodology (RSM) by white rot fungi and iron oxide coating material named IOCS (Iron Oxide Coating Sand) (Barlianti *et al.*, 2016). On the other hand, adsorption method was convenient, applicable, and operational low-cost in wastewater treatment, especially for decolorization process. Furthermore, the adsorbent in wastewater treatment ought to have high removal capacity, durable quality, good-natured and inexpensive material (Gisi *et al.*, 2016).

Moreover, activated carbon (AC) was famously and mostly recommended to be applied in the wastewater treatment caused by abundant pores that showed the ability to adsorb contaminants such as micro-pollutant, dyes, organic and inorganic compounds, etc. (Kumar and Jena, 2016). Supported by Li *et al.*, (2018), AC also owned low adsorption energy, tasteless, non-toxic, good regeneration, and sustainable material. Even though, decolorization of dyes utilized moving grained adsorbents was not conducive enough to optimize the degradation process so that it needed to modify in order to improve the efficient, effectiveness, and capacity of adsorbent performance.

More importantly, alginate as gel phase established significant results for degrading methylene blue synthetic dyes after the addition of activated carbon mixed by other minerals (Benhouria *et al.*, 2015). Alginate belonging to natural material, was composed by polysaccharide extracted from brown algae which frequently conducted as immobilization biomass material by creating "egg-box" structured and led ionic selective interaction (Mega, 2018; Wang *et al.*, 2018).

The composite consisted of activated carbon and alginate formed small granule called AC-alginate beads. The material means to immobilize activated carbon in order to make stable adsorbent for color decolorization of black liquor. Besides, other advantages of beads shape were larger porous volume than single material and escalated reusability until five times of using (Hassan *et al.*, 2014). Thus, the issues focus on finding the efficiency of activated carbon immobilized alginate and its properties as black liquor decolorization agent.

Materials and Methods

Black liquor sludge with lignin concentration up to 10,000; 30,000; and 50,000 mg/L was obtained from pretreatment process of bioethanol in Research Center for Chemistry, Indonesian Institute of Sciences. Then, commercial activated carbon in 200 Mesh was brought from market. Sodium alginate, calcium chloride ($CaCl_2$), Methanol, and distilled water were prepared from the laboratory.

AC-alginate beads

Sodium alginate 1.5 g was diluted in the 100 mL of distillated water and homogenized using magnetic stirrer on the hot plate. After that, 2 g activated carbon 200 Mesh was added into Sodium alginate solution, and mixed them well. The mixed solution was slowly dropped to Calcium chloride solution 5% in petri dish until beads form transformed. Ac-alginate beads was soaked in the $CaCl_2$ 5% for 2 hours. Next, beads was washed by distillated water three times and dried at room temperature for about 12 hours.

Characteristics of AC-alginate beads

Beads of activated carbon and alginate were crushed to smaller size. Subsequently, the functional groups of material was investigated by Infrared Spectrophotometer belong to FTIR Thermo-Scientific Nicolet iS5 iD5ATR.

Various contact times of black liquor decolorization process

Black liquor 100 mL with 10,000 mg/L was put in the Erlenmeyer 250 mL. Activated carbon-alginate beads as much 35 g was added and homogenized by shaker with 150 rpm at 30 °C for 4 hours. Black liquor solution that contacted with adsorbent subsequently was taken every 1, 2, 3, and 4 hour. Additionally, the samples were centrifuged for 30 minutes at 5,000 rpm and the supernatant measured by UV-Vis spectrophotometer.

Various contact times of black liquor decolorization process

Several concentrations of lignin solution, i.e. 10,000; 30,000; and 50,000 mg/L in which each had 100 mL of volume were poured to Erlenmeyer 250 mL. In the same way, 35 g of activated carbon-alginate beads was added and mixed by shaker rpm at 30°C for 4 hours with 150 rpm. After that, the solutions were examined each hour from 1 to 4 hours. For separating the supernatant so centrifuge used at 5,000 rpm for 30 minutes. The separated fluids were observed by UV-Vis spectrophotometer.

Reusability of activated carbon immobilized alginate

After decolorization process for 4 hours, the adsorbent was washed by distillated water and dried in oven for 12 hours. Next, beads were soaked by methanol in the Erlenmeyer 250 mL. In addition, the materials were rotated with shaker for 2 hours with 150 rpm. Activated carbon-alginate beads was splashed and dried again to reuse in the next decolorization process.

Results and Discussion

Characteristics beads of activated carbon-alginate

Fourier-Transform Infrared Spectroscopy (FTIR) was applied to understand specific functional groups of AC-alginate adsorbent that are described in Fig. 1. On absorbed strip of 3441 cm^{-1} indicated the existence of O-H group including phenolic cluster. Another wavelength number that captured was 2926 cm^{-1} which was a stretching vibration of the methyl (CH_3) group in CH or aliphatic forms. A stretching vibration explained the present of acetyl classification. The results showed that O-H and aliphatic of C-H was realness of activated carbon compound (Sahara *et al.,* 2017). Moreover, absorbed number of 2858 cm^{-1} described the bond between –C–CH_3– which involved on aldehyde groups. While

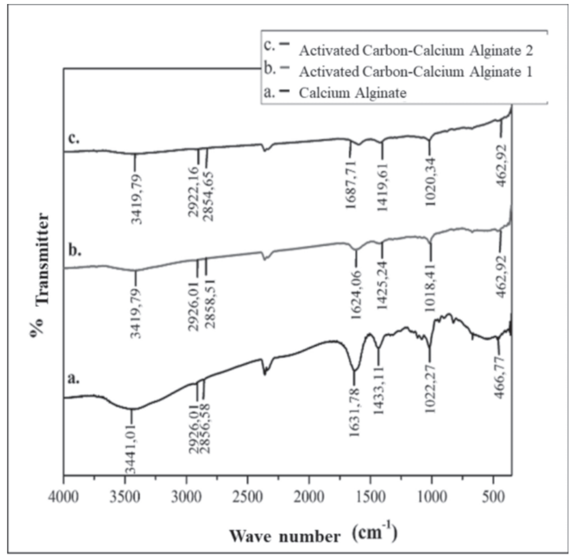

Fig. 1. FTIR Spectra (a) adsorbent of calcium alginate (b) adsorbent of activated carbon-calcium alginate 1 (before decolorization) and (c) adsorbent of activated carbon-calcium alginate 2 (after decolorization)

1631 cm^{-1} indicated vibration and stretching from asymmetric of C–O –O represented alginate molecules.

The blend of activated carbon and alginate material deserved adsorbed friction. The vibration frequency of O-H from carbon and alginate generates smaller or lower and peak of immersion. Furthermore, the effects of resonance of activated carbon material presence caused small wavelength number. As it can be seen from Fig. 1, the application of AC-alginate beads before and after decolorization process described not much significant differences. These merits supported the material to be used more times as agent of decolorization.

Decolorization of black liquor on various times and adsorbents mass

By comparing with alginate belongs to only 59%, activated carbon as obtained bigger points up to 80%. Nevertheless, activated carbon immobilized with alginate gained an enhancement of adsorption ability to 90%. As outlined in Fig. 2, the longer involving time of AC-alginate beads and black liquor, the larger lignin was adsorbed at the maximum contact time of 4h. Since the lignin adsorption process of black liquor was saturated, the interaction time was going to no longer have any effects (Heriono and Rusmini, 2016).

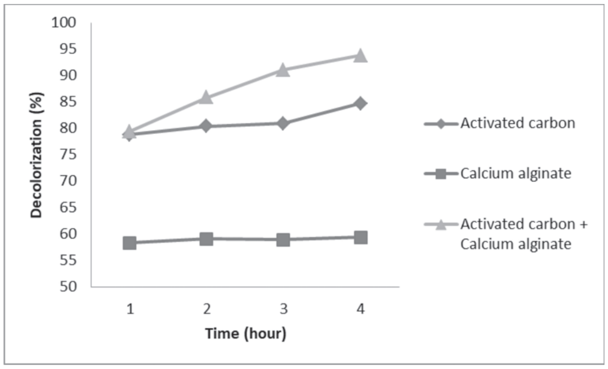

Fig. 2. Removal percentage of black liquor sludge in adsorbents and time varieties

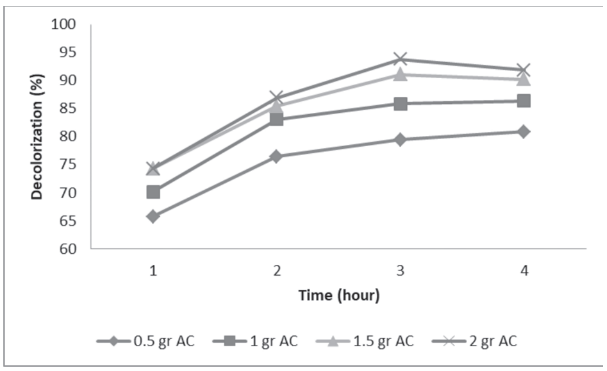

Fig. 3. Removal percentage of black liquor sludge in many kinds of activated carbon weight

On variety concentrations of black liquor were 10,000; 30,000; and 50,000 mg/L, the decolorization capacity of AC-alginate beads experienced dropped percentage of decolorization along with the rising of lignin concentration in the black liquor which were 93.77, 91.15, and 91.14%, respectively. The percentages of lignin degradation in the 30,000 and 50,000 mg/L was similar to each other. Even though, the concentration over than 10,000 mg/L affected to regeneration of beads where high lignin concentration of black liquor encouraged the composites to be easy saturated and defective so that the adsorbent was unable to reuse again. Based on the occurrence, the appropriate concentration for decolorizing and reusing of AC-alginate beads was no more than 10,000 mg/L.

Figure 3 described the mass variation of activated carbon in the composite making in order to investigate the most suitable composition between activated carbon and alginate to degrade black liquor color. The most qualified of lignin removal utilized by 2 g of activated carbon inside the composite. The ratio was found to noticeably affect to its processes. According to Anjani *et al.* (2014), the amount or mass of adsorbent tended to increase of adsorption capability. The greater mass of activated carbon mixed in the composite, the more effective decolorization of black liquor obtained. Also, the phenomenon was related to the ability of an adsorbent to dragg the amount of absorbant called adsorption force (Cahyaningrum, 2016), which in the study gained the optimum of adsorption force of 26.79 mg/g.

Langmuir and Freundlich isotherms

The Langmuir and Freundlich isotherms determined the lignin adsorption capacities in black liquor were presented in Fig. 4. Determinant value as R^2 of Langmuir isothermal equation is 0.7854 while Freundlich was 0.9954. Based on those findings, the lignin adsorption of black liquor by AC-alginate beads met suitably with Freundlich equation. Freundlich equation explained that adsorption occurred on the multilayer process through heterogeneous surfaces (Benhouria *et al.*, 2015). The maximum lignin adsorption capacity of black liquor was pointed at 344.827 mg/g.

Ayawei *et al.*, (2017) highlighted the adsorption process followed to Freundlich isotherm model utilized the assumption that the process happened physically. The Freundlich presumption suggested that the surface of adsorbent was heterogeneous and occurred in many physical layers named physisorption. Physical adsorptions implied the interaction between adsorbent and adsorbate based on Van der Waals force (Langenati *et al.*, 2012). Van der Waals force occurred due to the polarity among the compounds. Activated carbon-alginate beads had many active groups and were able to be categorized as polar matters. In addition, lignin structures also possessed numerous polar properties so that the process of lignin adsorption by AC-alginate beads came through Van der Waals interactions.

Thermodynamics and regeneration of activated carbon immobilized alginate

Gibbs free energy ($\Delta G°$) is one of thermodynamic parameters produced when one molecule is adsorbed by adsorbent and the values equivalent to negative of Gibbs free energy standard (Purnamasari, 2017). Lignin adsorption of black liquor by AC-alginate beads was obtained Gibbs free energy standard ($\Delta G°$) reached (-) 0.589983kJ/mol.

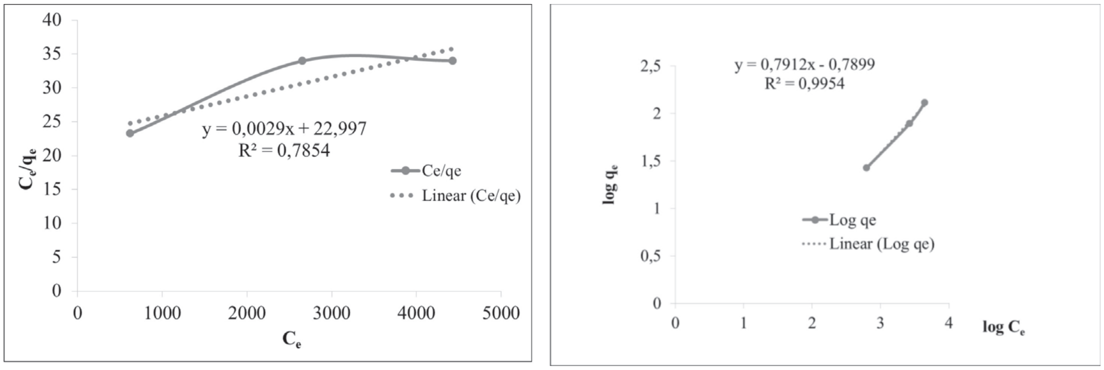

Fig. 4. Langmuir (right) and Freundlich (left) for activated carbon immobilized alginate of adsorption isotherms

A negative sign interpreted that the adsorption process of lignin took placed spontaneously in exothermic reaction with light disturbance system (Sari *et al.,* 2017).

Beads regeneration was the utilization of adsorbent material repeatedly after given a certain treatment. As mentioned before, adsorption process pursued Freundlich isotherm model based on physical interaction or Van der Waals force. Adsorption interactions belonged to Van der Waals bond whose adsorption properties was reversible because the absorbant could be released back into a solvent and resulted re-entering particles (Cahyaningrum, 2016).

The decolorization ability of AC-alginate beads in removing lignin of black liquor after treated by methanol appeared a remarkable decrease from first to third of application. However, AC-alginate beads remained to show their capability to be used more than once with percentage removal for three times utilization at 99.17, 77.84, and 61.91%, respectively. The falling potency of beads due to the reduction of active sites, the adhesion site of adsorbant attached on the composite, and also caused by declining of beads mass or weight along with many beads regeneration processes. Not with standing, activated carbon immobilized alginate in the beads shape owned more benefits and was easier separated between the solution and the adsorbent after decolorization process.

Conclusion

To sum up, the composite material consisted of activated carbon immobilized alginate was found functional group which supported their structures to prove degrading lignin of black liquor up to 90% of 10,000 mg/L in 4 hours. Equally important, the adsorption process was fitted to Freundlich model that mean efficient, effectiveness and capacity of adsorbent was noticeable during the decolorization process of black liquor until three times of material reusability more than 50%.

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