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Mechanism, adsorption kinetics and applications of carbonaceous adsorbents derived from black liquor sludge

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ABSTRACT

Pretreatment processes in second generation bioethanol production produce a lignin-based black liquor. Polyaluminum chloride (PACl) was employed to treat black liquor using coagulation, in which the generated sludge was converted to a carbonaceous adsorbent. The bioethanol black liquor sludge-based carbonaceous adsorbent (BBLS-CA) was characterized physically, and its adsorption mechanism, kinetics, and ability to absorb methylene blue (MB) were evaluated. Additional studies revealed the performance of BBLS-CA to treat peat water and landfill leachate. The results demonstrate that BBLS-CA decolorized a 100 mg/l solution of MB by 98% within 30 min. MB components reclaimed from BBLS-CA reveal the presence of NH_2, substituted and *p*-disubstituted benzene rings, and $=CH_2$, suggesting that physical and chemical mechanisms are operative during adsorption. Isotherm analysis reveals that adsorption equilibrium followed the Langmuir model and exhibited pseudo second-order kinetic behavior. BBLS-CA adsorbed 100% iron and manganese; and remediated 72% color and 67% COD in peat water, as well as 57% COD in landfill leachate. This report highlights a by-product from black liquor sludge that can be applied to the removal of wastewater pollutants. Further, the development of method is required to obtain activated carbon which fulfills standard properties of activated carbon.

1. Introduction

Wastewater treatment is required before its disposal to territorial waters due to its toxicity, poor esthetic characteristics, eutrophication, and negative outcomes to aquatic life [1]. Coagulation is a commonly used method to treat organic pollutants in wastewater. In this regard, polyaluminum chloride (PACl) has been found to be an effective coagulant to treat wastewater from pulp and paper mills and dyes. Indeed, reductions of approximately 84% and 92% in the COD and color of pulp paper mill wastewater were measured, respectively, when PACI was used, and approximately 99.5% of the suspended solid was precipitated [2]. Unfortunately, the inherent disadvantage of the coagulation method is the production of large quantities of sludge, which must be disposed of in landfills. However, this is not an ideal solution because the total dissolved salt content in the sludge creates additional landfill problems such as landfill leachate formation and long-term soil fertility reduction [3].

One valuable application of PACl may be found in second-generation bioethanol production in Indonesia. A total of 3000 l of black liquor is generated from the pre-treatment process for every 76.46 kg of bioethanol derived from oil palm empty fruit bunches [4]. Black liquor that contains a large amount of lignin must be treated effectively before it is discharged into territorial waters due to its negative environmental effects to aquatic ecosystems. Lignin is a complex organic polymer with strong molecular bonds. In alkaline solutions, the presence of lignin results from an alkaline pre-treatment process in bioethanol production, which contributes to the dark coloration of the liquor [5]. Such coloration inhibits the penetration of sunlight into water and reduces its aesthetical value.

Black liquor can be treated using physical, chemical, and biological methods [2,4,6]. Biological approaches have been used to degrade dissolved organic compounds and to reduce toxicity, but such methods are only useful when small concentrations of black liquor are present [4,6,7]. Employing the coagulation method for either black liquor or organic-based wastewater is usually the

Abbreviations: BBLS-CA, bioethanol black liquor sludge-based carbonaceous adsorbent; BET, Brunner–Emmett–Teller; FT-IR, Fourier transform infrared; MB, methylene blue; PACl, polyaluminum chloride; SEM, scanning electron microscopy; SEM-EDX, scanning electron microscopy-energy dispersive using X-ray; COD, chemical oxygen demand; LC–MS, liquid chromatography-mass spectrometry.

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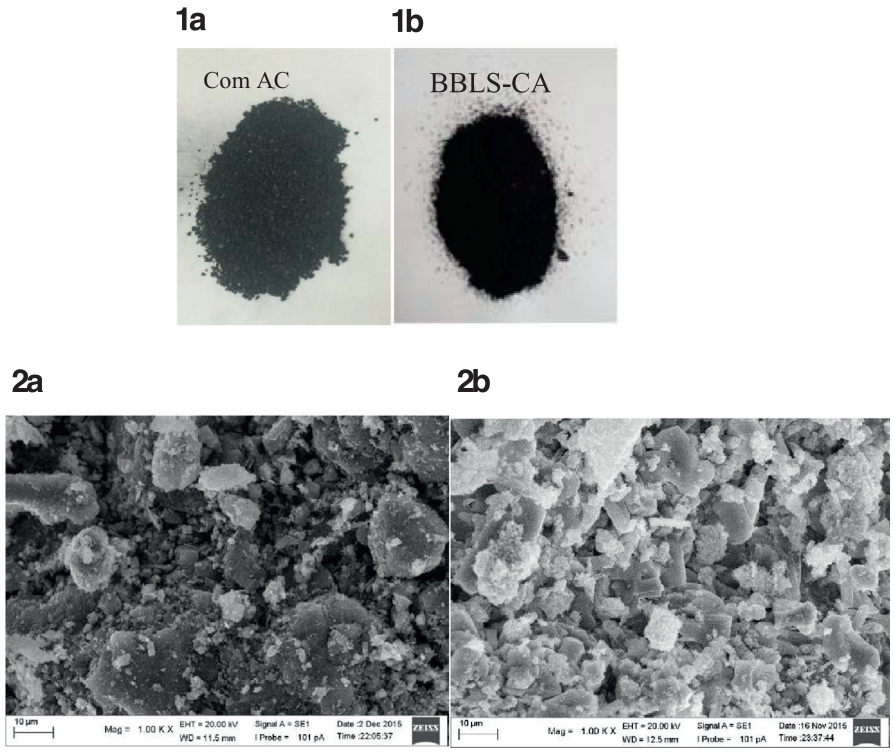

Fig. 1. (1a)–(2a): appearance and SEM of commercial activated carbon (1b)–(2b): appearance and SEM of BBLS-CA.

Table 1
Sludge component analysis.

Sludge samples	Dry Sludge (g/l)	Lignin (%)	Hemicellulose (%)	Ash (%)
Sludge from PACl	71.29	30.99 ± 0.456	–	0.1867 ± 0.100
Sludge from H_2SO_4	42	17.36 ± 0.330	7.313 ± 0.116	0.7567 ± 0.090

(Source: measurement and data from [5])

first treatment step [8]; hence, this process generates a significant amount lignin within the sludge. However, excess lignin in black liquor sludge is a precursor for activated carbon production since lignin contains a high carbon and low ash content, as well as a molecular structure that is similar to bituminous coal [9]. Activated carbon has a porous structure that can adsorb various pollutants, such as dyes and metal ions [10]. Applications like these stimulate great interest in activated carbon, or at least carbonaceous materials that produce activated carbon, which results in commercial activated carbon to be expensive. Thus, studies concerning the production of activated carbon materials have been widely investigated.

In addition to black liquor, the treatment of dye-based wastewater, which is produced from various industrial activities, is another problem that has increased significantly in Indonesia. In fact, this issue has even been placed on Indonesia's national agenda in an attempt to address its consequent environmental repercussions. As with black liquor, several methods have been developed to remove dyes from contaminated water, including physical, chemical, and biological approaches [4,11,12]. Clearly, access to clean water is vital to a healthy environment and lifestyle. However, the inhabitants of Riau, a province in Indonesia, experience a scarcity of clean water since almost 45% of this land is peat. Peat water may pose a serious environmental problem because of its taste and odor. In Riau, peat water is the area's primary water source, and humic acid is one its main components, which causes the water to be colored brown or yellow. The molecular structure of humic acid includes aromatic and aliphatic residues with numerous substituents such as OH groups, ketones, carboxylic acids, amino acids/peptides, saccharides, and amino saccharides [13]. Another issue concerning access to clean water involves landfills. Leachate is a liquid that passes through landfills and contains a large amount of organic and inorganic contaminants; thus, it is a significant threat to surface water and groundwater. For these reasons, landfill leachate treatment has been given significant attention in recent years, and collectively, methods to remove humic acid and landfill leachate for cleaner water represent ongoing research initiatives.

To this end, adsorption using activated carbon or carbonaceous adsorbents derived from waste is an alternative method to remove dyes and other organic pollutants from wastewater because of its economic feasibility and simplicity in design and operation. Fu et al. [14] reported the application of a lignin-based activated carbon to remove methylene blue, a dying agent used in the textile industry, from aqueous solution with a maximum adsorption capacity of 92.51 mg/g. To investigate this issue further, the present report aims to convert black-liquor-sludge-containing PACl-lignin into a carbonaceous adsorbent. The prepared adsorbent is then analyzed for its ability to adsorb conditioned wastewater containing methylene blue. A characterization of the carbonaceous adsorbent, its decolorization percentage of methylene blue solutions, and identification of the adsorption mechanism were analyzed by SEM-EDX, FT-IR, spectrophotometry, and LC–MS. Additionally, isotherms and the adsorption kinetics were also evaluated, and the carbonaceous adsorbent was applied to treat peat water and landfill leachate to ascertain its adsorption performance.