Biochar Modification with Cetyltrimethylammonium Bromide (CTAB) For Utilization in The Adsorption Process: A Mini-Review

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ABSTRACT

The properties of an adsorbent is important qualities that need to be determined before its utilization in adsorption studies. Biochar is one of the most applied adsorbent in adsorption studies with high removal performance often reported. However, biochar performance is considered weaker than other adsorbents e.g., activated carbon, especially for the removal of anionic pollutants. The performance of biochar in removing anionic pollutants can be enhanced through modification with cetyltrimethylammonium bromide (CTAB), a cationic surfactant. CTAB can be introduced on the biochar surface through ex-situ or in-situ method where the immobilization of the micelles on the biochar surface will enhance the interaction between the biochar and anionic pollutants and subsequently enhancing the removal performance.

Keywords: Biochar, adsorption, cationic surfactant, anionic pollutants, micelles.

1. INTRODUCTION

Adsorption is one of the most well-known methods utilized for the remediation of pollutants present in the environment. High preference for the adsorption method is attributed to its simple design and process, cost-effectiveness and high removal efficiency attained [1]. Various adsorbents have been utilized in adsorption process such as activated carbon, biochar, zeolite, etc., where good removal performance is often reported. The usage of biochar as an adsorbent in adsorption is highly appealing due to the simple production process in which no chemicals are required which resulted in a reduction of approximately 45% in cost [2]. The precursor employed in the production of biochar is widely available, mostly as waste from other processes [3]. This will result in the simultaneous production of valuable adsorbents and the reduction of unwanted waste in the environment.

Biochar has been reported to attain high removal efficiency in removing various pollutants, which can be attributed to its high surface area and good microporous structure [4]. However, the performance of biochar is considerably lower than that of other adsorbents, especially activated carbon, mainly due to the limited availability of adsorption sites [5]. Additionally, as biochar typically possesses a negative surface charge, its performance in removing anionic pollutants, e.g., anionic dye, metal anion, etc., is impoverished due to electrostatic repulsion between the biochar and the pollutants [6]. Therefore, various studies have suggested the modification of biochar with cationic surfactant, which will lead to an increase in positive charge on the biochar surface.

In the context of anionic pollutants, biochar should be modified with any chemicals that would alter the surface charge of biochar from negative to positive, thus allowing electrostatic attraction to occur between the adsorbent and pollutant [6]. Cetyltrimethylammonium bromide (CTAB) is

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a cationic surfactant containing both a positively charged polar hydrophilic head and a non-polar hydrophobic tail, as shown in Figure 1 [7]. CTAB has been employed in the production of modified biochar (also known as engineered biochar), which has resulted in an enhancement of layer spacing, improvement of surface area, and an increment of positive surface charge and hydrophobicity [8]. Positively charged CTAB micelles are attached to the surface of the biochar which allows the anionic pollutants to be strongly attracted and resulted in their removal. Due to the hydrophobic nature of CTAB-modified adsorbents, any pollutants with hydrophobic nature may also be removed through hydrophobic-hydrophobic interaction.

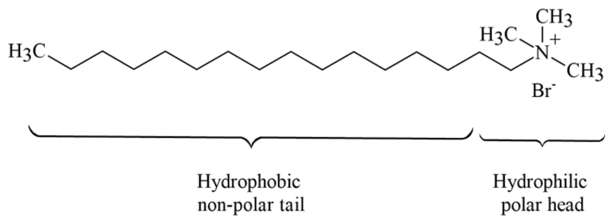

Figure 1. Molecular structure of CTAB.

This paper will serve as a summary of the methods utilized for the modification of biochar using CTAB, the mechanism of pollutant removal, and the list of studies employing CTAB-modified biochar in the adsorption of anionic pollutants.

2. MODIFICATION METHOD

CTAB may be introduced onto the biochar through two methods, namely: (i) ex-situ method, where CTAB is immobilized onto the adsorbent prior to adsorption; and (ii) in-situ method, where CTAB is added during the adsorption process.

Ex-situ method is widely reported in various studies where prepared biochar is completely soaked with CTAB solution and intensively stirred using appropriate instruments, e.g., incubator shaker, magnetic stirrer, orbital shaker etc., followed by filtration, washing, and drying process. Based on the literature, the duration of mixing and stirring of the CMC/biochar mixture varies from several hours up to 3 days at room temperature [7], [9]. The resultant is filtered by filter paper, washed by deionized water, and oven-dried (60 – 105 °C) [2], [10]. The only exception was reported by Hua *et al*. [8], where the mixing and stirring were conducted at a higher temperature (60 °C) for a short period of 2 hours. CTAB-modified biochar obtained is kept in appropriate containers prior to its use in the adsorption process.

On the other hand, the modification of biochar with CTAB using in-situ method is achieved by adding the CTAB solution into the pollutant-containing wastewater where the surfactant molecules added during the removal process are bonded concurrently onto the surface of the biochar and pollutants. The utilization of in-situ CTAB modification was reported by Li *et al*. [11] for the removal of orange II dye on sugarcane bagasse biochar and by Kamenická et al. [2] for the removal of flufenamic acid on commercial biochar, where the removal performance was significantly enhanced by introducing CTAB onto the wastewater during the adsorption process.

3. CTAB IMMOBILIZATION ON BIOCHAR

The introduction of CTAB was reported to increase the positive charge on the biochar surface and its hydrophobicity. To achieve this, the concentration of CTAB utilized should be higher than the critical micelle concentration (CMC) of CTAB (0.335 g/L), as the surfactant molecules will only sufficiently assemble to form micelles at CMC or higher while dissolving at a lower concentration. Figure 2 shows the micelles immobilization on the biochar surface at different CTAB concentrations.

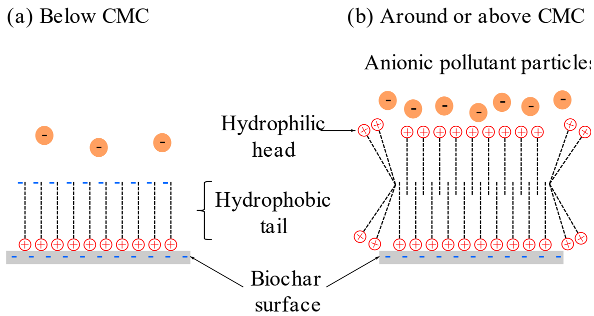

Figure 2. Micelles formation on biochar surface at different CTAB concentration.

As previously discussed, the surface of biochar typically contains a negative charge. During the mixing process where CTAB is introduced onto the biochar, the hydrophilic head of CTAB molecules was able to be attracted electrostatically to the negatively charged biochar surface, which subsequently resulted in the immobilization of CTAB and complete coverage of CTAB onto the biochar surface. At concentrations below CMC, the hemimicelles covering the biochar surface consist of a negatively charged polar hydrophobic tail in the outward position, as shown in Figure 2(a) [12], [13]. This configuration is detrimental to the adsorption of anionic pollutants due to the electrostatic repulsion phenomenon, which prevents anionic pollutants from being adsorbed onto the modified biochar.

With the increment of CTAB concentration up to CMC and beyond, the formation of admicelles takes place, which leads to a positively charged polar hydrophilic head being in the outward position as shown in Figure 2(b) [14]. The development of admicelles will allow electrostatic attraction between anionic pollutants and positively charged hydrophilic heads, which subsequently will result in an improvement in removal performance. However, increasing CTAB concentration beyond CMC is not necessarily beneficial to the adsorption process, as the admicelles may be formed in the CTAB solution without being immobilized on the biochar surface [12]. This will eventually result in insignificant modifications, as the removal performance obtained may be similar to that of unmodified biochar. This phenomenon has been reported by Nagireddi et al. [15] on the removal of palladium ions in chloride solutions ($PdCl^+$, $PdCl_2$, $PdCl_3^-$, $PdCl_4^{2-}$, $Pd(OH)_4^{2-}$) using CTAB concentrations between 1 CMC and 4 CMC, where the removal performance decreased beyond 2 CMC. Additionally, hydrophobic pollutants may also be adsorbed by CTAB-modified biochar due to hydrophobic interaction (π-π interaction) with the hydrophobic polar tail of CTAB molecules [9].

4. CTAB-MODIFIED BIOCHAR STUDIES

Various studies have been conducted and reported on the efficiency of CTAB-modified biochar in removing anionic pollutants present in wastewater, where significant enhancements in removal were attained compared to unmodified biochar. Table 1 summarizes related CTAB-modified biochar adsorption studies with their respective biochar and contaminants utilized.

Table 1 List of adsorption studies using CTAB-modified biochar

Biochar precursor	Contaminant	Ref.
Commercial	Flufenamic acid	[2]
Rice straw	2,4-dichlorophenol	[5]
Peanut shell	Hexavalent chromium	[6]
Coffee husk	Reactive yellow 145, reactive red 195, reactive blue 222	[7]
Orange peel	Congo red	[8]
Pine nut shell	Acid chrome blue K	[9]
Rice husk	Nitrate	[10]
Sugarcane bagasse	Orange II	[11]
Oil tea shell	Nitrate	[16]

The studies listed in Table 1 show that CTAB-modified biochar was able to enhance the removal of various groups of anionic pollutants, e.g., dyes, phenols, nitrates, heavy metals, and pharmaceuticals. This proves that CTAB-modified biochar is effective as an adsorbent for the remediation of various types of anionic pollutants. In the majority of these cases, the removal performance of the anionic pollutants was more than doubled compared to unmodified biochar. Li et al. [11] reported that the removal of orange II dye increased from 1.66 to 4.42 mg/g with the utilization of CTAB-modified sugarcane bagasse biochar. Kosaiyakanon et al. [7] showed in their study that the utilization of CTAB-modified coffee husk biochar were able to enhance the removal of three different reactive dyes by 9-fold. In the context of adsorption, the reusability of a particular adsorbent is an important parameter to determine the reusability and stability of the adsorbent. Hua et al. utilized CTAB-modified orange peel biochar for the removal of Congo red dye, where the modified biochar possessed good stability and reusability.

5. CONCLUSION

The performance of biochar in removing anionic pollutants, which can be considered weaker compared to other adsorbents, has been reported to be enhanced through modification with CTAB in various studies. CTAB-modified biochar has been successful in improving the removal efficiency of various anionic pollutants, e.g., dyes, phenols, nitrates, heavy metals, and pharmaceuticals; thus, it can be categorized as a promising adsorbent for remediating pollutants in wastewater. The utilization of surfactant-modified adsorbent, not solely restricted to CTAB, should be explored more on other pollutants, especially newly emerging pollutants, to determine its suitability and usability.

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