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Activated Low Rank Coal (LRC) Utilization as an Adsorbent for Synthetic Dye Removal

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Abstract. Among cationic and anionic dyes, Rhodamine-B (Rh-B) and Methyl Orange (MO) are commonly used in the chemical industry, such as textile industry. These dyes, especially Rh-B, are known to be toxic and carcinogenic, and their presence in water effluents has been widely studied. In this study, the adsorbent was prepared by activating East Kalimantan's low-rank coal (LRC) with a 30 % phosphoric acid solution (H3PO4). The aim of this research was to assess the effectiveness of activated LRC as an adsorbent in the adsorption process for Rh-B and MO dye removal. The best results for Rh-B and MO dye removal were obtained with an adsorbent dosage of 100 mg, a contact time of 10 minutes (for Rh-B) and 5 minutes (for MO), and a pH of 5 for Rh-B and 4 for MO. The Rh-B dye removal efficiency was 52.4405 % and 97.59 % for MO. The findings on the present investigation provide valuable insights into the use of activated East Kalimantan's LRC as an adsorbent for Rh-B and MO dye removal.

1 Introduction

The issue of water scarcity is indeed a significant global challenge that needs to be addressed. Chemical industries such as textile industries are one of the main sources of this issue that releases tremendous wastewater to water bodies without a pretreatment. One of the most abundant generators of dye in industrial textile wastewater is different types of reactive and synthetic dyes, like Rh-B and MO which are commonly used, have a complex aromatic molecular structure, making them less biodegradable, more stable, and resistant to water, light, weather, and detergents [1]. In general, their presence in wastewater induces high alkalinity, high concentration of organic materials, and strong color in comparison with other dyes. Directly releasing of synthetic dyes into the environment tend to significantly causes hazardous risks to human beings and aquatic life by affecting photosynthetic activity due to reduced light penetration [2].

To address this environmental issue, a different treatment techniques have been implemented to reduce the dye concentration of effluent wastewater including physical, biological, chemical and their hybrid processes [3] such as electrochemical oxidation [4], photocatalysis [5], membrane filtration [6], coagulation-flocculation [7] and adsorption

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[8,9]. Among them, the physical methods consists of the most economical techniques namely adsorption, coagulation, flocculation and filtration [10]. However, due to its simplicity, its high efficiency, low cost and flexible design, adsorption has evolved as an effective process in dye removal [11]. Moreover, the adsorption process can be cost-effective by using low-cost adsorbent materials that can be regenerated and reused, extending their lifespan and reducing waste [12]. Therefore, this study aims to assess the effectiveness of activated LRC as an adsorbent in the adsorption process for Rh-B and MO dye removal.

2 Method

The preparation of East Kalimantan's LRC as an adsorbent begins with the cleaning, crushing, and screening the particle in a 100 +120 mesh immediately. After that, the LRC is carbonized at 600 ^{0}C for 3 h using muffle furnace box QSH-1200M 200x200x200 mm resistance (made in Germany) before activated using 30 % concentration of H3PO4 for 8 h [7]. The immersion results were then washed to neutral pH and continued with heating process at 800 ^{0}C for 2.5 h in the furnace. Rh-B and MO was implemented for evaluating the adsorbent's effectiveness.

The Rh-B and MO dye adsorption were carried out in batch experiments utilizing activated LRC as an adsorbent with several process variable, such as adsorbent dosage (60 – 140 mg), contact time (5 – 60 minutes), and pH level (3 - 9), examined for 100mg/L initial dye concentration. Each erlenmeyer flask contained 100ml of dye solution with agitation kept at 150 rpm and 30^{o}C were carried out. In the end of the process, the shaker was switched off and the dye concentration (Rh-B and MO) was measured using Hitachi-double beam spectrophotometer UV-Vis U-2900/2910UV at maximum wavelength (λ_{max}) for Rh-B and MO dye.

3 Results and discussion

3.1 Results

Fig. 1 illustrates the effect of pH on the removal efficiencies of Rh-B and MO dyes. The results show that the maximum removal efficiencies were achieved at pH 5 for Rh-B and pH 4 for MO. **Fig. 2** presents the effect of adsorbent dosage, where the optimal removal for both dyes was obtained at an adsorbent dosage of 100 mg for an initial dye concentration of 100 mg/L. **Fig. 3** shows the effect of contact time, indicating that the maximum removal efficiencies were reached at 10 minutes for Rh-B and 5 minutes for MO.

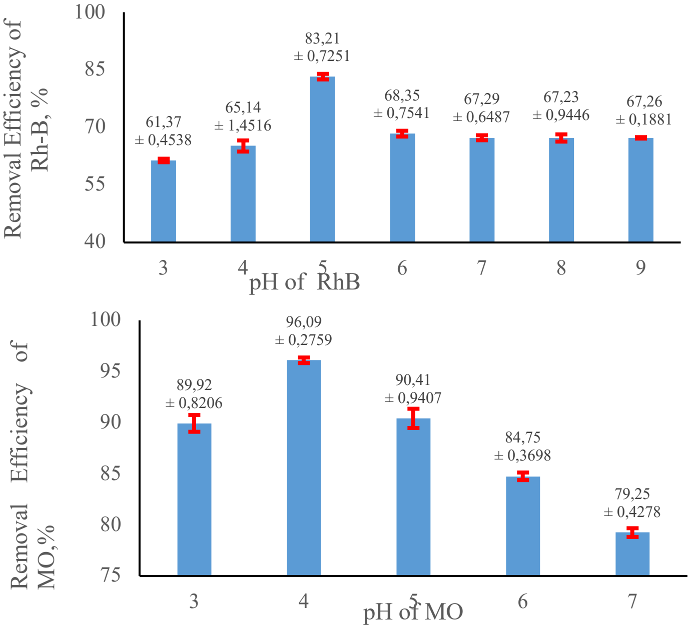

Fig. 1. The effect of pH on the removal efficiency

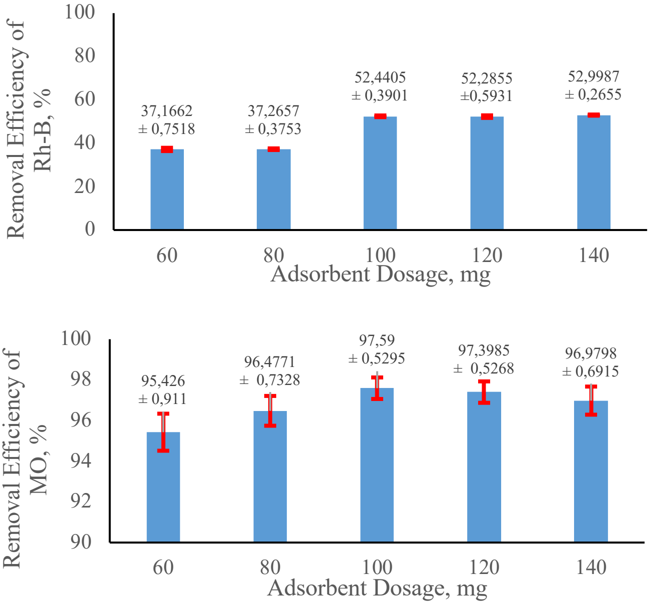

Fig. 2. The effect of adsorbent dosage on the removal efficiency

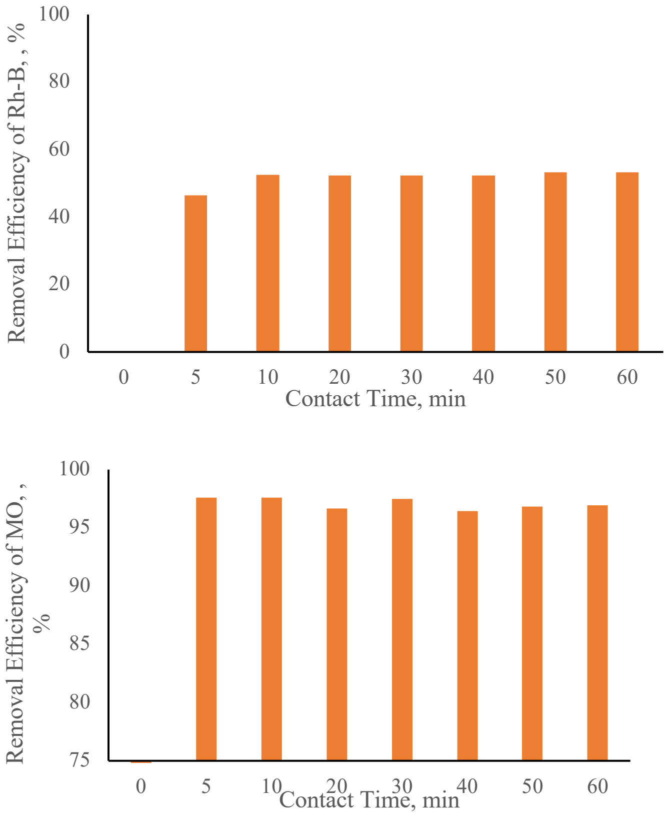

Fig. 3. The effect of contact time on the removal efficiency

3.2 Discussion

The pH of the dye solution is a critical parameter that strongly influences the adsorption process, particularly affecting the interactions between the adsorbent surface and the dye molecules, as well as the adsorption capacity and mechanisms. This behavior is closely related to the point of zero charge (pHpzc) of the adsorbent. The results for Rh-B and MO dyes show that dye removal increases with increasing pH, and then decreases beyond a certain pH value. The maximum dye removal of Rh-B for adsorption process was achieved at at pH 5 and for MO at pH 4. When pH of dye solutions > pH_{pzc} (the value of pH_{pzc} for activated LRC is 6.2), the cationic dye adsorption is favorable. On the other hands when pH of dye solutions < pH_{pzc}, the interaction between the Rh-B dye solution and the adsorbent surface will weaken, thereby reducing the Rh-B dye removal such as shown in **Fig. 1**. The MO dye solution's interaction with the adsorbent surface is similar. The adsorbent surface will be negatively charged when the pH of the MO dye solution is higher than the pH_{pzc} of the adsorbent, making it more effective in adsorbing cations, and vice versa.

Fig. 2 demonstrates the effect of adsorbent dosage on the respective Rh-B and MO dye removal efficiency. The experimental results showed that the Rh-B dye removal increased from 37.1662 ± 0.7518 % to 52.4405 ± 0.3901 % as the dosage increased from 60 mg to 100 mg for initial dye concentration of Rh-B 100 mg/L and then remained nearly constant after that point. The same condition with the MO dye removal which increases from 95.426 ± 0.911 % to 97.59 ± 0.5295 % as the dosage increased from 60 mg to 100 mg and then remained nearly constant after that point. The higher absorbent dosage provides greater surface area and subsequently provides more active binding sites for adsorption of the dyes. A further increase in the adsorbent dosage from 100 mg to 140 mg in 100 mg/L of initial dye concentration may causes more collisions between the adsorbent particles and due to decrease the adsorbed amounts of dyes. This phenomenon is often caused by the aggregation (clustering) of colliding adsorbent particles, which reduces the active surface area (the available active sites of the adsorbent become unsaturated or not fully utilized), resulting in a decrease of the adsorption capacity [13]. Finally, the maximum Rh-B and MO dye removal was achieved at 100 mg adsorbent dosage for 100 mg/L of the Rh-B and MO initial dye concentration.

The effect of contact time evaluated at the optimum acidity (pH 5 for Rh-B and pH 4 for MO) and 100 mg adsorbent dosage as shown in **Fig. 3**. Based on **Fig. 3**, up to the first 10 minutes of contact time, the adsorption of Rh-B dye on the adsorbent surface area increased. The adsorption process reached equilibrium at t=10 minutes, after the active sites of the adsorbent have been fully occupied with the Rh-B dye solution and are no longer active sites readily available for further adsorption process. So, further increase the contact time (from 10 to 60 minutes), the Rh-B dye removal remained nearly constant. The adsorption processes that reach equilibrium very quickly (within 5 - 10 minutes) usually follow the pseudo-second order (PSO) kinetic model. This model is based on the assumption that the rate-limiting step is chemisorption involving valence forces through the sharing or exchange of electrons between the adsorbate and the adsorbent [14]. The short equilibrium time indicates that the adsorption rate is not limited by slow pore diffusion, but rather by the availability of active sites on the adsorbent surface. Meanwhile, the adsorption process for MO dye reached equilibrium at t = 5 minutes, and the removal efficiency remained nearly constant with further increases in contact time. The shorter equilibrium time for MO can be attributed to differences in molecular size and weight between MO and RhB. MO has a smaller molecular size and lower molecular weight than RhB. In addition, MO has a more linear and planar structure, whereas RhB has a bulkier xanthene structure. As a result, RhB molecules tend to diffuse more slowly to the active sites of the adsorbent compared to the smaller and more linear MO molecules.

4 Conclusion

The utilization of activated East Kalimantan LRC as an adsorbent in the adsorption process is effective enough for Rh-B and MO dye removal. The findings revealed that under the best condition (pH of 5, an adsorbent dosage of 100 mg, a contact time of 10 minutes), the removal efficiency of Rh-B was 52.4405 % and the best condition for MO dye removal efficiency of MO was 97.59 % obtained at pH of 4, an adsorbent dosage of 100mg, a contact time of 5 minutes.

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