

Zinc Chloride Recovery for Synthesis of Porous Adsorbent from Lipid Condensate for Dye Removal

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Abstract. Zinc chloride (ZnCl_2) is one of the most frequently used chemical activators for the synthesis of porous adsorbent. However, ZnCl_2 activator is constrained by the corrosive nature of zinc cations (Zn^{2+}) and accumulation of chemical waste, posing a significant environmental concern. To address these issues, the potential of recycling the ZnCl_2 recovered from washing filtrate is explored as a resource utilization strategy. Lipid condensate, a by-product from the sterilization process in palm oil mill is proposed as a precursor for activation using the recovered ZnCl_2 washing filtrate. Preliminary insights suggest that the absorption performance of the adsorbent produced with recovered ZnCl_2 may exhibit a comparable result to that prepared using fresh ZnCl_2 . Nevertheless, further reuse of the activator beyond the first cycle of recovered ZnCl_2 may results in a significant decline of adsorption performance. This commentary highlights a practical approach for ZnCl_2 recovery aimed at reducing environmental burden while maximizing the utilization efficiency of ZnCl_2 .

Introduction

Palm oil mill effluent (POME) is recognized as one of the main contributors to water pollution in Malaysia, with a pollution load reported to be up to 100 times higher than municipal sewage [1,2]. In recent years, the palm oil industry has generated between 50 to 70 million m^3 of wastewater during its product processing [3]. Lipid condensate, a brownish effluent by-product generated from sterilization process in palm oil mill is one of the major sources of POME. It is rich in organic matter and content high amounts of chemical oxygen demand (COD), biological oxygen demand (BOD) and suspended solids [4,5]. If discharged without proper treatment, this waste can cause severe environmental issues such as eutrophication and soil pollution. One of the promising pathways of lipid condensate utilization is by converting this material into activated carbon (AC).

Its utilization as a precursor for AC synthesis through ZnCl_2 activation holds a promising valorization pathway for palm oil waste streams. However, during the impregnation and activation stage, a large volume of ZnCl_2 is typically consumed, leaving significant fraction remaining in the post-treatment effluent [6]. Frequent use of single-use ZnCl_2 leads to accumulation of chemical-laden wastewater, posing severe risks of ZnCl_2 leaching into aquatic ecosystems and impairing soil health. By developing a sustainable strategy to recover and recycle ZnCl_2 from lipid condensate derived AC, this helps in minimizing the environmental burden while simultaneously reducing the production cost of AC.



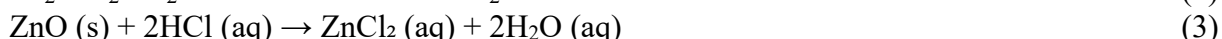
To address this issue, this study proposed a strategy for ZnCl_2 recovery from washing filtrate in post-activation stage as solution. The approach to recovered ZnCl_2 can still be able to perform effective activation, yielding results comparable with one produced with fresh ZnCl_2 . Several studies have proven the effectiveness of recycled ZnCl_2 in activation of AC [6,7,8]. In this study, the potential of ZnCl_2 recovery is reviewed for converting lipid condensate into AC for dye removal. The aim of this approach is to minimize the chemical effluent accumulated associated with ZnCl_2 , thus contributing to better sustainable management in activated carbon production. This solution aligns with the United Nations Sustainable Development Goal 12 emphasizing Responsible Consumption and Production, promoting a circular economy within the industrial sector.

Activation Mechanism of ZnCl_2

AC typically exhibits an amorphous and non-graphitic micro crystalline with a turbostratic structure [9,10]. This structure formed when AC undergoes two main stages: carbonization and activation [9,10,11,12]. During carbonization process, the precursor is heated at elevated temperature (500-700°C) in an inert atmosphere (e.g., nitrogen or argon) [9,13]. This process removes the volatile component within the precursor to produce a rudimentary carbon matrix. Meanwhile, activation process has role in developing porous structure and enhancing the surface area of the AC. Activation approaches are categorized into physical activation and chemical activation. Physical activation is a method of employing oxidizing gases such as CO_2 or steam at elevated temperature [14] while chemical activation involves the use of chemical activation such as ZnCl_2 , KOH and H_2SO_4 as dehydrating catalyst for pore formation development [9,10]. Prior studies have reported that chemical activation is among the preferred methods as it yields better results based on surface areas formation, pore size distribution and adsorption capacity at lower activation temperatures compared to physical activation [11].

Activation agents are mainly responsible for altering the thermal decomposition pathway and aid in developing micropores and mesopores in the carbon char upon impregnation. Different activators formed distinctive pore types and yield [10]. Among other activators, ZnCl_2 has been extensively employed in AC synthesis owing to its strong dehydrating capability and ability to produce well-developed porous carbon. Its unique characteristics as Lewis acid help in lowering the decomposition temperature of lignocellulosic and cellulosic components in precursor [11,15]. This helps in facilitating the breakdown of precursor while removing moist without melting it during heat treatment (carbonization). The strong dehydration effect plays role in removing oxygen and hydrogen in the form of water while stabilizing the carbon structure. The presence of zinc ions (Zn^{2+}) is responsible for assisting the aromatization of carbon structure while ZnO prevents the carbon structure from collapsing [12]. As the structure stabilizes, more microspores and mesopores are developed within carbon structure, resulting in high surface area.

During activation stage, ZnCl_2 acts as dehydrating agent to react with water released from scission of glycosidic bond and elimination of carboxyl and hydroxyl groups to form intermediates $\text{Zn}_2\text{OCl}_2 \cdot 2\text{H}_2\text{O}$ [6,16]. This intermediate, resembles a cement like material is mainly in amorphous phase with minor of crystalline phase, can be found within the AC at temperature of 400-500°C [16]. Subsequently, at temperature above 400°C, the intermediate is decomposed into volatile ZnCl_2 , ZnO and steam under pyrolysis [6,16]. Eqs. (1)-(2) show the chemical reactions involved. After activation, the unreacted ZnCl_2 and ZnO remain within the carbon structure which needs to be removed through washing procedure.



Recovery of ZnCl_2 can be achieved by washing with either water or dilute acid (commonly HCl). When washing the with water, the unreacted ZnCl_2 remain within the carbon structure

dissolved into the washing filtrate. While washing with acid like HCl will further converts ZnO back into ZnCl₂ as shown in Eq. (3). Thus, the washing filtrate will contain both regenerate ZnCl₂ (for acid washing) and unreacted ZnCl₂ which can be recycled for subsequent activation. This procedure also assists in clearing the blocked pore channels, exposing additional pore and helping to neutralize the AC [6].

Material and Methods

Lipid condensate was obtained from the sterilizer of palm oil mill in Johor state of Malaysia. The chemicals used, zinc chloride (ZnCl₂) and methylene blue were supplied by R&M Chemicals (Essex, UK). All the chemicals were analytically graded and used directly as received.

A10 g of lipid condensate was mixed with ZnCl₂, as the activator according to predetermined ratios of 1:2 (lipid condensate: activator). The mixture was stirred thoroughly to ensure even distribution of the activation agent within the lipid condensate. The obtained samples undergo pyrolysis in a furnace at 600°C for 1.5 h, fostering porosity and the desired activation level in the carbon material. The resulting AC was washed with distilled water on a hot plate stirrer to ensure complete elimination of the activating agent. Subsequent to the washing procedure, the sample was dried in an oven overnight. The recovered ZnCl₂ from washing filtrate was reused for another activation process. A new batch of 10 g of lipid condensate was mixed with the recovered ZnCl₂ and dried in an oven overnight before undergoing activation in the furnace, following the same conditions as the initial procedure. This step was repeated for another second recovered ZnCl₂ cycle. The surface area of the lipid condensate AC was measured by BET at liquid nitrogen adsorption of 77 K, using Micromeritics ASAP 2020 analyzer.

The preparation of methylene blue (MB) solution was carried out by dissolving the dye in distilled water to produce a series of concentrations ranging from 10 mg/L to 500 mg/L. The adsorption experiment was conducted by introducing 20 mg of activated carbon into 20 mL of the MB solution. The mixture was maintained at room temperature and allowed to equilibrate for 7 days. The equilibrium adsorption capacity (q_e) was calculated using Eq. (4),

$$q_e = \frac{(C_o - C_e)V}{W} \quad (4)$$

where C_o denoted as initial concentration (mg/L), C_e as equilibrium concentration (mg/L), V as volume of dye solution (L) and W as mass of adsorbent (g).

Results and Discussion

Characteristics of AC

The yield and surface area of lipid condensate AC are presented in Table 1. Lipid condensate AC prepared with fresh ZnCl₂ produced the highest yield compared to ACs obtained using recycled ZnCl₂ (ZR1: 21.96%; ZR2: 18.64%). This trend exhibited a gradual reduction of yield in subsequent activation of AC, implying that the effective amount of ZnCl₂ available becomes lesser with each reuse. During pyrolysis process in subsequent activations, some parts of ZnCl₂ may have volatilized and evaporated while some remained trapped within the carbon channels or on the surface [17]. This reduced the recovery efficiency of the activator. Thus, limited amount of ZnCl₂ was present during activation to facilitate the release of volatile matter, which resulted in lowered yield of recovered samples.

In contrast with the surface area values, sample ZR1 generates higher surface area (205.74 m²/g) in comparison with sample Z2 (25.44 m²/g) and ZR2 (8.99 m²/g). These data suggest that the first cycle of recovered ZnCl₂ has promoted further pore development during subsequent activation. According to [6], ZnCl₂ is not consumed during activation stage as it is regarded as dehydrant. ZnCl₂ is converted into intermediates known as Zn₂OC₂·2H₂O and further decompose into ZnO [6,16]. Thus, during washing procedure, the washing filtrate is concentrated with recoverable ZnCl₂, as large portion of unreacted ZnCl₂ dissolves in the effluent due to its high-water solubility.

This indicate that the first cycle of recovered ZnCl_2 can still performed it capability in pore development. However, the surface area of second cycle of AC (ZR2) shows a drastic decline compared to other samples, likely due to partial pore collapse as low amount of ZnCl_2 remaining in the washing filtrate.

Table 1 Yield and surface area of lipid condensate AC samples.

Sample	This work			Palm kernel shell [8]		Lotus root [6]	
	Z2	ZR1	ZR2	F-AC ^c	R-AC ^d	F-AC ^c	R-AC ^d
Yield (%)	25.44	21.96	18.64	70.70	51.40	33.50	48.70
Surface area (m ² /g)	107.62	205.74	8.99	858	345	1560	908.8

^cAC activated by fresh activator, ^dAC activated by recovered activator

These findings highlight the importance of ZnCl_2 as activator in facilitating the yield and porosity development in AC synthesis. Similar findings can be observed from prior studies on the use of recovered activators in AC adsorption. A study by [8] has showed that ZnCl_2 can be effectively recovered and reuse through washing with water for subsequent activation. In this study, the recycled ZnCl_2 can still produce good surface area of 345 m²/g compared to 858 m²/g obtained using fresh ZnCl_2 for methylene blue removal. Although the recycled ZnCl_2 resulted in a lower surface area, the adsorption performance remained acceptable while significantly reduced chemical cost. Acid washing procedure, on the other hand provides higher recovery efficiency yet generates acidic wastewater that requires neutralization. A study by [6] found that activation with recycled ZnCl_2 through acid washing higher yield (48.7%) compared to activation from fresh ZnCl_2 (33.5%), with surface area of 908.08 m²/g which is comparable to the first-round activation (1560 m²/g). Another method for ZnCl_2 recovery includes modified vacuum pyrolysis (MVP) [7]. In his work, it reported to achieved recovery of ZnCl_2 over 99.99% without generating wastewater, while displaying higher adsorption capability compared to traditional pyrolysis method. However, this method is constrained by its complex vacuum system, extensive energy usage as well as tight control of temperature-pressure conditions which makes it unsuitable for low-cost operations.

Fig. 1 depicts the surface morphology of the samples obtained from scanning electron microscopy (SEM). The effectiveness of sample adsorption performance surface area corresponds to the pore size distribution and surface functionality. As observed, sample Z2 and ZR1 display clear pores, cracks and widened openings formed during pyrolysis process. This is due to the presence of ZnCl_2 which act as dehydrating agent and facilitates removing the volatile matters from the carbon matrix. As the result, irregular pores and non-uniform pore channels were formed within the samples. Meanwhile for sample ZR2, the sample shows a more compact surface area with fewer distinguishable pores due to partial pore collapse and limited activation in second recovery cycle. These observations correspond well with the surface area results, where sample ZR1 recorded at the highest result, followed by sample Z2 while sample ZR2 exhibits lower surface area due to limited ZnCl_2 availability in the washing filtrate for the second recovery cycle. Overall, with the pore structure as shown in sample Z2 and ZR1, these AC able to promote better accessibility for larger MB molecules during adsorption process.

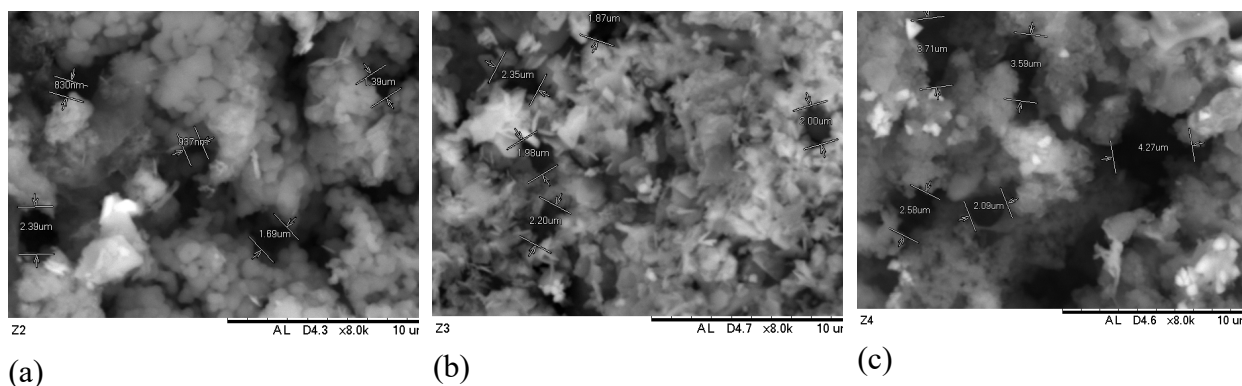


Figure 1 SEM images of (a) Z2, (b) ZR1 and (c) ZR2.

Equilibrium adsorption

Fig. 2 shows the equilibrium adsorption of MB dye by lipid condensate AC. In general, the adsorption process takes place when methylene blue molecules transfer from aqueous phase to the solid surface, where the molecules interact with active site of the AC and subsequently diffuse into the internal pores. In this work, the AC samples were tested with MB concentrations ranging from 5 to 500 mg/L. An increase in dye concentration resulted in higher adsorption capacity of AC, with dye concentration gradient acting as the driving force.

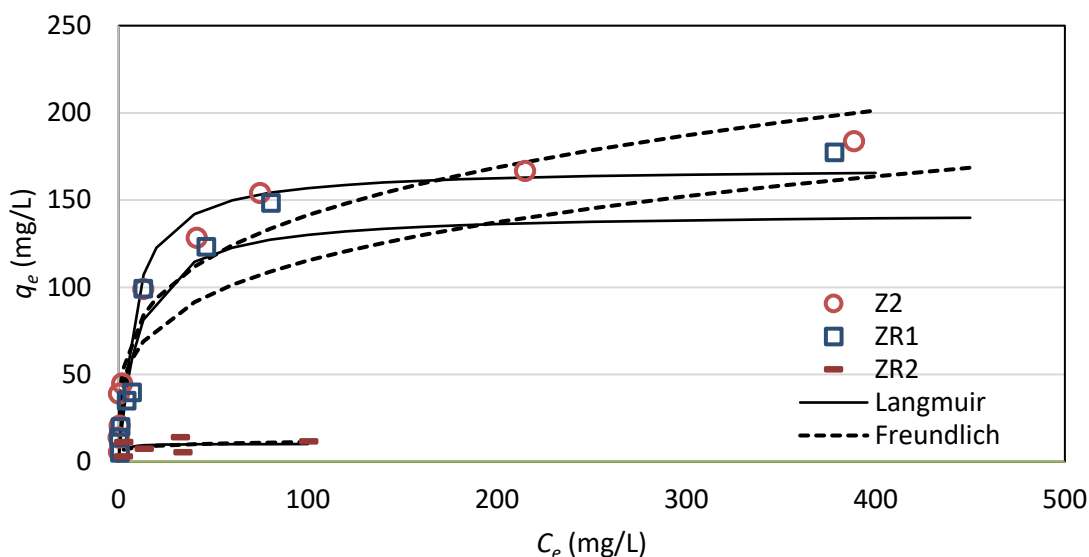


Figure 2 Equilibrium adsorption of MB dye onto AC.

Table 2 Isotherm constant for MB adsorption by lipid condensate AC.

	Z2	ZR1	ZR2
Langmuir			
q_m (mg/g)	168.669	142.911	10.24
k_L (L/mg)	0.133	0.101	0.811
R^2	0.968	0.951	0.116
Freundlich			
k_F (mg/g)(L/mg) ^{1/n}	43.629	36.0	6.051
n	3.918	3.957	7.374
R^2	0.947	0.796	0.165

At higher dye concentrations, the movement of dye molecules was enhanced by the stronger concentration gradient, thus overcoming the mass transfer resistance at solid phase [18,19].

The variation in adsorption performance can be observed among the AC samples even though they were prepared at the same impregnation ratio. The differences were mainly due to the recovery cycle of ZnCl_2 . Sample Z2 displayed the highest maximum adsorption capacity of 183.73 mg/g, followed by ZR1 with 177.16 mg/g meanwhile ZR2 only showed low capacity of 11.74 mg/g. Sample Z2 and ZR1 performed superior results due to larger numbers of accessible pores and active site presence in the AC. While sample ZR2 poor performance is due to its underdeveloped porosity and limited surface area. These findings demonstrate the importance of pore developments in adsorption performance of AC.

The findings were further fitted to Langmuir and Freundlich models to understand the adsorption mechanism of the AC. These data were calculated through non-linear regression using *Solver* of MS Excel. Table 2 summarizes the isotherm constants of Langmuir and Freundlich models for methylene blue adsorption by lipid condensate AC. From Table 2, Langmuir model provided the best fit for adsorption data compared to Freundlich model where sample Z2 and ZR1 recorded with high coefficient of determination (R^2) of 0.968 and 0.951, respectively. This suggests that adsorption of these samples had mainly occurred through the monolayer coverage on homogeneous surface [20]. In contrast with sample ZR2, both models displayed poor agreement results, confirming that the sample is not an effective AC under the tested conditions. The Langmuir constant, k_L is a significant parameter that reflects the adsorption affinity between the adsorbent and dye molecules at low concentrations. Table 2 shows that sample Z2 ($k_L = 0.133$) and ZR1 ($k_L = 0.101$) have relatively high affinity toward methylene blue dye, indicating stronger interactions at low concentrations.

The Freundlich isotherm constants also demonstrated a favourable adsorption result where n values of sample Z2 and ZR1 were recorded as 3.918 and 3.957, respectively. Yet, sample ZR2 showed an unusually high n value (7.374) with poor correlation, suggesting unreliable fitting. The Freundlich constants, k_F values for sample Z2 (43.6) and ZR1 (36.0) were also higher in comparison to sample ZR2, validating its stronger adsorption capacity and affinity at the stated conditions.

Conclusion

This study demonstrated the recovery and reuse of ZnCl_2 for lipid condensate-based AC synthesis. The results showed that the first cycle of recovered ZnCl_2 produced AC with higher surface area (205.74 m^2/g) compared to lipid condensate activated with fresh ZnCl_2 (107.62 m^2/g), while maintaining comparable adsorption capacity (177.16 mg/g) and yield (21.96%). However, the subsequent activation using recovered ZnCl_2 resulted in a drastic decline in both surface area (18.64 m^2/g) and adsorption capacity (11.74 mg/g), indicating the limited availability of ZnCl_2 remained in the recovered solution for effective activation. Overall, these findings highlight the potential strategy for minimizing reliance on single-use chemicals while offering a practical and scalable pathway for sustainable AC production by reducing costs, improving resource efficiency and supporting cleaner processing of palm oil industry waste.

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