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Evaluating The Adsorption Efficiency Of Pelletized And Powdered Clinoptilolite For Methylene Blue

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ABSTRACT

The widespread use of dyes in various industries such as clothing, manufacturing, cosmetics, and printing has raised concerns about their negative impact on the environment. Adsorption is a practical method used in industries to treat this type of discharge on a large scale. However, the conventional powder format raises practical concern. This paper examines the adsorption capacity of clinoptilolite prepared as both pellets and powders for removing methylene blue. Both formats showed a consistent increase in adsorption capacity as the mass increased due to the increased number of adsorption sites attracting the methylene blue. However, compared to the powder format, the adsorption capacity of the pelletized clinoptilolite was significantly lower as the mass increased. The difference in adsorption capacity between the pellet and powder widened with increasing mass. This is because increasing the pellet mass only contributes to small increases in surface area from the slight increase in pellet thickness, whereas the powder format effectively uses all the exposed surface area of each powder unit as adsorption sites. Additionally, the methylene blue does not completely penetrate the inner structure of the pellet, further lowering its adsorption capacity. This study suggests that the adsorption capacity of clinoptilolite pellets can be enhanced to match the performance of the powder format if the mass is decreased. It shows that there is significant potential for improving clinoptilolite pellets to perform as well as the powder format.

1. Introduction

Adsorption is a fundamental surface phenomenon where molecules or particles from a fluid (gas or liquid) adhere to the surface of a solid or liquid. It plays a crucial role in a wide range of industrial applications, including water treatment, gas purification, catalysis, and the removal of contaminants from air and wastewater [1]. This is because it is an inexpensive operation compared with the others and superior in terms of operating cost, flexibility and simplicity of design, ease of operation and insensitivity to toxicity of pollutants [2].

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There are a variety of materials commonly used for adsorption in aqueous media such as biomass [3], activated carbon [4], zeolite [5], biochar [6], aerogels [7], composite [8] and many others. Each material has its advantages and disadvantages. Activated carbons typically exhibit superior performance due to their high porosity characteristics. However, synthesis of the activated carbon releases non-environmentally friendly gases and byproducts. Biochar shows similar trends but at lower cost. Aerogels also deliver excellent performance due to their highly interconnected pore structure which promotes fluid flow. However, their complex synthesis process and associated chemicals raise practical concerns.

Clinoptilolite, as one of natural zeolite is one of the most used adsorbents in water treatment and adsorption study [9]. It can naturally attract catanionic substances such as methylene blue, by electrostatic attractions [10] [11]. Another advantage is that it can be modified in terms of its surface to attract anionic and organic substances [12] [13]. Compared to other adsorbent materials, the natural clinoptilolite does not require synthesis process.

Artificial dyes are usually used for dyeing fabrics in clothing, textile industries, dyeing papers and leather. A large volume of methylene blue dye containing wastewater is discharged into groundwater and surface water. Methylene blue is categorized as synthetic dye and, in the formation, the chemical reactions are effective [12]. Cationic dyes that are extremely poisonous and can have mutagenic, carcinogenic, and teratogenic impacts on ecosystems of humans and aquatic life and will penetrate the surface of the material by chemical or physico-chemical processes [14].

Most of the study in adsorption revolving around activated carbon or other adsorbent materials focused on powder form. Dinu and coworkers realized that powder form offers impractical solutions should larger units of adsorption be implemented [15]. One of the disadvantages is the requirement of post filtration, leaching, posing risk of sedimentation across the post units such as pumps and valves, thus increasing maintenance needs and costs. As a solution, they produced adsorbent in the form of microbeads. However, the microbeads faced stability issues in regeneration since the regeneration requires the use of acid interactions such as low concentration HCl or CH_3COOH [15]. From a sustainability perspective, regeneration is a crucial aspect of adsorption technology, offering significant benefits such as enhanced cost-effectiveness, waste reduction through adsorbent reusability, and potential recovery of the adsorbed pollutants for further use or safe disposal.

As an alternative to microbeads that require complicated processes and regeneration issues, this paper proposed an adsorbent in a form of pellets. The aim of this paper is to evaluate and compare the adsorption capacities of clinoptilolite pellets and clinoptilolite powder for the removal of methylene blue from aqueous solutions in removing methylene blue.

2. Methodology

2.1 Materials

The clinoptilolite granules were purchased from ACME Sdn Bhd. The methylene blue powder was purchased from Sigma Aldrich.

2.2 Preparation of Clinoptilolite Powder

The granular clinoptilolite was first cleaned and washed using tap water. The last several washes used distilled water. Then, the granular clinoptilolite was dried overnight at 100 °C. After that, the clinoptilolite granules were powderized using a ball mill (Pulverisette 6, Fritsch). The process was run for 5 hours under 550 rpm using tungsten carbide balls. The approximate size of the powder was 0.420 micrometre measured by Zetasizer Nano ZS90 (Malvern Panalytical).

2.3 Preparation of Clinoptilolite Pellet

Hydraulic press was used to produce the clinoptilolite pellet. A press pressure of 1 ton was applied onto the clinoptilolite powder placed inside a mold. The pellet thickness was adjusted by varying the mass of the powder. Each pellet had a diameter of 6 mm. The pellet was then heat-treated to 400°C for 48 hours. Finally, the pellet was let cool down to room temperature. Table 1 shows the details of each sample.

Table 1. Details of samples produced for adsorption capacity experiment

No.	Sample format	Mean mass (g)	Mean thickness (mm)	Sample ID
1	powder	0.05	-	Pd5
2	powder	0.07	-	Pd7
3	powder	0.09	-	Pd9
4	pellet	0.05	1.60	Pe5
5	pellet	0.07	1.96	Pe7
6	pellet	0.09	2.96	Pe9

Figure 1 shows images of the pellet taken from the top and side views. The thickness was estimated using ImageJ software. In this context, the thickness refers specifically to the height of the flat, cylindrical portion of the pellet, excluding the convex surfaces on the top and bottom.

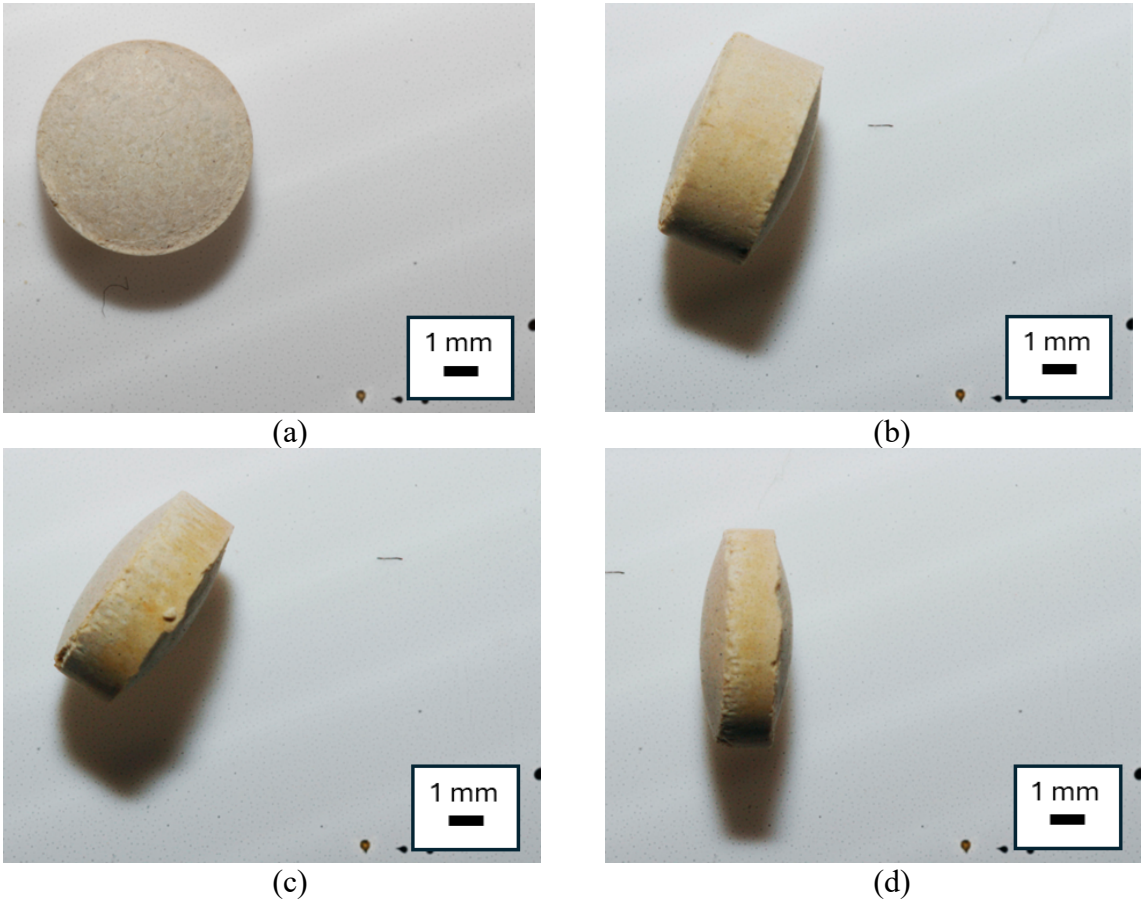


Fig. 1. Images of clinoptilolite pellets from its top view (a), and side view of Pe9 (b), Pe7 (c), and Pe5 (d)

2.4 Adsorption capacity experiment

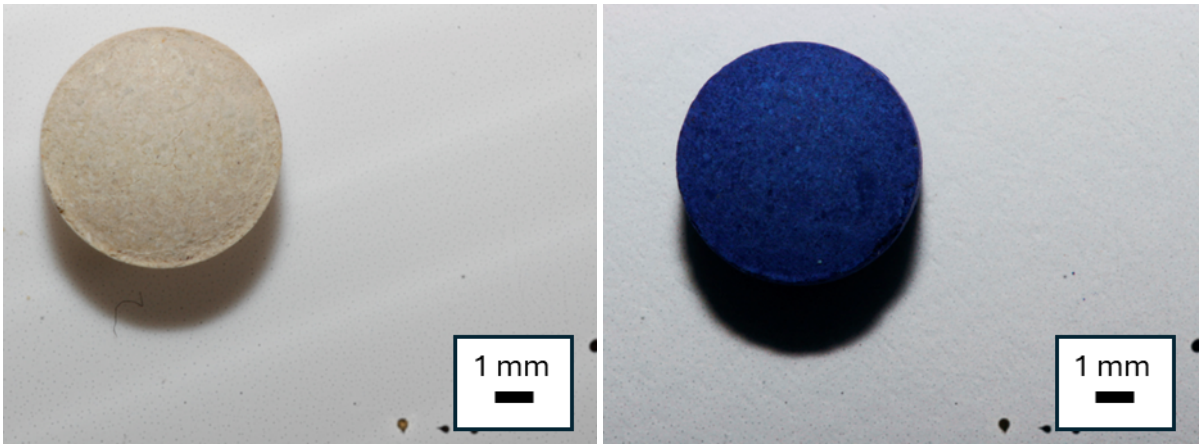
A stock solution of 20 mg/L methylene blue was prepared. The adsorption test was conducted in two batches. The first batch used clinoptilolite pellets. The second batch used clinoptilolite powder with similar mass. Each clinoptilolite sample was added into a 100 ml flask of 50 ml of 20 mg/L methylene blue solution. They were continuously shaken at 100 rpm using an orbital shaker [16]. The initial pH of the prepared 20 mg/L methylene blue was 6.98 ≈ 7.00. The temperature was room temperature. The adsorption was allowed to run until the concentration of the methylene blue solution became constant [17]. In this study, both sample types were run for 164 hours to ensure equilibrium. UV-Vis spectrophotometer was used to obtain concentration. Each different sample was duplicated triplite. The standard deviations were calculated and depicted by error bars in **Figure 3**. The adsorption capacity was calculated using the following **Eq. 1** [18] :

$$q_e = \frac{(C_i - C_e)}{m} \times V \tag{1}$$

where q_e is the adsorption capacity, C_i is the initial concentration of the methylene blue, C_e is the concentration of methylene blue at equilibrium, m is the clinoptilolite mass added into the solution, and V is the volume of the methylene blue solution.

3. Results

Figure 2 shows the condition of the pellet before and after the adsorption of methylene blue. The methylene blue covered the surface of the clinoptilolite pellet.



(a) (b)

Figure 2. Condition of the clinoptilolite pellet before and after the adsorption of methylene blue

Figure 3 shows the adsorption capacity of clinoptilolite powder and clinoptilolite pellets. For clinoptilolite powder, the trend showed consistent increment as the mass of the powder was increased. This is due to increased adsorption sites as the quantity of adsorbent increases. Increased adsorption sites provided an increased amount of adsorbates attracted to the surface of the adsorbent. The value of the adsorption capacity of the powder format is comparable with previous works [19], [20], [21].

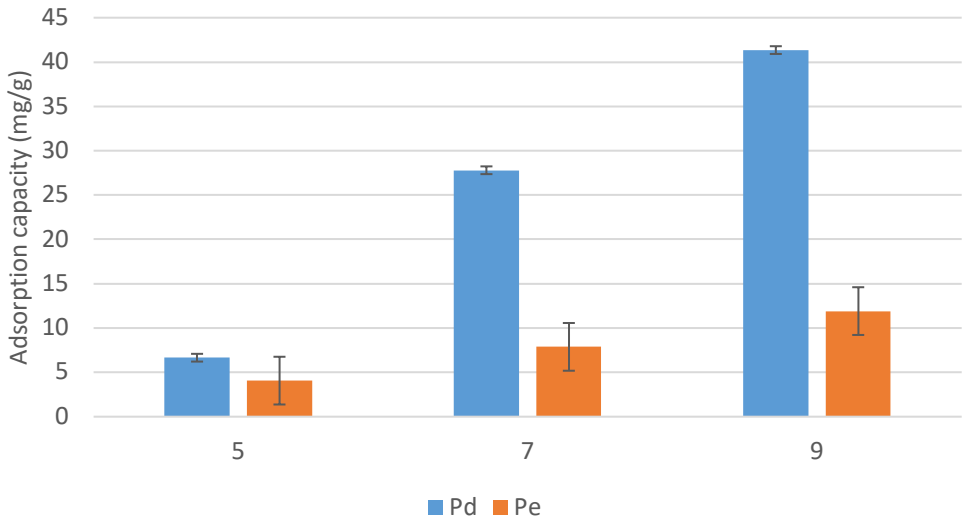


Fig. 3. Adsorption capacity of Pd5, Pd7, Pd9, Pe5, Pe7, and Pe9

For clinoptilolite pellets, the trend follows a similar increment as that of powder. Increased mass of pellets provided thicker pellets which increased its dimensional surface area. This as well, provides a higher amount of adsorption sites, thus increasing the number of adsorbates attracted to the surface. Compared to the clinoptilolite powder, the adsorption capacity provided by the clinoptilolite pellets showed higher inconsistency as indicated by the error bars. This might be due to the inconsistent surface structure produced during the powder pressing into pellets. The analogue mode of the bar gauge of the hydraulic press potentially caused parallax error.

However, the increment of the pellet against its mass is not as significant as its powder counterpart. It shows that using pellets highly reduced the adsorption capacity. In terms of mass-to-mass comparison between the Pd5 and Pe5, the difference is smaller compared to Pd7 and Pe7, and Pd9 and Pe9 as shown in **Table 2**. The difference in terms of adsorption capacity became highly significant as the mass increased. This is due to the increase of dimensional surface area of the pellet is not as high as the increasing amount of powder when the masses were increased. It shows that the effective surface area is lower.

Table 2
Difference in percentage for adsorption capacity of clinoptilolite on methylene blue relative to pellet, for powder and pellet formats

Powder and pellet format	Difference in percentage for adsorption capacity relative to clinoptilolite pellet
Pd5 and Pe5	-64
Pd7 and Pe7	-253
Pd9 and Pe9	-247

Another factor that causes poorer adsorption capacity of the pellet is penetration resistance towards the methylene blue as adsorbate. The hydraulic pressing produced more compacted structure, especially the inner and central regions. This is shown in **Figure 4**. According to our estimation, the methylene blue only reached 0.32 – 0.37 mm deep from the surface. There is a high portion of the inner structure of the pellet is unreachable. If we assume the powder format utilization in the methylene blue adsorption is 100%, the utilization of the adsorbent capacity for the pellets are 61.1%, 28.3%, and 28.8%, for the Pe5, Pe7, and Pe9, respectively. This finding suggests that utilization of up to 100% can be achieved if the pellet thickness is approximately 0.64 to 0.74 mm. This compaction likely impairs adsorption significantly compared to the powder form due to poor pore connectivity. However, systematic studies examining the effects of different pressing pressures on adsorption capacity are needed to confirm this assumption supported by porosity analyses such as mercury intrusion porosimetry.

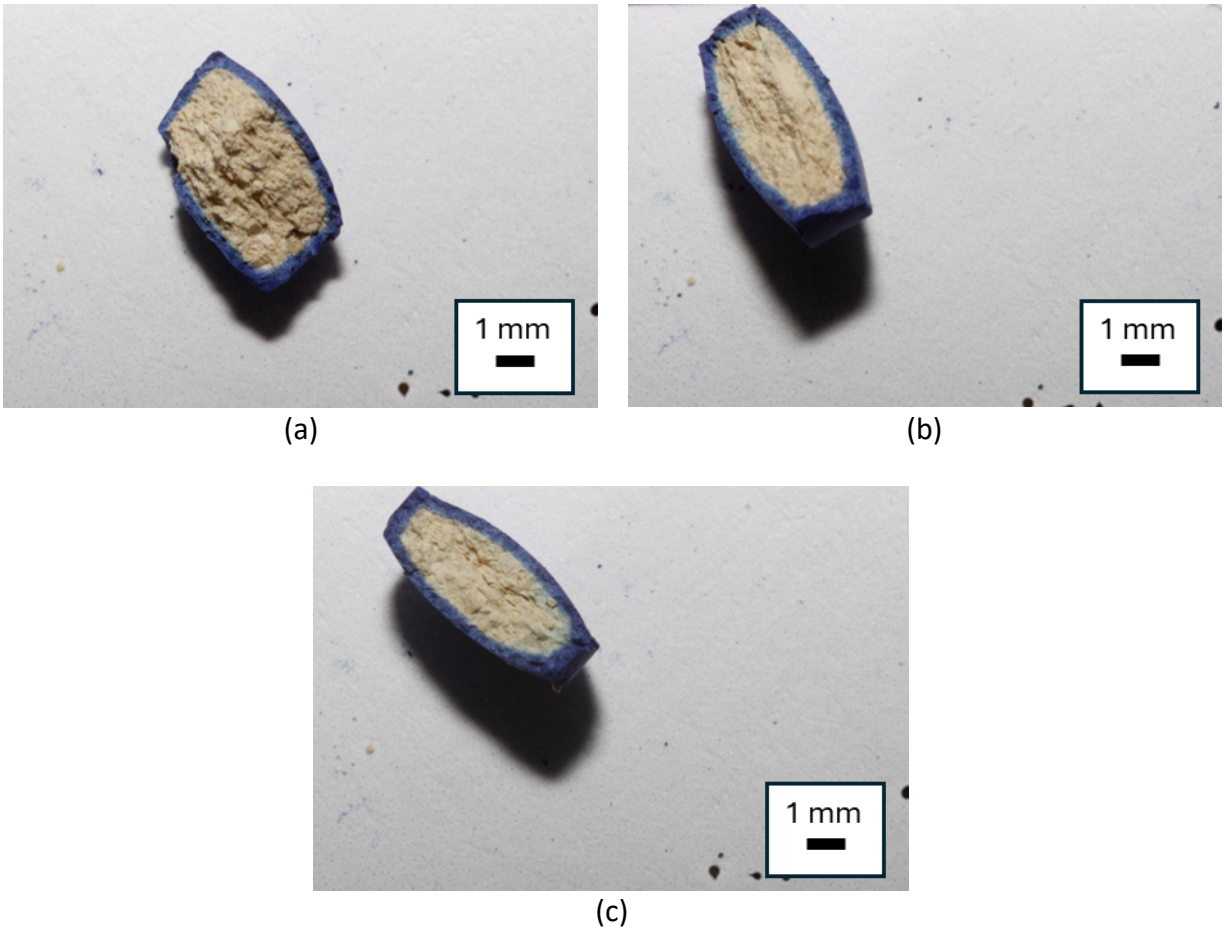
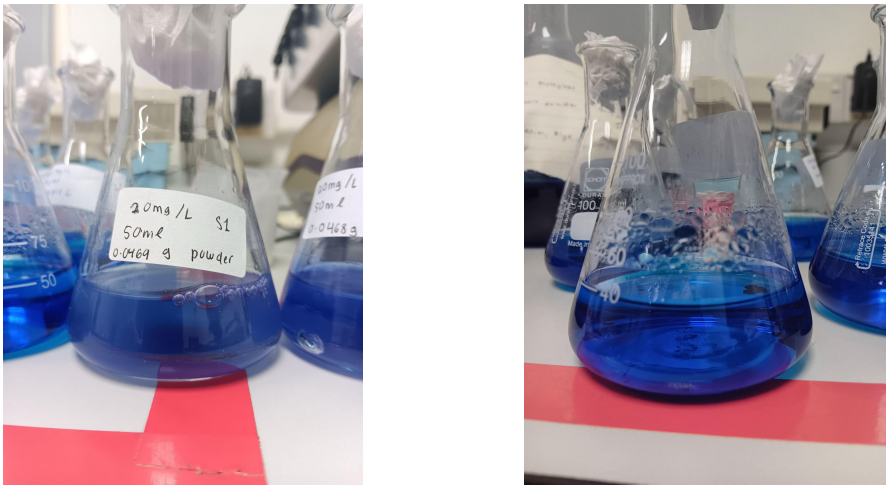


Fig.4. Images of cross section of the pellet after adsorption of Pe9 (a), Pe7 (b), and Pe5 (c)

Figure 5 shows the image of the methylene blue solution after the adsorption using Pe5 and Pd 5. The Pd5 solution was cloudy and required post separation prior to data collection, while Pe5 showed a transparent and clear blue solution which does not require any further treatment.



(a) (b)

Fig. 5. Condition of solutions treated using clinoptilolite powder (a) and clinoptilolite pellet (b)

Table 3 presents a performance comparison of methylene blue adsorption between this study and previous studies. As expected, the pellet scored relatively low. In comparison to other adsorbent materials, such as activated carbon, which possesses a high surface area and porosity and relies on several contributing mechanisms to promote methylene blue adsorption, including Van der Waals forces [22], electrostatic attraction [23], pore filling/trapping [22] and possible chemical bond [22]. Differed from activated carbon, clinoptilolite utilized its negatively charged element to attract the methylene blue of polarized dimethylamino groups, a small positive charge when they come into contact with water molecules in an aqueous solution [24]. Moreover, clinoptilolite does not possess high surface area and pore volume unless further chemical treatment is applied[13].

Therefore, several strategies are currently being developed to address this issue. First, we are incorporating pore formers to enhance pellet porosity, thereby improving adsorbate diffusion and surface interaction. Second, we are treating the pellet surface with surfactants to capture anionic compounds more effectively. Lastly, we are focusing on reducing the pellet's thickness to promote faster mass transfer, increase utilization, and improve overall adsorption efficiency.

Table 3
Adsorption capacity of methylene blue in single system adsorbate by adsorbents of clinoptilolite and other adsorbent materials

Adsorbent	Format	Highest experimental value of adsorption capacity (mg/g)	Reference
Clinoptilolite	powder	20.66	[19] (2019)
Clinoptilolite	powder	22.78	[25] (2023)
Clinoptilolite	powder	24 – 46	[20] (2018)
Aerogel cylinder	small cylinder	163.84	[7] (2025)
Biochar powder	powder	84.2	[6] (2025)
Activated carbon	powder	164.8	[26] (2025)

Activated carbon/zeolite composite	powder	14.28	[27] (2025)
Clinoptilolite/Alginate microbead	microbead	151.73	[15] (2017)
Clinoptilolite	powder	41.34	This study
Clinoptilolite	pellet	11.91	This study

4. Conclusions

The adsorption capacities of clinoptilolite pellets and powder for methylene blue were evaluated and compared. Both pellets and powder showed a similar trend with their adsorption capacity increasing as the mass increased due to the increased number of adsorption sites. However, the difference in adsorption capacity between pellets and powder widened with increasing mass. The lower increment of the adsorption capacity of the pellets was mainly due to the poor increment of effective surface area and increased resistance to methylene blue penetrating the inner structure of the pellets. This difference, however, can be minimized by using a lower mass when fabricating the pellets. This would also reduce the resistance to methylene blue penetrating the inner structure of the pellets. These findings suggest significant potential for enhancing the performance of clinoptilolite pellets to match that of the powder format.

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