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Efficient Adsorptive Removal of Methylene Blue Using Acid- and Alkali-Modified Clinoptilolite–Alginate Beads: High-Capacity Monolayer Adsorbents for Wastewater Treatment and Potential Membrane Applications

Nur Fatin Atikah Abdul Mutalib[a], Dauren Kulbatyrova[b], Assylbek Kanbetova[b], Temirkhanova Gulden Yerlanovna[b], Azat Seitkhan[c], Muhammad Bisyrul Hafi Othman[a], Norliyana Mohd Salleh[d], Siti Khadijah Hubadillah[e], Mohd Riduan Jamalludin[f], Mohd Ridhwan Adam[a*]

[a]Materials Technology Research Group (MaTReC), School of Chemical Sciences, Universiti Sains Malaysia, 11800, Minden, Penang, Malaysia
[b]Non-profit JSC, Atyrau Oil and Gas University named after S. Utebayev, Atyrau, Kazakhstan
[c]Laboratory of Engineering Profile, Satbayev University, 22 Satbayev Str., Almaty, Kazakhstan
[d]Academic Research Management, Group Technology and Commercialisation, PETRONAS Research Sdn Bhd, 43000 Bandar Baru Bangi, Selangor, Malaysia
[e]School of Technology Management and Logistics, Universiti Utara Malaysia, 06010 Sintok, Kedah, Malaysia
[f]Faculty of Mechanical Engineering Technology, Universiti Malaysia Perlis (UniMAP), Kampus Alam UniMAP, Pauh Putra, 02600 Arau, Perlis, Malaysia

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ABSTRACT

Methylene blue (MB) is a hazardous pollutant with severe impacts on human health and marine ecosystems. To solve these issues, this work investigates the removal of MB from wastewater using sodium alginate beads embedded with natural zeolite clinoptilolite (NZC) modified with HCl and NaOH. To comprehend the changes in NZC physicochemical properties, it was modified with different concentrations of HCl and NaOH (0.5, 1.0, 3.0, and 5.0 M) and extensively characterized using Fourier-transform infrared spectroscopy (FTIR-ATR), and nitrogen adsorption analysis. Both HCl-NZC and NaOH-NZC beads achieved 100% MB removal efficiency, with maximum adsorption capacities of 45.80 mg/g and 45.09 mg/g, respectively. The adsorption process followed the Langmuir isotherm model with high correlation value (R^2) of 0.9952 (HCl-NZC) and 0.9907 (NaOH-NZC), indicating monolayer adsorption on a homogeneous surface. This study serves as a preliminary investigation into the adsorption behavior of acid- and base-modified NZC encapsulated in alginate beads for MB removal. The findings demonstrate that the modified beads exhibit strong adsorption capacity and stability, suggesting their potential application as fillers or active components in future zeolite-based composite membrane systems for efficient dye removal.

Keywords: Natural zeolite clinoptilolite, adsorption, methylene blue, isotherm, alginate beads

1.0 INTRODUCTION

Methylene blue (MB) is a cationic dye frequently used in the paper, leather, and textile industries. Considered a highly hazardous, cancer-causing, and mutation-inducing water contaminant [1]. The presence of MB in aquatic

* Corresponding to: M. R. Adam (email: mohd.ridhwan@usm.my)
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environments can lead to many environmental problems, including decreased penetration of light and oxygen transfer, which adversely affect aquatic life [2]. Long-term human exposure to MB can also have negative health effects, including skin irritation, respiratory problems, and possibly even cancer. Consequently, removing MB from wastewater has grown to be a significant health and environmental concern.

Numerous techniques, such as adsorption, photocatalysis, coagulation, ion exchange, ozonation, irradiation, membrane filtration, and electrochemical destruction, have been developed to treat wastewater contaminated with dyes [3]. Among these, adsorption has emerged as a preferred method due to its simplicity, cost-effectiveness, and high efficiency across a wide range of dye concentrations.

Adsorbents play a crucial role in adsorption processes, and natural materials have attracted significant attention for their availability, affordability, and eco-friendliness. Activated carbon, biochar, clay minerals, and advanced materials are some of the most studied adsorbents for wastewater decontamination. These materials possess the necessary features to be used for this purpose, e.g., high surface area, negative electric charge (clay minerals), and micro-mesoporous (carbon-based) materials [4]. However, their large-scale application is often hindered by limitations such as high cost and complex processing.

Alginate, a naturally derived biopolymer, and zeolite, a microporous aluminosilicate mineral, have been extensively studied for their adsorptive properties [5]. Brown seaweed-derived alginate, known for its exceptional gel-forming ability and biocompatibility, forms hydrogels in the presence of divalent cations such as calcium. These hydrogels can be processed into beads, which have been used to remove various contaminants, including dyes and heavy metals. However, pure alginate beads often exhibit limited adsorption capacity, necessitating modifications to enhance their performance.

Zeolites, particularly clinoptilolite, are natural aluminosilicate minerals with a unique porous structure that facilitates the adsorption of various contaminants. Their high cation exchange capacity and selectivity make them effective in removing heavy metals, ammonium ions, and dyes from wastewater [6]. Although zeolites can be used directly, challenges related to handling and recovery from treated water can arise due to their fine powder form, which often requires additional post-treatment processes for separation.

In this study, adsorptive alginate beads embedded with acid-modified and base-modified natural zeolite clinoptilolite (NZC) were fabricated for the removal of MB from wastewater. Encapsulation of the modified zeolite within the alginate matrix effectively addresses the common challenges of natural zeolite powders, such as handling, separation, and recovery. The adsorption performance of the beads, including the effects of acid and base modification, contact time, and initial MB concentration, was investigated. Additionally, the adsorption capacities of HCl-3.0NZC and NaOH-1.0NZC beads were compared with those reported in previous studies, demonstrating that these modified beads offer a cost-effective solution for wastewater treatment. While natural zeolite-based adsorbents show great potential in water purification, their application can be further advanced through integration into membrane

systems. The modified zeolite-alginate beads developed in this study provide a foundation for future incorporation into composite membranes, which could synergistically combine adsorption and filtration processes for more practical and continuous wastewater treatment applications.

2.0 METHODS

2.1 Materials

The Natural Zeolite Clinoptilolite, with a particle size less than 70 μm, was directly procured from Shijiazhuang Mining Trade Co. Ltd, located in Liaoning Province, China. Hydrochloric acid (HCl) with a concentration of 37%, sodium hydroxide pellets (NaOH), methylene blue (MB), and sodium alginate were obtained from Sigma-Aldrich. Anhydrous calcium chloride ($CaCl_2$), with a purity of 97% or greater, was purchased from Quality Reagent Chemicals (QReC). Distilled water was used as the solvent in all experiments. All these materials were used directly without any purification.

2.2 Modification of NZC using HCl and NaOH

Approximately 10 g of NZC were weighed and mixed with 100 mL of 0.5 M HCl in an Erlenmeyer flask, maintaining a solid-to-liquid ratio of 1:10. The Erlenmeyer flask was then covered with aluminium foil, and the solution was stirred for 24 hours. Subsequently, the solution was repeatedly washed with water until a neutral pH of 7 was achieved. The modified NZC was transferred to a small beaker, covered with perforated aluminium foil, and left to dry in an oven at 70°C. Finally, the dried sample was stored and labelled in a small plastic container. This procedure was repeated using HCl solutions with concentrations of 1.0 M, 3.0 M, and 5.0 M, as well as NaOH solutions with concentrations of 0.5 M, 1.0 M, 3.0 M, and 5.0 M.

2.3 Preparation of Alginate Beads Embedded with Modified NZC

A solution was prepared by dissolving approximately 1 g of sodium alginate in 50 mL of distilled water and stirring it with a glass rod using a magnetic stirrer for 15 minutes on a hot plate. Subsequently, 1 g of modified zeolite was gradually added while stirring continued to ensure even dispersion. The mixture was then sonicated at 60 °C for 10–15 minutes to ensure uniform dispersion. The mixture was dropwise added into a 200 mL $CaCl_2$ solution using a syringe under continuous stirring (300 rpm) at room temperature. The formed beads were rinsed several times with distilled water to remove residual $CaCl_2$ and finally stored in distilled water until further use.

2.4 Characterization of Unmodified and Modified NZC

Fourier-transform infrared attenuated total reflectance (FTIR-ATR) analysis was performed using a Shimadzu IRSpirit FT-IR spectrophotometer equipped with a Universal ATR Sampling Accessory and LabSolutions IR software to identify the functional groups of natural and modified NZC samples. Spectra were recorded in the range of 4000–400 cm^{-1}**.** Surface area, pore size, and pore volume were measured using a Micromeritics ASAP 2020 analyzer based on the Brunauer–Emmett–Teller (BET) technique after degassing at 350°C for 3 hours**.**

2.5 Adsorption Performance of Modified NZC

The concentration of methylene blue (MB) dye was determined by measuring its absorbance at 668 nm using a Perkin Elmer Lambda 35 UV–Vis spectrophotometer**.** The adsorption experiments were carried out by varying several parameters, including the type of modification (acid or base), contact time, and initial dye concentration [7]. The removal efficiency of MB, R (%) for each parameter was then calculated using Equation 1**.**

$$\boldsymbol{R = \frac{C_i - C_e}{C_i} \times 100} \qquad 1$$

Where *%R* is the percentage removal of MB, Ci and Ce are the initial and equilibrium concentrations of MB (mg/L). Furthermore, the adsorption capacity of MB using modified NZC can be determined using the following equation:

$$q_e = \frac{(C_i - C_e)}{M} \times V \qquad 2$$

In this equation, C_i represents the initial concentration of MB (mg/L), C_e represents the equilibrium concentration of MB (mg/L), M represents the mass of the adsorbent (g), and V represents the volume of the solution used (L).

3.0 RESULTS AND DISCUSSION

3.1 Physicochemical Properties of Unmodified and Modified NZCs

The functional groups of the unmodified, acid-modified (HCl-NZC) and base-modified (NaOH-NZC) NZCs were evaluated using FTIR-ATR, as shown in Figure 1.

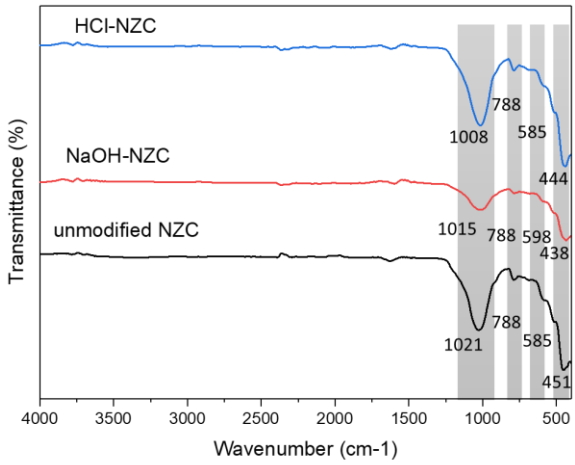

Figure 1 FTIR spectra of unmodified, base-treated, and acid-treated NZCs

The bands at 788 cm^{-1}, 585 – 598 cm^{-1}, and 438 – 451 cm^{-1} correspond to the symmetric stretching vibration of O-Si-O, double rings of tetrahedra bending vibration, and symmetric bending vibration of T-O bonds in TO4 tetrahedra (where T = Si or Al) [8]. A strong peak near 1000 cm^{-1}, observed across all samples, is attributed to the asymmetric stretching vibrations of Si-O tetrahedra [9]. For the base-modified NZC, the Si-O stretching intensity was significantly reduced, indicating a loss of Si from the framework due to the desilication process. Notably, the band initially observed at 1021 cm^{-1} in the unmodified NZC shifted to 1008 cm^{-1}

with a slight increase in intensity after acid modification. This shift and intensity change highlight the structural transformation caused by dealumination, wherein Al is removed from the Si-O-Al bonds, leading to the formation of new Si-O-Si linkages. These new bonds signify the reorganization of the framework structure and the enrichment of silicon within the acid-modified NZC [10].

The surface area of unmodified, acid-modified, and base-modified NZC beads was examined and evaluated through the analysis of N_2 adsorption-desorption isotherms. As shown in Figure 2, the unmodified NZC, HCl-NZC, and NaOH-NZC beads exhibit BET adsorption isotherms classified as type IV based on the International Union of Pure and Applied Chemistry (IUPAC) classification. Additionally, the hysteresis loops observed in both cases are categorized as H4 type [11]. The presence of H4 hysteresis loops indicates the presence of compounds containing both mesopores and micropores in the samples [12].

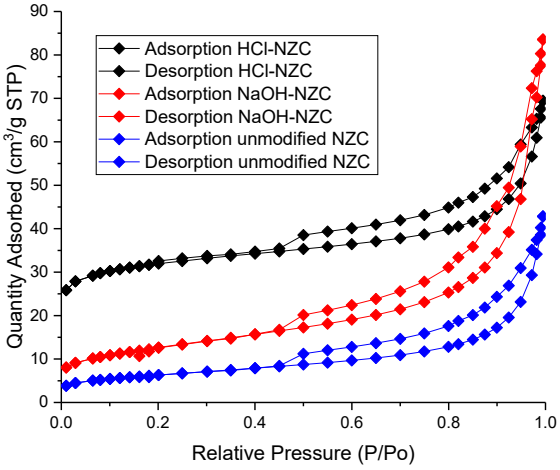

Figure 2 N_2 adsorption-desorption isotherms for unmodified NZC, HCl-NZC, and NaOH-NZC beads

Table 1 shows the BET surface area, total pore volume, and pore size for unmodified, acid-modified, and base-modified NZCs. The surface areas were 22.0423 m^2/g for unmodified NZC, 81.6088 m^2/g for acid-modified NZC, and 45.6059 m^2/g for base-modified NZC. The increase in surface area for treated NZCs is due to acid modification, which enhances the surface area by removing exchangeable cations and impurities that block pores, while base modification causes desilication of the zeolite framework, creating mesopores but resulting in a smaller overall increase in surface area, which improves their ability to adsorb MB dye [13, 14]. Moreover, the total pore volumes were 0.0662 cm^3/g for unmodified NZC, 0.1708 cm^3/g for acid-modified NZC, and 0.1293 cm^3/g for base-modified NZC. Acid modification increased the pore volume by removing aluminum (dealumination), while base treatment did so, it was attributed to the desilication process within the framework [15, 16]. Nevertheless, pore sizes were 12.0204 nm for unmodified NZC, 4.7466 nm for acid-modified NZC, and 10.8562 nm for base-modified NZC. All the observed pore sizes fall into the mesoporous

classification. The smaller pore size in acid-modified NZC is due to improved porosity and the removal of pore-blocking substances [17]. In contrast, the slight reduction in pore size for base-modified NZC indicates a less pronounced effect [15].

Table 1 BET analysis data for unmodified NZC, acid-modified NZC and base-modified NZC

Adsorbent	BET Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Pore Size (nm)
Unmodified NZC	22.0423	0.0662	12.02
HCl-NZC	81.6088	0.1708	4.75
NaOH-NZC	45.6059	0.1293	10.86

3.2 Effect of Acid and Base Modification

Figure 3 shows the removal efficiency of MB using acid-modified NZC beads at different HCl concentrations, which were 0.5 M, 1.0 M, 3.0 M, and 5.0 M.

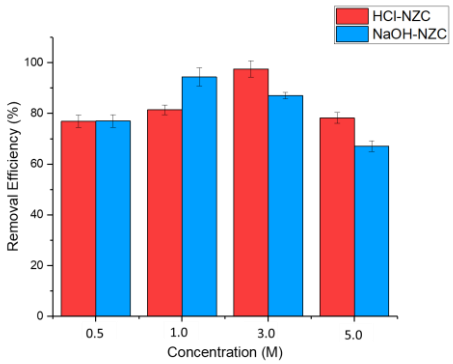

Figure 3 The effect of acid and base modification on percentage removal of MB (Adsorbent dosage = 0.1 g, Initial MB concentration = 20 mg/L, contact time = 60 min, pH = 7) (n = 3)

The recorded removal percentages were 76.87% for 0.5 M, 81.45% for 1.0 M, 97.53% for 3.0 M, and 78.22% for 5.0 M. As seen in the figure, the MB removal percentage improved progressively from 0.5 M to 3.0 M before declining at 5.0 M. The observed increase in removal efficiency from 0.5 M to 3.0 M was due to the HCl modification, which significantly enhanced the adsorbent's surface area. This modification created additional binding sites for MB molecules to attach to the modified NZC. Moreover, the interaction between HCl and NZC promoted the replacement of exchangeable cations like Mg^{2+} and Ca^{2+} with hydrogen ions, further contributing to the surface area increase [18. 19]. On the other hand, the drop in removal efficiency at 5.0 M is attributed to structural damage in the NZC framework caused by the excessive leaching process of Al3+ ions resulting from the diffusion of HCl into the voids [15].

As shown in Figure 3, the MB removal percentages for base-treated NZC beads at NaOH concentrations of 0.5 M, 1.0 M, 3.0 M, and 5.0 M were 77.05%, 94.41%, 87.05%, and 67.05%, respectively. The data indicate that MB removal efficiency increased from 0.5 M to 1.0 M, then declined from 1.0 M to 5.0 M. The improvement in removal efficiency from 0.5 M to 1.0 M can be attributed to the base activation effect of NaOH, which modified the crystallinity of the natural zeolite [20]. Conversely, the reduction in MB removal efficiency beyond 1.0 M suggests structural degradation of the NZC framework. This decline is linked to excessive leaching of Si^{4+} ions caused by NaOH infiltration into the

material's voids, resulting in a decrease in surface area and fewer adsorption sites [21]. According to the graph, 3.0 M acid-modified (HCl-NZC) and 1.0 M base-modified (NaOH-NZC) NZC beads were the most effective modified NZC beads for further study, as they exhibited the highest percentage of MB removal. These concentrations provide stable and efficient adsorbents for wastewater treatment applications by significantly increasing the zeolite's surface area and active sites while maintaining its structural integrity.

3.3 Effect of Contact Time

The effect of contact time on the adsorption of MB by acid-modified and base-modified NZC beads was investigated over a period of 0 to 180 minutes, as shown in Figure 4.

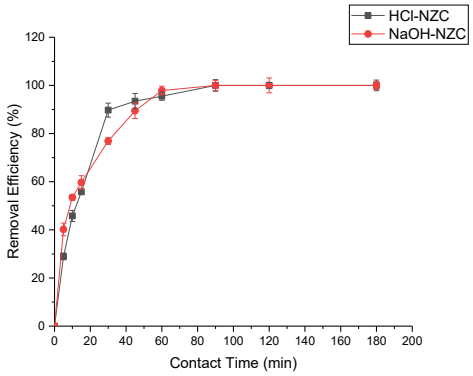

Figure 4 The effect of contact time on the removal efficiency of MB (Adsorbent dosage = 0.1 g, Initial MB concentration = 20 ppm, pH = 7) (n = 3)

The removal efficiency of both acid and base-modified NZC beads increased rapidly during the initial phase, from 0 to 60 minutes, due to the quick adsorption of MB molecules onto the abundant active sites available on the modified NZC beads. By 90 minutes, equilibrium was achieved, with both types of modified NZC beads successfully removing 100% of MB. This result highlights the significant MB removal capacity of the modified NZC beads, as evidenced by the steady approach to equilibrium following the initial rapid adsorption phase. This trend aligns with findings reported in previous adsorption studies [22]. Therefore, 90 minutes was selected as the optimal contact time for subsequent studies.

3.4 Effect of Initial Concentration

Figure 5 illustrates the removal efficiency of acid-modified and base-modified NZC beads for MB dye. The results indicate that the highest percentage of MB removal, 100%, was achieved when the initial dye concentration increased from 5 to 20 ppm for both types of modified beads.

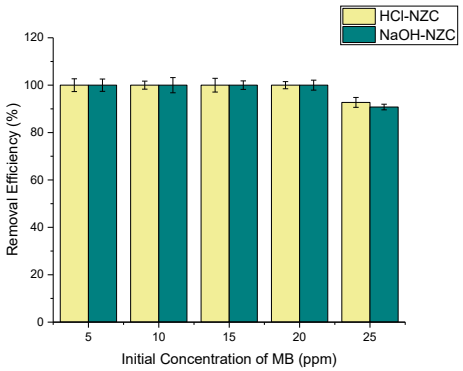

Figure 5 The effect of initial dye concentration on the removal efficiency of MB (Adsorbent dosage = 0.1 g, contact time = 90 minutes, pH = 7) (n = 3)

This finding suggests that increasing the initial dye concentration within this range positively influences MB removal efficiency. However, a decline in removal efficiency was observed when the dye concentration was further increased to 25 ppm. This reduction can be attributed to the limited availability of adsorption sites as the dye concentration rises. At higher concentrations, the adsorption

sites on the adsorbent become saturated, leading to a decrease in the percentage of MB removal [23]. These findings emphasize the importance of optimizing the initial dye concentration in adsorption processes. While an increase in dye concentration can enhance removal efficiency up to a certain level, excessively high concentrations may result in diminished performance due to the saturation of adsorption sites. Therefore, the optimal initial dye concentration for achieving the highest MB removal efficiency in this study is 20 ppm, where a remarkable 100% removal was recorded. This concentration represents the ideal balance between maximizing removal efficiency and ensuring efficient utilization of available adsorption sites.

3.5 Adsorption Isotherm Studies

The experiments were conducted by varying the initial MB concentration from 5 to 180 ppm, keeping the contact time 180 minutes, and using 0.1 g of adsorbent. The graphs shown in Figure 6 illustrate the Langmuir, Freundlich, and Redlich-Peterson isotherm models, following the equations reported in previous studies [22]. The Redlich–Peterson model was applied to evaluate the adsorption behaviour because it combines features of both the Langmuir and the Freundlich models, allowing assessment of whether the adsorption process follows ideal monolayer behaviour or exhibits heterogeneous surface characteristics. The non-linear plots of Langmuir, Freundlich, and Redlich-Peterson isotherm models of MB adsorption on unmodified NZC, HCl-NZC, and NaOH-NZC beads are shown in Figure 5 (a-c), respectively. The best fit model of the adsorption process was determined by comparing the R^2 values of the isotherm models. As we can see in Table 2, the adsorption process data fitted well by the Langmuir model, with values of 0.9952 (HCl-NZC) and 0.9907 (NaOH-NZC), compared to the other models. These results validated that the adsorption is homogeneous and forms a monolayer. The order of the models, based on the R^2 correlation coefficient, is Langmuir > Redlich-Peterson > Freundlich. Hence, it was concluded that the adsorption of MB on HCl-NZC and NaOH-NZC beads is a monolayer, as the data were best fitted to the Langmuir model.

The MB adsorption capacities of HCl-NZC and NaOH-NZC beads were compared with those of other adsorbents reported in previous studies, as shown in Table 3. The maximum adsorption capacities increased to 45.80 mg/g for HCl-NZC and 45.09 mg/g for NaOH-NZC beads, compared to 30.91 mg/g for unmodified NZC beads. This improvement is primarily attributed to the significantly larger specific surface area and pore volume of the modified samples, which enhance MB adsorption, with HCl–NZC exhibiting slightly higher capacity due to more exposed active sites and accessible Si–OH groups that strengthen electrostatic attraction, while NaOH modification also increases surface hydroxylation, providing additional sites for dye binding, but resulted in a marginally lower number of accessible active sites. Furthermore, the use of low-cost materials such as NZC highlights the economic feasibility of these modified adsorbents. A comparison of the results from this study with those reported in previous literature (Table 3) demonstrates that the modified NZC bead exhibits excellent adsorption capacity, making it a cost-effective solution for dye removal.

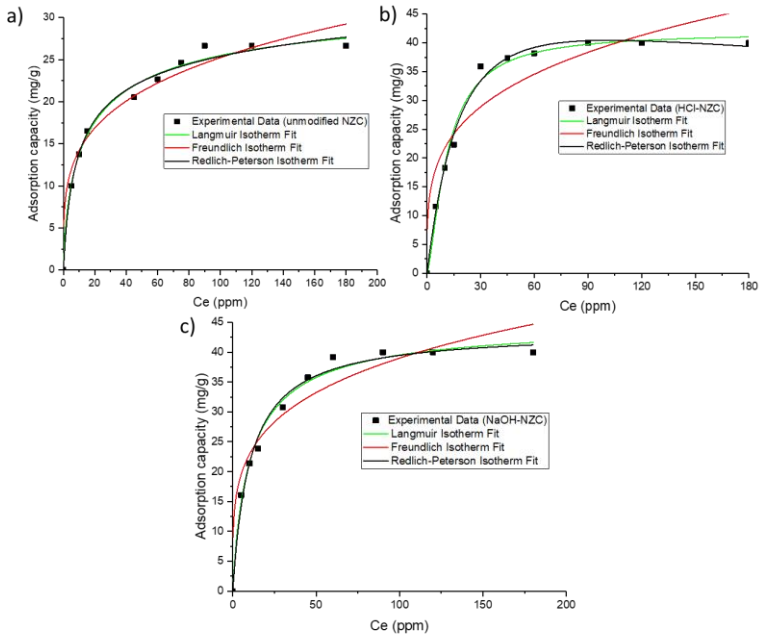

Figure 6 Adsorption isotherm model plots of Langmuir, Freundlich, and Redlich-Peterson for the adsorption of MB on (a) unmodified NZC, (b) HCl-NZC, and (c) NaOH-NZC beads

Table 2 Parameters of the equilibrium isotherm models for the adsorption of MB dye on unmodified NZC, HCl-NZC and NaOH-NZC beads

Isotherm Models	**Parameters**	**Unmodified NZC**	**HCl-NZC**	**NaOH-NZC**
Langmuir	q_{max} *(mg/g)*	30.9061	45.7952	45.0868
	K_L *(L/g)*	0.6823	1.4364	0.8920
	R^2	0.9910	0.9952	0.9907
Freundlich	n	4.0048	3.8770	4.3290
	K_F *(L/mg)*	7.9929	12.0139	13.4639
	R^2	0.9437	0.8059	0.8920
Redlich-Peterson	K_R	3.8788	2.4669	4.2108
	a_R	0.2261	0.0212	0.0973
	b	0.95	1.19	0.99
	R^2	0.9903	0.9936	0.9898

Table 3 Comparison of maximum adsorption capacities of MB with other adsorbents

Adsorbent	**Maximum adsorption capacity, q_e (mg/g)**	**References**
Acid-treated zeolite	2.11	[15]
Base-treated zeolite	1.09	[15]
Magnetic NaY zeolite composite	2.05	[24]
Modified pumice	15.87	[25]
Ni-O Nanoparticles (NPs)	166.67	[26]
Fly ash	5.72	[27]
Acid-treated coal fly ash	8.0	[28]
Fe_3O_4/ZA nanocomposite	40.46	[29]
Unmodified NZC	30.91	This study
HCl-NZC	45.80	This study
NaOH-NZC	45.09	This study

4.0 CONCLUSION

The modified HCl-NZC and NaOH-NZC beads were successfully synthesized for the removal of MB from wastewater. Acid and base modifications significantly enhanced the adsorptive properties of NZC by increasing its surface area and pore volume, as confirmed by FTIR-ATR and BET surface area analysis. The maximum adsorption capacities of 45.80 mg/g and 45.09 mg/g, along with high correlation coefficients (R^2 values of 0.9952 and 0.9907) for HCl-NZC and NaOH-NZC, respectively, indicated strong agreement with the Langmuir isotherm model, suggesting monolayer adsorption on a homogenous surface. In addition, incorporating the modified zeolite into alginate beads effectively overcame handling and recovery challenges, providing better mechanical stability and ease of separation. Overall, the modified NZC alginate beads present a cost-effective and practical adsorbent for dye removal from wastewater.

This preliminary study demonstrates the effectiveness of acid- and base-modified NZC beads in removing MB dye from aqueous solutions. Given their stability and strong adsorption performance, these modified beads can potentially be incorporated into membrane matrices to form hybrid adsorptive–filtration systems. Future work will focus on developing and evaluating zeolite-based composite membranes derived from these modified beads for advanced wastewater treatment applications.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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