

Article

Virgin Volcanic Rock: Kinetics and Equilibrium Studies for the Adsorption of Methylene Blue

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Abstract

Dye removal from aqueous solutions remains a major global environmental challenge. Among the various remediation techniques, adsorption using natural materials has gained significant attention. In this study, the adsorption of methylene blue (MB) by a natural volcanic rock (VR) adsorbent—collected from the Cerro Blanco volcano in Divisaderos, Sonora, Mexico—was investigated, and the process efficiency was evaluated at different temperatures. The comprehensive characterization revealed a rough and irregular porous surface via SEM, while the EDS elemental data and the CIPW normative calculations identified the material as a silica-saturated tholeiitic basalt, primarily composed of bytownite (An_{71}) and pyroxenes. This petrological classification was cross-validated by XRD and FTIR spectra, which exhibited vibrational modes characteristic of mafic silicate. The surface analysis via the BET method indicated a specific surface area of $12 \text{ m}^2 \cdot \text{g}^{-1}$, while a BJH analysis indicated a mesoporous structure (average pore diameter of 3.75 nm), and a Type IV isotherm with H3-type hysteresis, suggesting narrow, slit-shaped pores. Batch adsorption experiments demonstrated an exceptional removal efficiency of 99.99% for $50 \text{ mg} \cdot \text{L}^{-1}$ MB within only 30 min. The equilibrium data and the adsorption kinetics followed the Langmuir isotherm and a pseudo-second-order model, respectively. Cytotoxicity assays confirmed the VR is biosafe. The combination of high removal efficiency, low cost, and environmental safety positions this material as high-potential adsorbent for sustainable water remediation processes.

Keywords: kinetics; isotherms; thermodynamics; water remediation; dye



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1. Introduction

Currently, water pollution is one of the primary concerns worldwide; it is estimated that approximately 80% of global wastewater is discharged into water bodies without proper treatment [1]. In particular, the dye industry contributes significantly to water pollution, as it utilizes persistent synthetic compounds, which can have an adverse impact on both aquatic organisms and human beings, given that dyes can reduce sunlight transmission and hinder photosynthetic processes [2].

To address these challenges, various techniques have been implemented for dye removal from aqueous solutions, including coagulation–flocculation, biological processes, membrane filtration, ion exchange, adsorption, electrochemical methods, photocatalysis, and advanced oxidation processes [3]. Conventional methods, such as coagulation–flocculation, are simple initially and are cost-effective; however, they generate significant amounts of sludge that require further handling [4]. Biological treatments (aerobic and anaerobic) offer an environmentally friendly and economical alternative, yet their efficiency is often limited by the recalcitrant nature of many synthetic dyes. Similarly, while membrane filtration and ion exchange processes provide high removal efficiencies, their practical application is hindered by membrane fouling and high maintenance costs [5]. In recent years, electrochemical techniques (electrocoagulation and electrooxidation) and photocatalytic processes have gained attention due to their ability to achieve high mineralization; however, they remain expensive due to considerable energy requirements [6].

Among these, adsorption has gained significant attention, owing to its operational simplicity, high efficiency, and the potential for adsorbent regeneration [7]. While carbonaceous materials are widely utilized due to their remarkable adsorption capacity, their high production costs often limit large-scale application. Consequently, there is an urgent need to explore more economical and sustainable natural alternatives [8].

Volcanic rock is emerging as a promising natural adsorbent due to its widespread lithological availability and unique physicochemical properties, including high porosity, significant surface area, and exceptional chemical stability [9]. Recent studies have demonstrated that the multi-component mineralogy of volcanic rock facilitates the adsorption of various contaminants, such as heavy metals and organic dyes, positioning volcanic rock as a sustainable and cost-effective candidate for advanced wastewater treatment [10].

The application of volcanic rock as a natural adsorbent for dye remediation has yielded promising results. Nevertheless, its performance is highly contingent upon critical operational parameters, including the solution pH, the initial adsorbate concentration, and the solid–liquid contact time [11]. These variables fundamentally govern the adsorption kinetics and the thermodynamic equilibrium, ultimately determining the overall efficiency of the sequestration process [12].

This study evaluates the adsorbent properties of volcanic rock (VR) sourced from the Cerro Blanco volcano, located in Divisaderos, eastern Sonora, Mexico [29.600° N, −109.516° W]. A petrological and mineralogical analyses identified this material as a silica-saturated tholeiitic basalt, primarily composed of bytownite (An_{71}). Notably, mechanical processing and crushing of the rock generate a mesoporous silica-rich structure [13], which, combined with its intrinsic porosity, suggests a significant potential for the sequestration of cationic dyes. Beyond its structural advantages, the VR exhibits intrinsic photoluminescence properties, an unconventional feature in natural mineral adsorbents. This natural fluorescence is attributed to the presence of specific active centers within the bytownite lattice, such as structural defects or trace element activators [14].

Methylene blue (MB) is a prominent cationic organic dye widely used in the textile, pharmaceutical, paper, and plastic industries [15]. Due to its stable aromatic structure, MB is highly resistant to natural biodegradation, and its presence in aquatic systems disrupts

photosynthetic processes by blocking sunlight [16]. Furthermore, exposure to MB can cause adverse health effects in humans, including respiratory distress and digestive disorders [17]. Testing its removal is therefore a critical case study for evaluating the efficiency of VR as an adsorbent.

2. Materials and Methods

2.1. Chemicals

Sodium chloride (NaCl 99%, Sigma-Aldrich, Toluca, México), sodium hydroxide (NaOH 97.0%, pellets, Sigma-Aldrich), ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$ 99.5%, Sigma-Aldrich), nitric acid (HNO_3 70%, Sigma-Aldrich) and hydrochloric acid (HCl 37%, Sigma-Aldrich) were obtained from commercial sources and used as received. Deionized water (DW) was employed in all experimental procedures. The methylene blue dye ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\cdot 3\text{H}_2\text{O}$, 82%) produced by Sigma-Aldrich was used without any purifying procedures. By combining 1.2195 g of MB with one liter of deionized water, a stock solution with a concentration of 1000 mg/L was created.

2.2. Material Source

The volcanic rock (VR) used in this investigation was obtained from the Cerro Blanco volcano, located near the municipality of Divisaderos in the eastern region of Sonora State, Mexico, a region recognized for its extensive volcanic formations. The volcano coordinates are 29.600° N , -109.516° W and it is part of the geological formation named Sierra Madre Occidental.

Material was collected from the flank of the volcano, ensuring that selected rocks exhibit homogeneity in terms of appearance and size. Subsequently, rock samples were packed, labelled, and transported to the research laboratory under controlled conditions.

2.3. Preparation of Volcanic Rock Particles

Figure 1 illustrates the milling procedure for the VR particles. The rock samples, each weighing approximately 4 g, were introduced into a Fritsch Pulverisette 7 ball mill for comminution at a rotational speed of 800 rpm. Subsequently, to remove dust impurities from the comminuted particles, these were immersed in 30 mL of deionized water and subjected to agitation for 15 min. Finally, the mixture was filtered with paper to recover the VR particles.

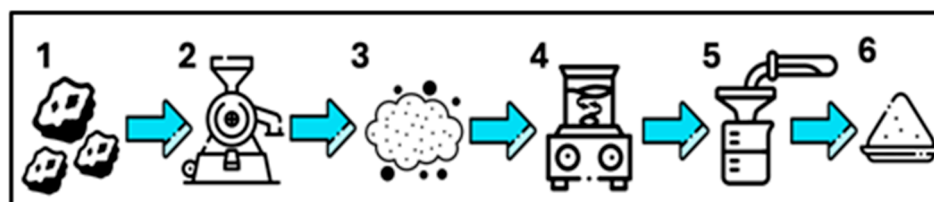


Figure 1. Fabrication procedure for VR particles.

2.4. Characterization

The surface morphology of the VR was characterized using the following techniques: Scanning Electron Microscopy (SEM) with a JEOL JSM-5410LV (Tokyo, Japan) equipped with an INCA system and an Oxford Instruments, Energy-Dispersive X-ray Spectroscopy (EDS) detector operating at 15 kV (before the analysis, samples were coated with a gold layer of approximately 20 nm to prevent charge build-up), and elemental analysis using the EDS detector.

Chemical composition of the sample was determined using a Perkin-Elmer Model 1600 ATR-FTIR spectrometer with an ATR accessory. Spectral data were acquired in the range of 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1} .

Crystalline structure of the sample was determined using a Bruker Discover D8 X-ray diffractometer, employing $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). Angular measurements were performed through a range of 10° to 70° , with the X-ray tube operating at 40 kV and 30 mA.

The specific surface area was determined through nitrogen adsorption–desorption isotherms, obtained at 77 K using a Quantachrome NOVA analyzer. Pore size distribution and average pore diameter were assessed using the BJH method.

The pH at the point of zero charge (pHpzc) was determined by adding 0.1 g of the sample to 10 mL of a 0.01 M NaCl solution. The initial pH was adjusted within the range of 2–12 using 0.1 M HCl or 0.1 M NaOH. The suspension was then stirred, and the final pH was measured after 24 h. The pHpzc value was obtained from the intersection in the graph of ΔpH vs. initial pH curve.

2.5. Adsorption Experiments

2.5.1. Adsorption Kinetics

To evaluate the effect of the solution pH on the MB adsorption with 0.25 g volcanic rock at 298.15 K, experiments were conducted over a pH range of 3 to 11. The pH was adjusted by the controlled addition of 0.1 M HCl or 0.1 M NaOH solutions.

Sorption experiments used 50 mL of a 50 $\text{mg}\cdot\text{L}^{-1}$ MB solution with 0.25 g of adsorbent at different temperatures (298.15, 308.15, and 318.15 K), which were equilibrated for 24 h, and samples were collected at predetermined time intervals. Then the suspension was centrifuged at 5000 rpm for 5 min. The supernatant was analyzed by UV-Vis spectrophotometry (Agilent 8453). The absorbance value of methylene blue was read at the wavelength of 664 nm. All experiments were conducted in triplicate, and the mean value was used for data analysis of the experimental design.

The sorption capacity of the adsorbent sample for dye (q , mg/g) at equilibrium conditions was calculated using Equation (1).

$$q = \frac{(C_0 - C_e)V}{w} \quad (1)$$

The initial concentration (C_0) and the equilibrium concentration (C_e) of MB are given in $\text{mg}\cdot\text{L}^{-1}$, the volume of the solution (V) is expressed in L, and the mass sample (w) is expressed in g. The reproducibility was verified by triplicate analysis. The MB removal percentage was obtained using Equation (2).

$$\text{Removal (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

2.5.2. Equilibrium Studies

The adsorption isotherms were obtained by employing 50 mL of MB solutions with concentrations ranging from 20 to 100 $\text{mg}\cdot\text{L}^{-1}$, which were mixed with 0.25 g of adsorbent at 298.15, 308.15 and 318.15 K. The mixtures were then subjected to different temperatures for 30 min. The regeneration and reuse of the samples were evaluated as follows: 0.5 g of a sample was added to 50 mL of 50 $\text{mg}\cdot\text{L}^{-1}$ MB solution. Adsorption was performed at 298.15 K and 150 rpm for 30 min until saturation was achieved.

2.5.3. Desorption Studies

After MB adsorption process, VR adsorbent was centrifuged, dried, and desorbed before being reused. Effects of solvent (deionized water, ethanol, nitric acid, hydrochloric

acid, and sodium hydroxide) were studied. The desorption of MB was determined by loading 0.25 g of adsorbent with 50 mL of MB solution in a solvent at 318.15 K. These samples were agitated at 150 rpm for 50 min. Amount of dye desorbed was determined by use of a spectrophotometer at 664 nm.

After identifying the ideal desorption circumstances, adsorbent was reused for adsorption with optimized adsorption conditions, and the number of reuses of volcanic rock was then calculated. Desorption capacity (q_{de}) was calculated using Equation (3):

$$q_{de} \text{ (mg} \cdot \text{g}^{-1}) = \frac{(C_f)V}{w} \quad (3)$$

2.5.4. Statistical Analysis

The experiments were performed in triplicate, and the results were presented in form of mean $\pm$ standard deviation (SD). Significant differences between different samples were examined by one-way analysis of variance (ANOVA) with F-test and T-test.

2.6. Cytotoxic Assays of VR Particles

Human dermal fibroblasts from the Detroit 548CCL-116 cell line were cultured with initial density of 5×10^5 cells $\cdot$ mL $^{-1}$ using Dulbecco's Modified Eagle Medium (DMEM; Sigma-Aldrich). The culture medium was enriched with 10% fetal bovine serum (FBS; Sigma-Aldrich) and 1% antibiotic-antimycotic solution containing 100 U $\cdot$ mL $^{-1}$ penicillin and 100 μ g $\cdot$ mL $^{-1}$ streptomycin (Thermo Fisher Scientific). Cells were maintained at 310 K in a humidified incubator under a 5% CO $_2$ atmosphere.

To assess the cytotoxicity of the VR particles, the material was sterilized by subjecting it to four consecutive cycles of ultraviolet (UV) irradiation of 15 min each. Following sterilization, particles were washed with methanol and left to air-dry, following the method described by Vuong et al. in 2016 [18]. Particles were subsequently suspended in DMEM containing 1% FBS and dispersed in ice-cooled water by applying sonication for 20 min.

For cytotoxicity testing, fibroblasts were placed in 96-well plates at a density of 5000 cells per well. Once the cells were adhered to the substrate, the culture medium was replaced with fresh medium containing VR particles at different concentrations (0, 12.5, 25, 50, 100, 200 and 300 mg $\cdot$ L $^{-1}$). Cell viability was evaluated after 24 h using a resazurin-based assay, which measures metabolic activity via absorbance readings at 570 nm and 600 nm, in accordance with the method of Giordano et al. [19].

3. Results

3.1. Characterization

Figure 2 shows an SEM micrograph of the VR particles displaying an irregular morphology, with angular edges and a surface texture consisting of fragmented volcanic materials. The particle size distribution spanned from 10 to 100 μ m. The most abundant particles were found within the 30 to 50 μ m size fraction.

The Energy-Dispersive X-ray Spectroscopy (EDS) spectrum (Figure 3) revealed the elemental composition of the sample VR, which was primarily composed of 46.59% oxygen and 21.49% silicon, followed by 9.89% iron, 9.41% aluminum, 5.35% calcium, 2.63% magnesium, 3.01% sodium, 1.33% titanium, and 0.30% potassium. The EDS analysis was performed in triplicate on different areas of the sample. The reported values correspond to the average composition. Some variability was observed among the replicates, particularly in the oxygen content, which may be attributed to surface heterogeneity, particle topography, and possible surface hydration effects. The estimated uncertainty is ± 1 –3 wt% for major elements, with a detection limit of approximately 0.1 wt%.

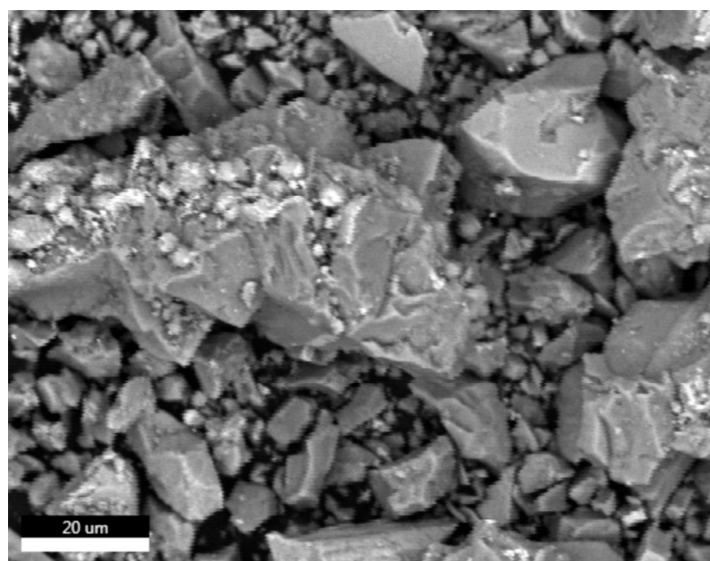


Figure 2. SEM micrograph of volcanic rock.

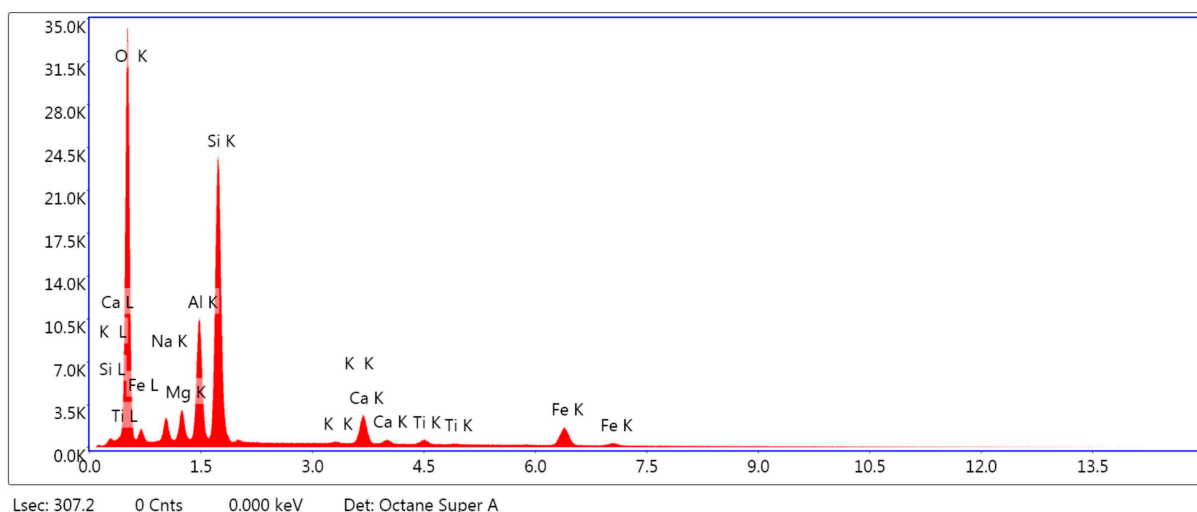


Figure 3. EDS analysis of volcanic rock.

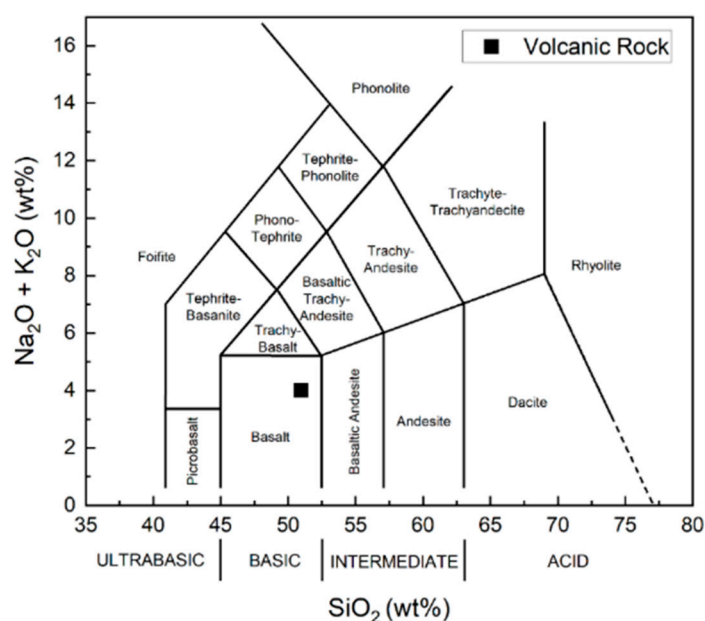
From these data, the corresponding oxide weight percentages (wt%) were calculated and are summarized in Table 1. The resulting oxide concentrations indicate contents of 50.95% SiO_2 , 11.45% total iron oxide (FeO) and 5.04% magnesium oxide (MgO). These data were subsequently employed for petrological classification and geochemical modelling through the Total Alkali–Silica (TAS), Alkalis–Ferrum–Magnesium (AFM), and Cross–Iddings–Pirsson–Washington (CIPW) normative analysis. The integration of these chemical parameters allowed a precise determination of the magmatic series and the crystallization environment of the VR.

As shown in Figure 4, the coordinates (50.95, 4.0) identify the VR as basalt, a classification that is in strict agreement with the TAS scheme for volcanic materials [20]. This position within the basaltic field confirms the basic nature of the rock and provides the necessary geochemical framework to proceed with the identification of its magmatic series and normative mineralogy.

Table 1. Oxide weight percentages and normative moles in VR.

Sample	Element	wt% (EDS)	Oxide Factor	Oxide	Oxide wt%	Normative Moles (PMol)
Volcanic Rock	Si	23.82	2.1393	SiO ₂	50.95	0.8735
	Al	9.70	1.8895	Al ₂ O ₃	18.33	0.1875
	Fe	8.90	1.2865	FeO	11.45	0.1713
	Ca	5.51	1.3992	CaO	7.71	0.1467
	Mg	3.04	1.6581	MgO	5.04	0.1382
	Na	2.82	1.3481	Na ₂ O	3.8	0.0641
	Ti	1.51	1.6681	TiO ₂	2.52	0.0353
	K	0.17	1.2046	K ₂ O	0.20	0.0025

Note: Total iron is expressed as FeO for normative and petrological classification purposes.

**Figure 4.** TAS diagram showing the VA as a basalt.

The AFM diagram, presented in Figure 5, and the information of the normalized oxide percentages, presented in Table 1, locates the VR within the tholeiitic series, according to the boundary established by Kuno. The coordinates (19.55, 55.98, 24.44) were calculated following the method of Santos and Hartmann [21], confirming a significant iron enrichment relative to magnesium, which is a diagnostic feature of tholeiitic magmatism.

According to the CIPW normative calculations presented in Table 2, the VR consists of quartz (Qz), orthoclase (Or), albite (Ab), anorthite (An), diopside (Di), hypersthene (Hy), magnetite (Mt) and ilmenite (Il). This mineralogical assemblage confirms a silica-saturated basalt belonging to the tholeiitic series [22]. The normative presence of Qz and Hy, coupled with its iron-rich nature, is characteristic of continental rift formation rather than Mid-Ocean Ridge Basalts (MORBs).

Figure 6 shows the X-ray diffraction (XRD) pattern corresponding to the VR sample. This diffractogram reveals several prominent reflections characteristic of volcanic mineralogy. In accordance with the TAS and AFM diagrams as well as the CIPW norm calculations, which classified the sample as a tholeiitic basalt, the identified mineral phases include Qz, Or, Ab, An, Hy, Il, Mt, and Di.

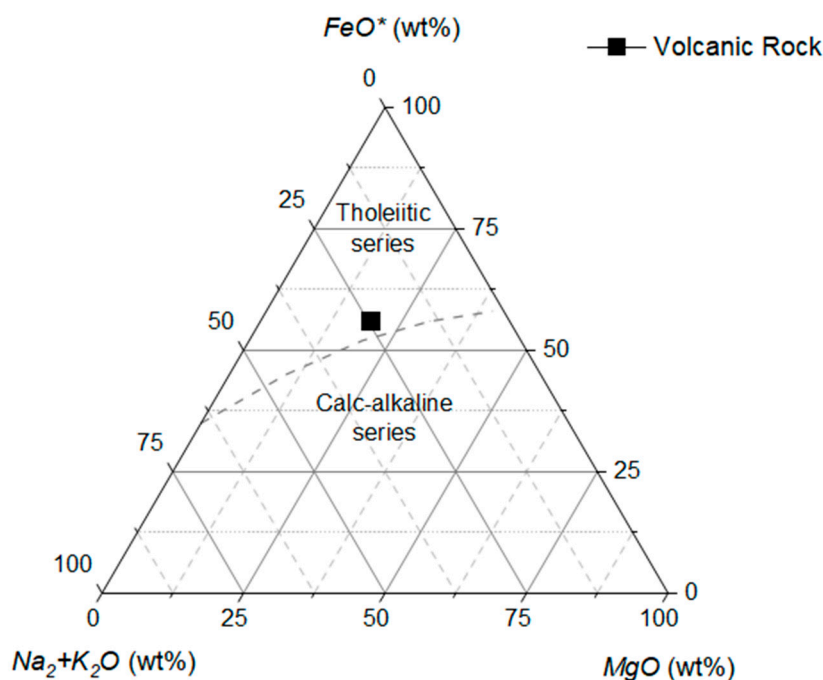


Figure 5. AFM diagram locating the VR in the tholeiitic series.

Table 2. Calculated CIPW normative mineralogy for tholeiitic basalt.

Mineral Phase	Crystal System	Formula	wt%
Quartz	Trigonal	SiO ₂	5.23
Orthoclase	Monoclinic	KAlSi ₃ O ₈	0.30
Albite	Triclinic	NaAlSi ₃ O ₈	6.83
Anorthite	Triclinic	CaAl ₂ Si ₂ O ₈	16.51
Diopside	Monoclinic	CaMgSi ₂ O ₆	2.50
Hypersthene	Orthorhombic	(Mg, Fe) SiO ₃	16.63
Magnetite	Cubic	Fe ₃ O ₄	0.35
Ilmenite	Trigonal	FeTiO ₃	3.92

Note: Values indicate the calculated normative weight percentage for each mineral phase.

In the XRD reflections, several material phases were identified by their specific interplanar *d*-spacings and Miller indices (*hkl*), as summarized in Table 3. The predominance of reflections associated with An and Hy strongly confirms the tholeiitic nature of the VR unit, which exhibits high crystallinity as evidenced by the sharp peaks persistent even at diffraction angles exceeding 60° (2θ). The presence of Mt and Il, albeit in minor proportions, corroborates the Fe–Ti oxide content determined by the CIPW norm, comprising a primary mineral paragenesis with no significant evidence of secondary alteration or detectable amorphous phases.

The most abundant mineral in the VR sample is An, exhibiting a primary diffraction peak at 27.76° (2θ). This position indicates that a triclinic structure dominates the rock matrix, characteristic of calcic plagioclases. The overlap between the An and Ab signals suggests a non-pure phase, consisting instead of an intermediate-composition plagioclase where sodium is integrated into the crystal lattice of the predominant feldspar.

Coexisting with this matrix, a significant presence of Hy is observed, with reflections in the 30–33° (2θ) range, confirming the stability of the iron–magnesium silicates as orthopyroxene. Additionally, Di occurs as a minority phase between 30 and 64° (2θ); its occurrence as a calcium-rich clinopyroxene demonstrates that the silica-oversaturated matrix of the VR unit provides the necessary environment for the stability of diverse crystalline structures.

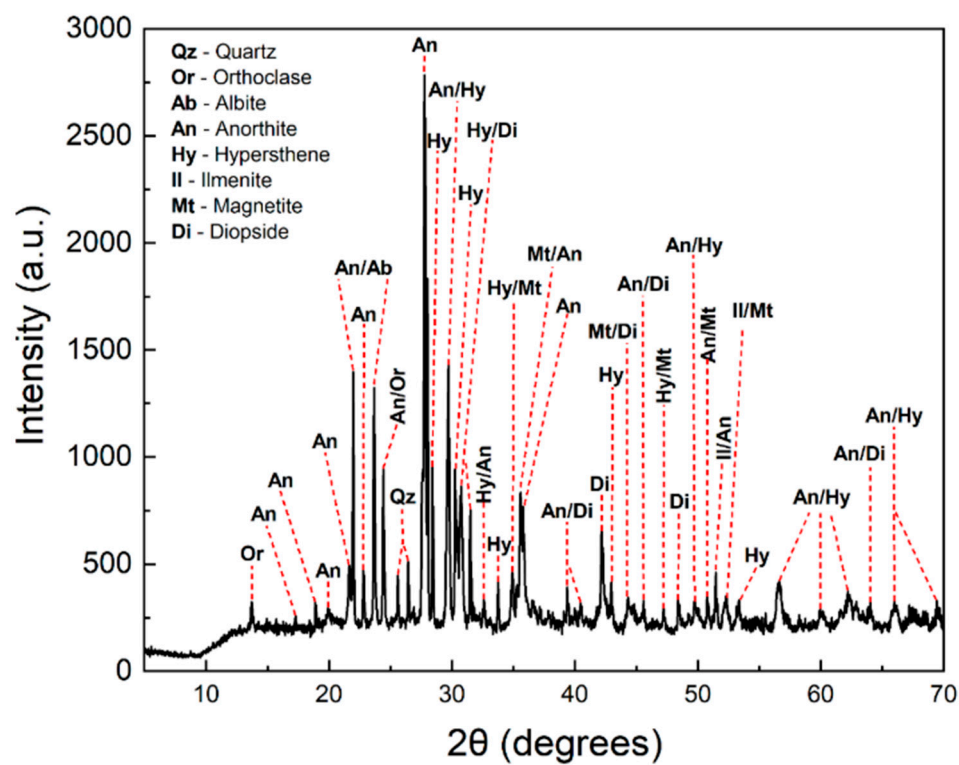


Figure 6. X-ray diffractogram of volcanic rock.

Table 3. Mineral phase identification, interplanar *d*-spacings, and Miller indices (*hkl*) for the XRD pattern of the VR.

Mineral Phase	2θ (°)	d-Spacing (Å)	Miller Indices (hkl)	Mineral Phase	2θ (°)	d-Spacing (Å)	Miller Indices (hkl)
Quartz	25.6	3.47	(011)	Diopside	30.74	2.91	($\bar{2}21$)
	26.44	3.37	(101)		31.5	2.84	(310)
Orthose	24.42	3.64	(111)	Hypersthene	28.42	3.14	(211)
	27.76	3.21	($\bar{2}01$)		29.72	3.01	(311)
Albite	21.98	4.04	($\bar{0}22$)		30.26	2.95	(411)
	23.68	3.75	(002)		30.74	2.91	(511)
Anorthite	21.98	4.04	($\bar{0}22$)	Magnetite	31.5	2.84	(321)
	23.68	3.75	(002)		34.92	2.57	(311)
	24.42	3.64	(111)		35.58	2.52	(311)
	29.72	3	(131)		44.32	2.04	(400)
	39.38	2.28	($\bar{2}42$)		47.2	1.93	(331)
	40.46	2.22	(151)		51.46	1.78	(116)

Regarding the oxides, Mt is manifested through its primary reflection at 44.32° (2θ), corresponding to the (400) plane of its cubic spinel structure. Conversely, Il is subtly identified at 51.46° (2θ), overlapping with the high-resolution signals of the An phase. The crystallization of these minerals suggests that the VR magma possessed a moderate oxygen fugacity (*f*O₂), which allowed iron to be partitioned into two distinct environments: the cubic spinel lattice of Mt and the rhombohedral structure within the trigonal system of Il.

This information reveals a holocrystalline rock, characterized by narrow, high-intensity peaks, indicating slow to moderate cooling that allowed for excellent atomic ordering. The identified mineralogical assemblage (calcic plagioclase + orthopyroxene + clinopyroxene + Fe-Ti oxides) is diagnostic of a tholeiitic basalt.

Based on the normative values of Ab (6.83) and An (16.51), an An content of 70.74% (An₇₁) was determined. This result allows for the classification of the dominant phase as bytownite (0.71 CaAl₂Si₂O₈ · 0.29 NaAlSi₃O₈), situated at the compositional boundary with labradorite. This highly calcic nature is consistent with the position of the observed diffraction maximum at 27.76° (2θ), which shows a mineral shift relative to the pure An pattern, confirming the mafic character and tholeiitic signature of the VR unit. This data is coherent with the whole-rock geochemistry (AFM diagram), reinforcing the interpretation of the sample as a primary volcanic product with scarce magmatic diffraction.

The FTIR spectrum of the VR is presented in Figure 7. The absorption bands at 757, 650, and 540 cm^{−1} correspond to the vibrational modes of the Si-O bond in the ring linkages within the silicate network, a characteristic feature of minerals such as feldspar [23]. The absorption peak observed at 472 cm^{−1} is attributed to the Si-O-Fe vibrational modes, indicating the potential presence of ferromagnesian minerals, including Mt and Il, for which absorption in this spectral region has been previously documented [24]. The principal absorption band at 1014 cm^{−1} is associated with the stretching vibrations of Si-O and Al-O linkages, which are characteristic of the aluminosilicate framework commonly found in minerals such as feldspar, and its precise position changes depending on the structural degree order within the material [25].

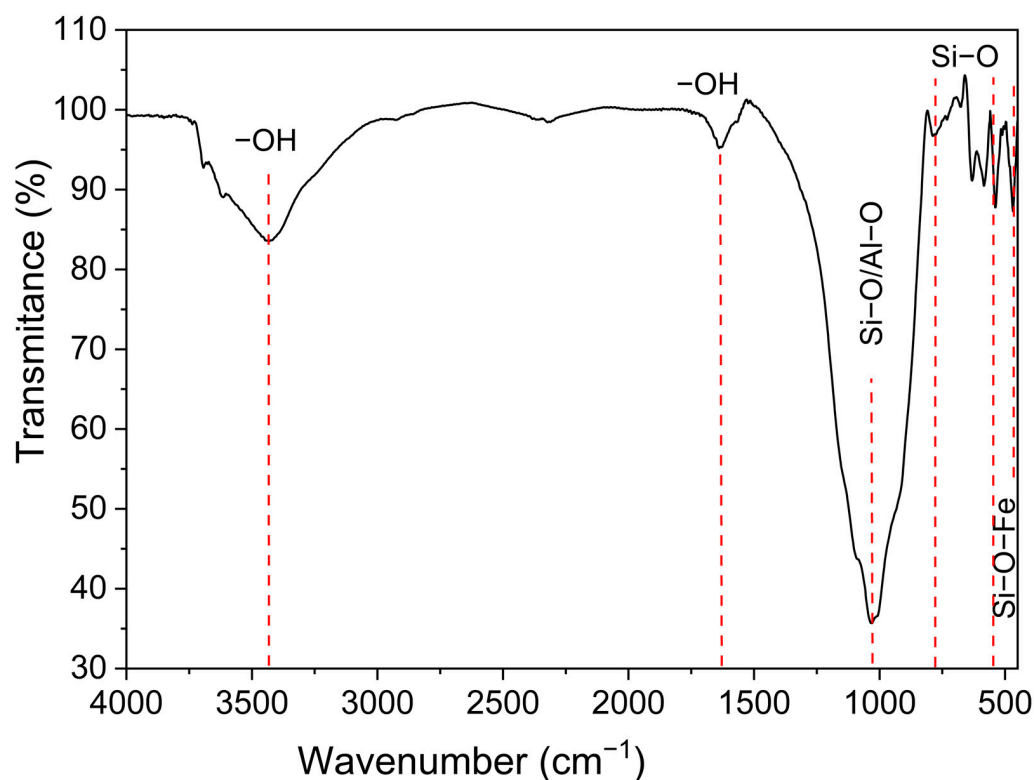


Figure 7. FT-IR spectrum of volcanic rock. The red dotted line indicates the wavelength corresponding to absorption bands.

Furthermore, the absorption bands at 3420 and 1630 cm^{−1} correspond to the stretching and bending vibrations of O-H bonds in water molecules. These spectral features may be associated with either the hydration of minerals within the VR or the presence of adsorbed water on its surface, a phenomenon commonly reported in studies of both zeolites and phyllosilicates. These hydroxylated surfaces are crucial for the functionalization of the VR unit, providing the necessary active sites for its interaction with nanomaterials.

In calcic plagioclases such as bytownite, the substitution of S^{4+} by Al^{3+} in the tetrahedral sites creates a charge imbalance that is typically compensated by Ca^{2+} . However, at the surface level, this configuration often leads to the presence of reactive sites. The absorption bands observed at 3420 and 1630 cm^{-1} indicate that, despite the anhydrous nature of the primary bulk mineralogy, the VR unit possessed a hydroxylated surface.

Figure 8 shows the N_2 adsorption–desorption isotherm at 77 K and the corresponding pore size distribution of the VR. The isotherm is type IV, according to the BDDT classification with H3-type hysteresis that describes a material with slit-shaped pores, as can be observed in Figure 2 [26]. The specific surface area of the VR was calculated to be $12\text{ m}^2\cdot\text{g}^{-1}$ using the Brunauer–Emmer–Teller (BET) method, and the average pore diameter and total pore volume are 3.75 nm and $0.037\text{ cm}^3\cdot\text{g}^{-1}$, respectively, using the Barrett–Joyner–Halenda (BJH) theory for mesopore analysis. This indicates that the surface of the VR has pores, with mesopores being the dominant type.

These are the results of the particle size reduction by ball milling, which causes the silicate chains to fracture and rearrange, leading to the formation of cavities.

The pH of the dye solution, which is a critical factor affecting dye removal, can change the degree of ionization of the adsorbent and the molecular structure of the dye [27].

According to the prevailing pH conditions and the molar fraction of dye molecules in the aqueous solution, MB can be present either as a cationic (MB^+) or neutral (un-charged) (MB^0) species, as displayed in the speciation diagram. The MB^0 species predominates (86%) at $\text{pH} = 3.0$, whereas both MB^0 (50%) and MB^+ (50%) species coexist at $\text{pH} = \text{pK}_a = 3.8$. On the other hand, MB^+ is practically the only species present at $\text{pH} > 6.0$ [28]. Therefore, the removal of MB from aqueous solutions by the addressed adsorbent was mainly controlled by the prevailing pH conditions, as shown in Figure 5.

The pH_{pzc} indicates the pH at which an adsorbent surface has no net electrical charge [29]. The pH_{pzc} was determined from the intersection of the ΔpH versus the initial pH curve. All the measurements were performed in triplicate, and the results are presented as the mean $\pm$ the standard deviation. The pH_{pzc} of the adsorbent was determined to be 6.89 (Figure 9a). The adsorption experiments for a $50\text{ mg}\cdot\text{L}^{-1}$ sample of MB were done in a pH range from 3 to 11, and we observed a 99.9% removal of MB. The adsorption is higher when the pH conditions get closer to the pH_{pzc} (Figure 9b). Then, the pH solution significantly controls the adsorption process by influencing the chemistry of the solid phase, modifying the binding sites on the adsorbent surface. At low pH conditions, the Al-O and Si-O groups of the material can be protonated, repelling the MB molecules at the adsorption sites, thereby decreasing dye adsorption efficiency. Below the VR pH_{pzc} , protons (H^+) and MB molecules compete for active adsorption sites, which restricts the extent of dye adsorption [30]. As the pH increases, a larger surface area of the adsorbent repels protons, acquiring negative charges, reducing the repulsion of MB molecules, and favoring their adsorption. This study shows that pH control is a factor improving the MB dye molecule adsorption process into the VR adsorbent material. Although electrostatic attraction is the main mechanism governing the adsorption of MB by the investigated adsorbents, hydrogen bonding and π - π interactions [31] (between the two benzene rings of the adsorbent and MB) may also be important, particularly at pH values below the pH_{pzc} . Hydrogen bonding can occur either between the H-donor (hydrogen of the amino groups on the surface of adsorbents) and the H-acceptor (nitrogen atoms of the MB) or between the surface amino groups of the adsorbents and the aromatic ring of the MB [32].

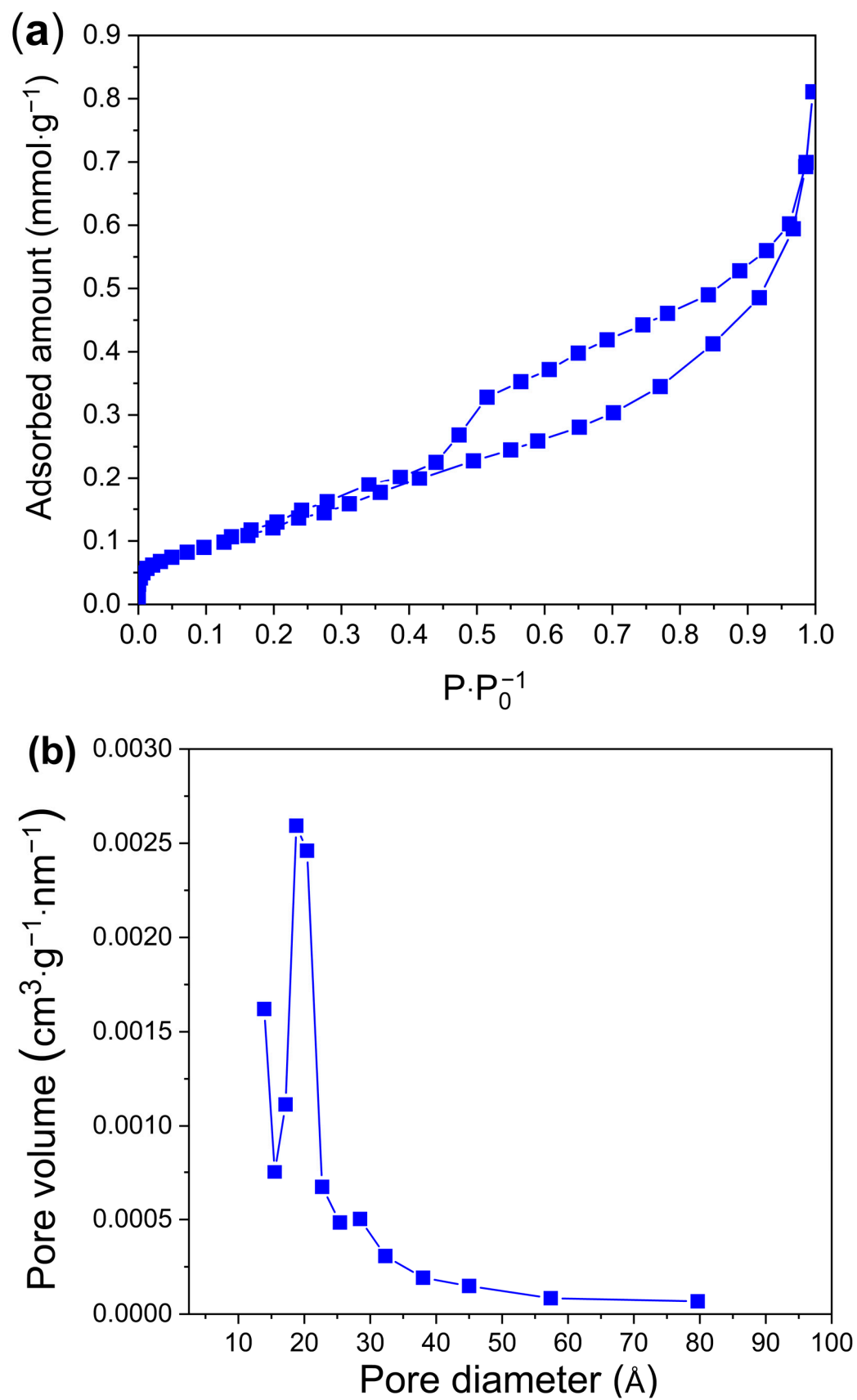


Figure 8. (a) N₂ adsorption–desorption isotherm at 77 K and (b) corresponding pore size distribution of VR.

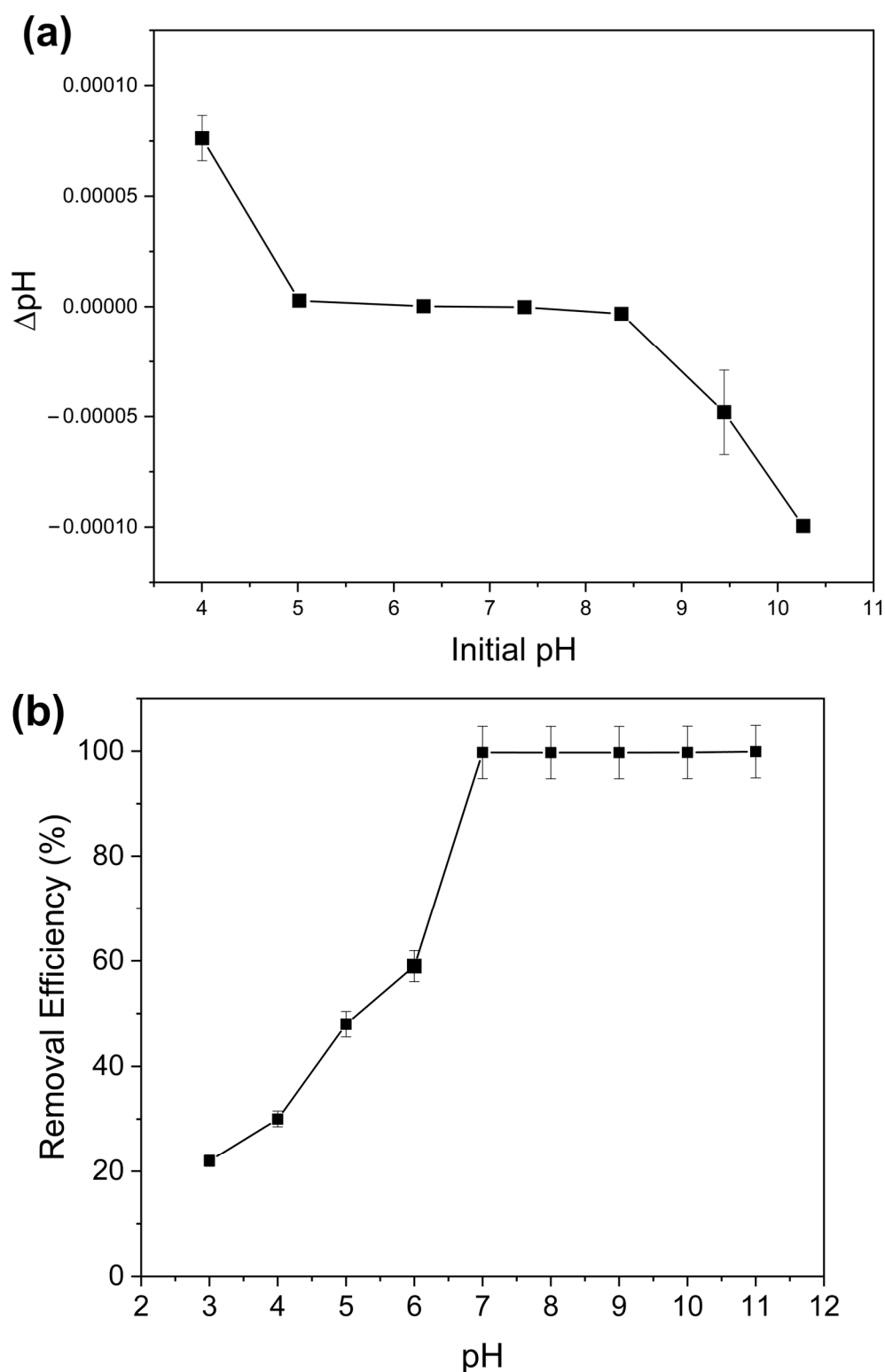


Figure 9. Determination of the influences of (a) point of zero charge and (b) pH on the adsorption of MB on VR. Experimental conditions: temperature 298.15 K, equilibrium time 30 min, mass to volume ratio 5 g/L, initial concentration of $50 \text{ mg} \cdot \text{L}^{-1}$, stirring 150 rpm.

In addition, this behavior can be described by the following mechanisms: ion exchange between the cationic dye and the protons of surface hydroxyl groups of natural zeolite and ion exchange between the metallic species and the exchangeable cations (Na^+ , Ca^{2+} , etc.) associated with plagioclase and other mineral phases. These may participate in dye uptake and balance the negative charges of each AlO_4 or SiO_4 tetrahedron in the framework.

Surface complexation and specific interactions between the MB molecules and the Fe- and Al-containing active sites are present in the aluminosilicate matrix.

3.2. Adsorption Study: Kinetics and Equilibrium

Figure 10 presents the adsorption kinetic curves for MB on the VR sorbent at three different temperatures. At the same sampling adsorption time, the amount of adsorbed dye decreased as the temperature increased. The process starts with an initial MB concentration of $50 \text{ mg}\cdot\text{L}^{-1}$, and it can be observed that in 30 min, the VR removes approximately 99% of the dye. This rapid response suggests that an effective interaction takes place between the dye and the active surface of the adsorbent. The effectiveness of VR as the adsorbent can be associated with the hydroxyl groups Si-O and Al-O on its surface and its specific surface area.

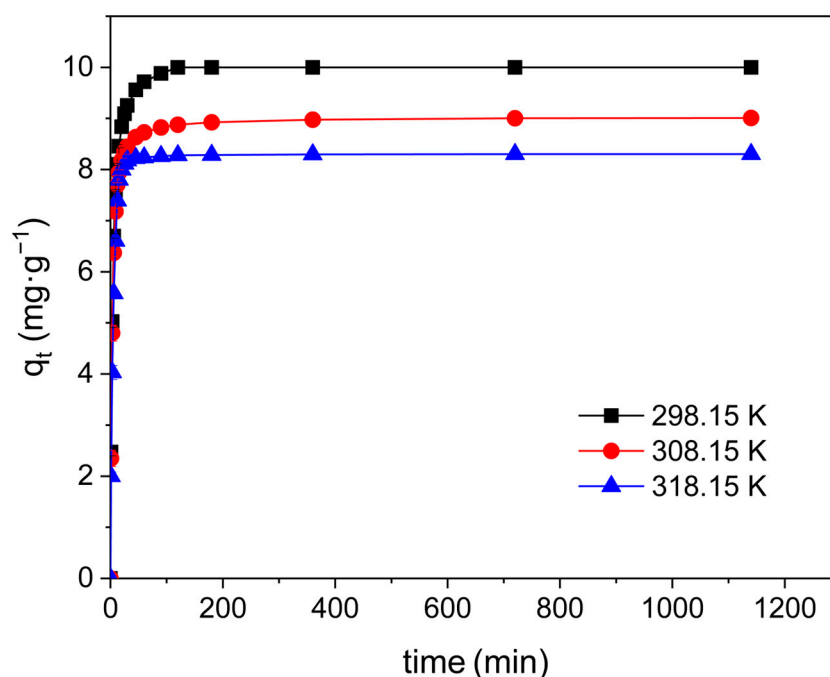


Figure 10. Adsorption kinetics of MB on VR as a function of the temperature. Symbols represent experimental data points, and lines the predicted pseudo-second order model. Experimental conditions: pH 9, equilibrium time 24 h, mass to volume ratio 5 g/L, initial concentration of $50 \text{ mg}\cdot\text{L}^{-1}$, stirring 150 rpm.

Applying pseudo-first and pseudo-second order kinetic models to the experimental data, the fitting parameters were obtained (Table 4). An analysis of these parameter values reveals that the pseudo-second order model accurately describes the data, suggesting that diffusion of MB dye into the absorbent pores is the dominant mechanism in the adsorption process. In the pseudo-second order model, the VR adsorbent material exhibits an equilibrium capacity (q_e) value of $10 \text{ mg}\cdot\text{g}^{-1}$. Simultaneously, the kinetic constant (K_2) reached 17.47, a value related to the larger pore size in the material.

This behavior suggests that the structural characteristics of the VR favor the effective diffusion of the dye in its pores, exerting a positive influence on MB removal from aqueous solutions. The apparent activation energy (E_a) was calculated using the Arrhenius equation (Equation (4)) [33].

$$\ln \frac{K_{T1}}{K_{T2}} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (4)$$

Table 4. Kinetic models for MB adsorption on the synthesized adsorbents at different temperatures yielded values for the adsorbed amount and rate constants.

Sample	T (K)	Pseudo-First Order			Pseudo-Second Order		
		R ²	K ₁ (min ^{−1})	q _e (mg·g ^{−1})	R ²	K ₂ (g(mg·min ^{−1}))	q _e (mg·g ^{−1})
Volcanic rock	298.15	0.915	0.0432	3.780	0.9980	0.045	10.030
	308.15	0.971	0.1291	6.450	0.9985	0.054	9.025
	318.15	0.992	0.1715	7.685	0.9983	0.096	8.313

Initial concentration (C₀); temperature (T); correlation (R²); pseudo-first constant (K₁); equilibrium adsorbed amount (q_e); pseudo-second constant (K₂).

In this equation, K_{T1} and K_{T2} are the pseudo-second order constants at 298.15 and 318.15 K, respectively, and R is the gas constant ($R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). The calculated E_a value for the VR is $30 \text{ kJ} \cdot \text{mol}^{-1}$. Additional information can be obtained using the intraparticle diffusion model equation (Equation (5)) [34].

$$q_t = k_{id}t^{\frac{1}{2}} + I \quad (5)$$

In Equation (4), k_{id} ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5}$) represents the intraparticle rate constant, and I ($\text{mmol} \cdot \text{g}^{-1}$) corresponds to the thickness of the boundary layer. Figure 11 shows the plot of q_t versus $t^{0.5}$, and k_{id} is obtained from the slope.

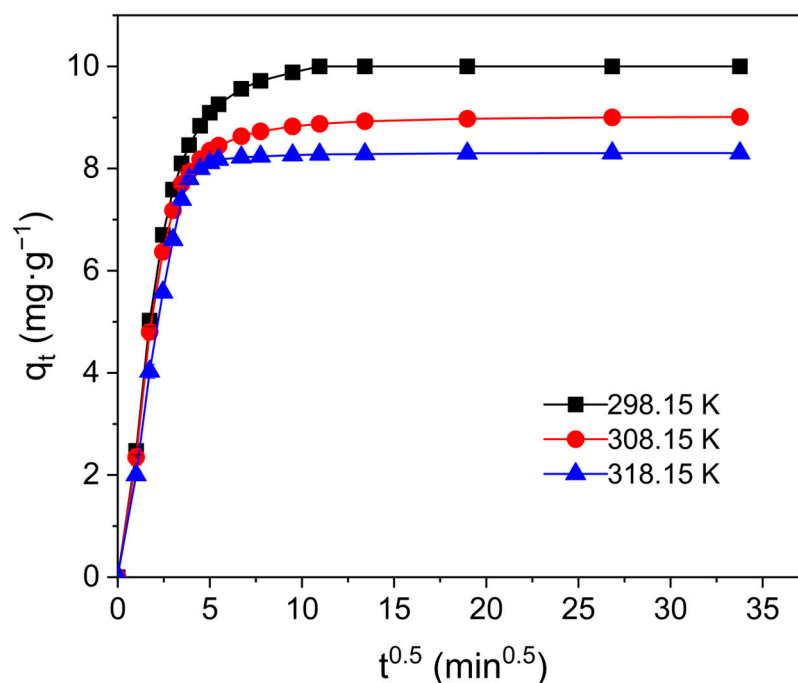


Figure 11. Intraparticle diffusion plots of MB adsorption in volcanic rock. Experimental conditions: pH 9, equilibrium time 24 h, mass to volume ratio 5 g/L, initial concentration of $50 \text{ mg} \cdot \text{L}^{-1}$, stirring 150 rpm.

The rate constant for the VR decreases when the temperature increases, which could be attributed to the pore size of the adsorbent (Table 5).

Table 5. Intraparticle diffusion rate constant for MB adsorption in VR at different temperatures.

Sample	C_0 ($\text{mg}\cdot\text{L}^{-1}$)	T (K)	k_{id} ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$)	I ($\text{mg}\cdot\text{g}^{-1}$)	R^2
Volcanic rock	50	298.15	0.8553	0.8767	0.9989
	50	308.15	0.8518	0.8803	0.9993
	50	318.15	0.8567	0.8754	0.9991

Initial concentration (C_0); temperature (T); intraparticle rate constant (k_{id}); thickness of the boundary layer (I); correlation (R^2).

The adsorption isotherms of MB at different temperatures using the VR are reported in Figure 12. According to the Giles classification, these isotherms belong to class “L” type 2 [35], suggesting favorable adsorption onto the Si-O and Al-O groups of the adsorbent material surface. The adsorption capacity is significantly higher in the experiment at 298.15 K, where the MB adsorbed by the VR reaches a value of $10 \text{ mg}\cdot\text{g}^{-1}$. The efficiency of the MB dye adsorption decreases as the temperature increases, because the interaction forces between the organic compound and the water molecules are weaker. Therefore, the interaction forces are reduced by the temperature.

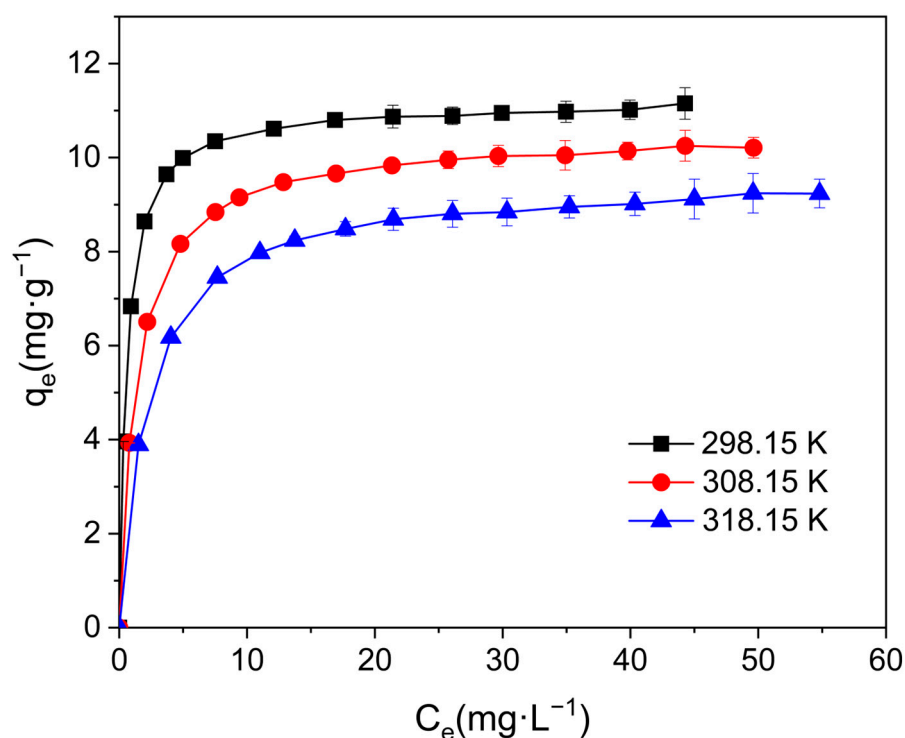


Figure 12. Adsorption isotherms of MB on VR adsorbents at different temperatures. Experimental conditions: pH 9, equilibrium time 24 h, mass to volume ratio 5 g/L, initial concentration of $50 \text{ mg}\cdot\text{L}^{-1}$, stirring 150 rpm.

The Langmuir and Freundlich equations provide the fitting parameters for the MB dye adsorption isotherms, as indicated by the experimental data reported in Table 6. The Langmuir model provides the best fit, indicating that adsorption occurs in a monolayer on a homogeneous surface, without interaction between the adsorbed molecules and a limited number of adsorption sites.

Table 6. Constants and correlation coefficients of Langmuir and Freundlich isotherms.

Sample	Model									
	C_0 (mg·L ⁻¹)	C_e (mg·L ⁻¹)	K_d	T (K)	Langmuir			Freundlich		
					q_{max} (mg·g ⁻¹)	K_L (L·mg ⁻¹)	R^2	K_F (L·mg ⁻¹)	N	R^2
volcanic rock	100	44.26	693.25	298.15	11.22	1.57	0.9985	6.62	6.08	0.7813
	100	49.6317	302.11	308.15	10.50	0.72	0.9981	5.27	5.10	0.8382
	100	54.79	241.13	318.15	9.60	0.44	0.9979	4.37	4.81	0.8607

Initial concentration (C_0); equilibrium concentration (C_e); equilibrium adsorption constant (K); temperature (T); adsorbed amount (q_{max}); interaction constant (K); correlation (R^2); adsorbed amount (N).

According to Equation (6), the equilibrium adsorption constant (K_d) values can be calculated [36].

$$K_d = \frac{\text{dye concentration in the adsorbent at equilibrium (mg·g}^{-1}\text{)}}{\text{dye concentration in solution at equilibrium (mg·mL}^{-1}\text{)}} \quad (6)$$

Table 7 shows the K_d values for dye adsorption onto the adsorbent, which can exhibit variations with initial dye concentrations. The K_d values increase as the initial MB dye concentration in the solution rises. The values of K_d were calculated at different temperatures and, using these values, the thermodynamic parameters for standard free energy, ΔG^0 , and standard enthalpy, ΔH^0 , were obtained using Equations (7) and (8) [37,38].

$$\Delta G^0 = -RT \ln K_d \quad (7)$$

$$\ln K_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (8)$$

Table 7. The thermodynamic parameters for MB adsorption on VR at different temperatures.

Sample	T (K)	ΔG^0 (kJ·mol ⁻¹)	ΔH^0 (kJ·mol ⁻¹)	ΔS^0 (J·mol ⁻¹ ·K ⁻¹)
volcanic rock	298.15	−13.72	−14.57	−2.84
	308.15	−13.71	-	-
	318.15	−13.66	-	-

T, temperature; ΔG^0 , standard free energy; ΔH^0 , standard enthalpy; ΔS^0 , standard entropy.

The dimensional units for ΔG^0 and ΔH^0 are (kJ·mol⁻¹) and (kJ·mol⁻¹), respectively. The ΔH^0 value was calculated from the slope of the linear plot of $\ln K_d$ versus $1/T$, and it is shown in Figure 13.

With the standard free energy, ΔG^0 , and the standard enthalpy, ΔH^0 , the values of the standard entropy, ΔS^0 , were determined using the Gibbs–Helmholtz equation (Equation (9)).

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (9)$$

The ΔG^0 , ΔH^0 , and ΔS^0 values for MB adsorption on the VR at the different temperatures are reported in Table 7. The negative values of ΔG^0 and ΔH^0 indicate that the dye adsorption process is spontaneous and exothermic, while the negative result of ΔS^0 suggests a decrease in order at the adsorbent/liquid interface for MB adsorption.

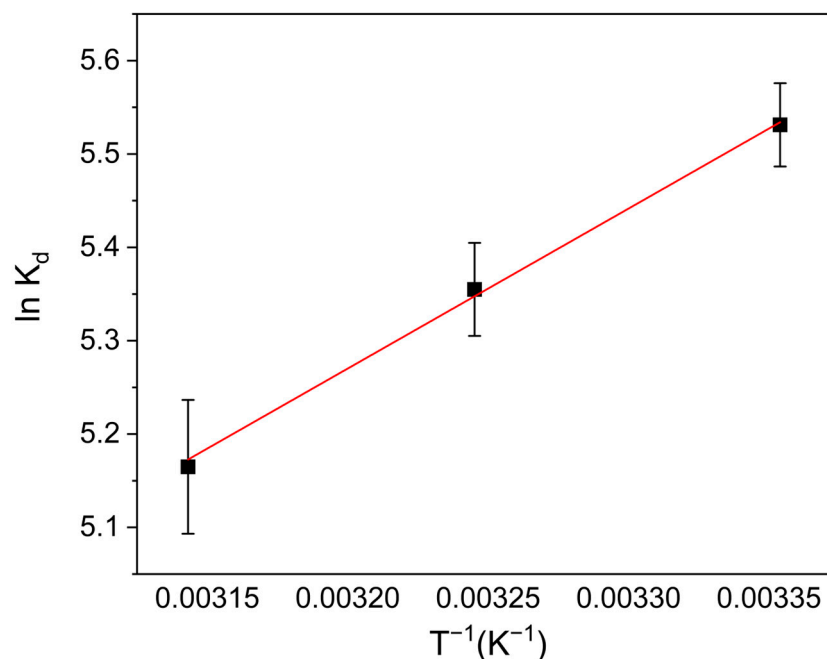


Figure 13. Plot of $\ln k_d$ versus $1/T$ for determining thermodynamic parameters.

3.3. Analysis of Desorption Properties

Figure 14a shows the desorption efficiencies of 0.25 g adsorbent loaded with MB and 50 mL of different eluents (deionized water, anhydrous ethanol, 0.2 M nitric acid solution, 0.2 M hydrochloric acid solution, or 0.2 M sodium hydroxide solution) at 318.15 K for 60 min. The removal efficiency of methylene blue adsorbed on the material follows the order 0.2 M HNO_3 > 0.2 M HCl > anhydrous ethanol > 0.2 M $NaOH$ > deionized water. These results indicate that nitric acid is the most effective desorption agent and is therefore the most suitable for regenerating the volcanic rock after methylene blue adsorption.

Figure 14b shows that the adsorption capacity of the material gradually decreases with an increasing number of adsorption–desorption cycles. After the first cycle, the removal efficiency of methylene blue reaches 95%. However, after five cycles, the efficiency decreases to approximately 90%. Despite this decline, the material retains significant adsorption capacity, confirming its reusability and highlighting the stability and potential of volcanic rock as a sustainable and reusable adsorbent for methylene blue removal.

To determine the stability of volcanic rock, the XRD patterns obtained after the first and fifth cycles were analyzed. These patterns are shown in Figure 15. The adsorbent was exceptionally stable, because no variations were detected in the diffractogram peaks after the MB adsorption.

3.4. Adsorption Mechanism

Figure 16 shows the possible adsorption interactions of the MB molecules on the VR adsorbent. Electrostatic interactions occur between the partially negative sulfur (S) and nitrogen (N) groups of the MB molecules with the potassium (K), silicon (Si) and aluminum (Al) groups on the surface of the material and a positive partial interaction of nitrogen (N) with oxygen (O) in the material [39].

3.5. Study of Cytotoxicity

The cytotoxic effects due to the VR particles on fibroblast cells was evaluated at 0, 12.5, 25, 50, 100, 200, and 300 $mg \cdot L^{-1}$ (Figure 17). The results showed that the VR particles did not induce significant cytotoxicity, as cell viability remained above 100% following

24 h of exposure, and there was no significant difference between the VR particles and the untreated control ($p \leq 0.05$), even at the highest concentration tested ($300 \text{ mg}\cdot\text{L}^{-1}$). On the contrary, an increase in cell viability was observed as the concentration of VR particles increased. In this study, a VR concentration that enables an effective MB adsorption and exhibits non-toxic behavior under the experimental conditions was selected.

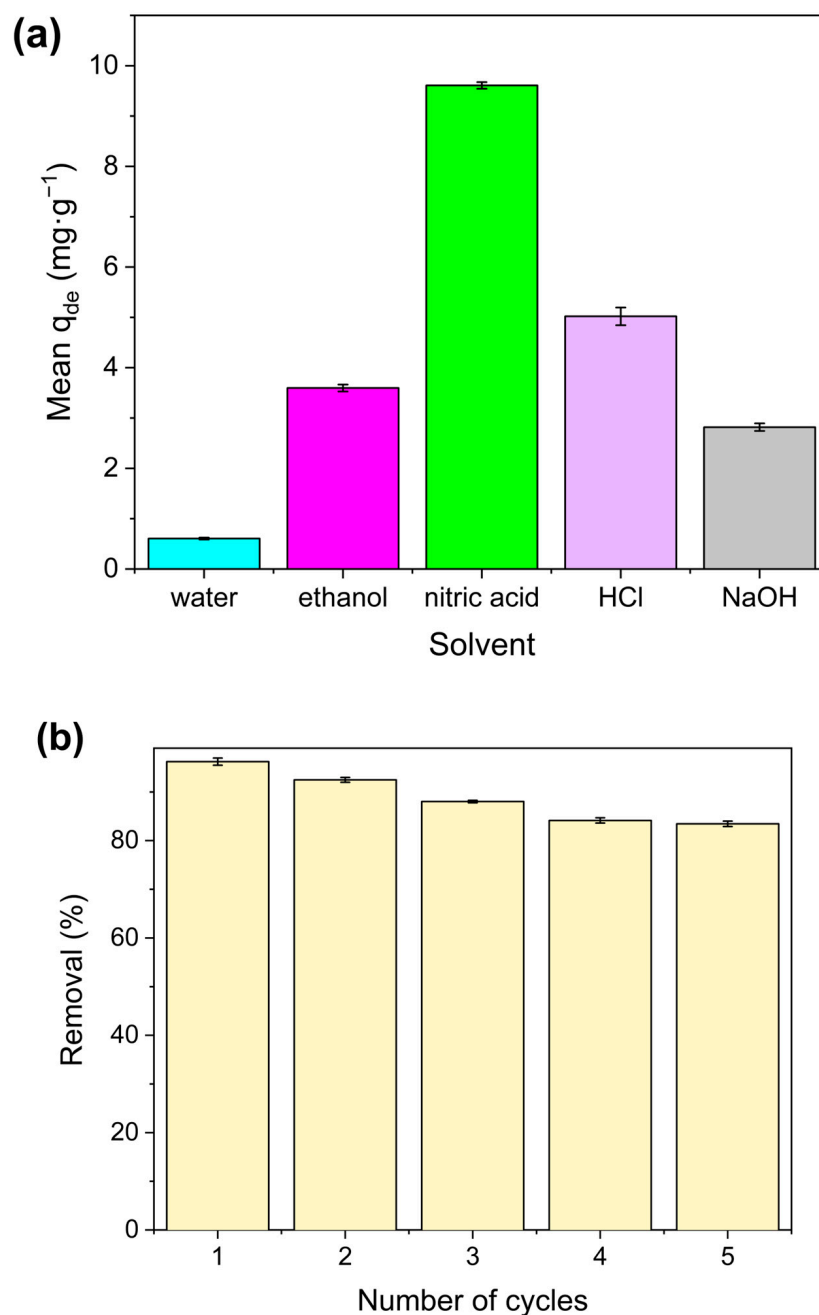


Figure 14. Reusability of volcanic rock. (a) Desorption effectiveness of different eluents. (b) Effect of different adsorption–desorption cycle numbers on adsorption of methylene blue by adsorbent. Experimental conditions: temperature: 318.15 K, pH 3, equilibrium time 1 h, mass to volume ratio 5 g/L, initial concentration of $50 \text{ mg}\cdot\text{L}^{-1}$ of nitric acid, stirring 150 rpm.

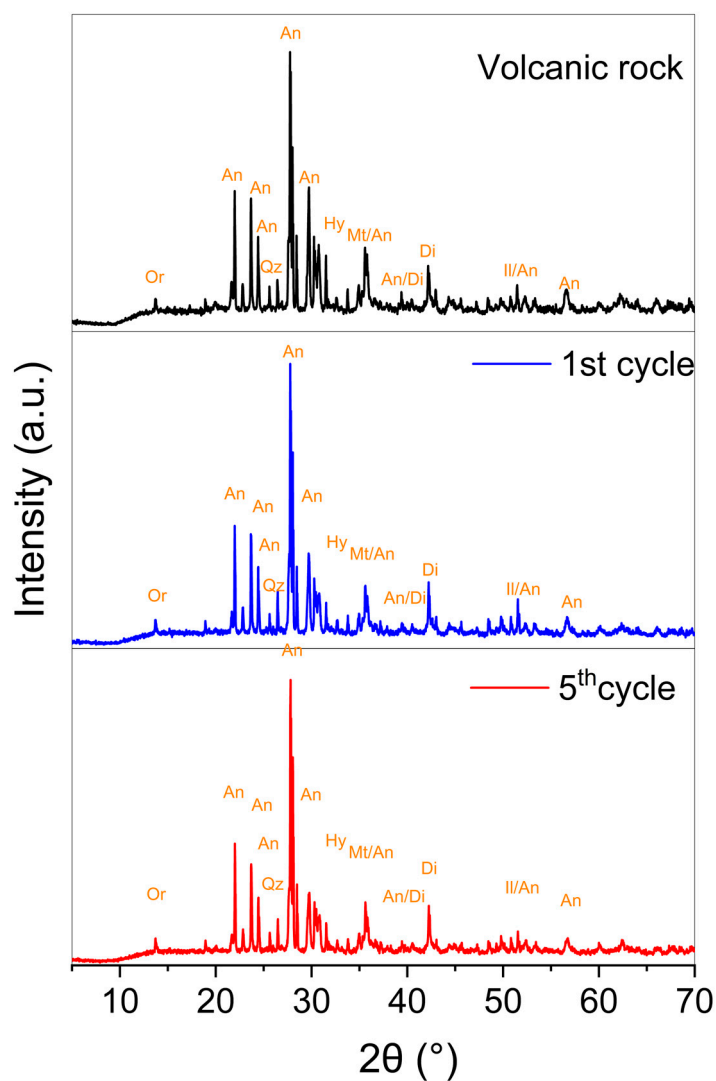


Figure 15. XRD patterns of recycled MB adsorption on volcanic rock after of the 1st and 5th cycles.

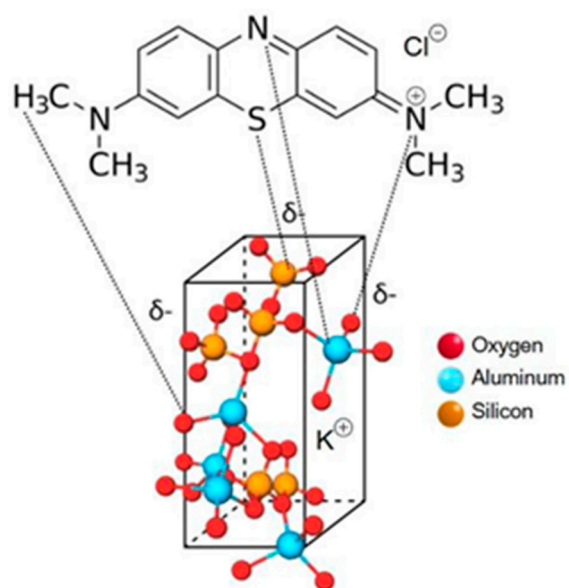


Figure 16. Functional groups involved in the adsorption mechanism of MB dye.

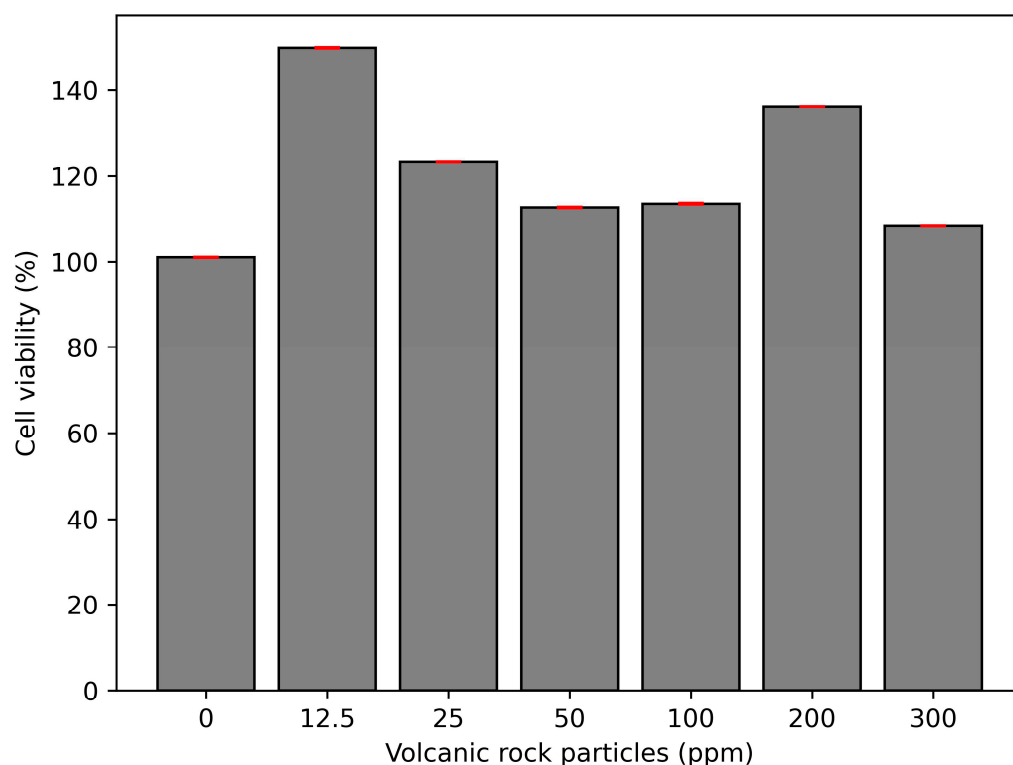


Figure 17. Cell viability percentage of fibroblast cells exposed to various concentrations of VR particles.

In other studies, the volcanic ash exhibited lower toxicity and did not induce significant inflammatory responses. The results indicated a decrease in cell viability upon exposure to ash concentrations of 100–300 $\mu\text{g mg}\cdot\text{mL}^{-1}$, with significant reductions observed at 48 and 72 h [40]. Horwell et al. conducted a comparative toxicity study demonstrating that volcanic ash particles are significantly less cytotoxic than pure crystalline silica [41]. In vitro assays using macrophages and A549 cells revealed that volcanic ash did not elicit a strong inflammatory response or significant cell death, indicating relatively low biological reactivity. These findings suggest that many types of volcanic ash are not inherently hazardous and may be considered biosafe under specific exposure conditions. The results demonstrate that the VR particles possess a favorable biosafety profile, indicating their suitability for applications such as water remediation, with negligible cytotoxic effects on endothelial human cells. Wilson et al. reported an assessment of toxicity from volcanic ash, collected at Montserrat Mountain, on human lung epithelial cells (A549) [42]. The results indicated that volcanic ash represents a relatively low health risk, supporting its potential consideration as a biosafe material for specific environmental or technological applications. So far, the results from the toxicity evaluation of the VR confirm that the material is biosafe; therefore, it is possible to consider the potential use of the VR particles in the field of water remediation.

One limitation of the cytotoxicity assay is that it was evaluated exclusively using a resazurin-based metabolic assay. Since particulate materials may interfere with colorimetric measurement through dye adsorption, light scattering, or sedimentation, the observed increase in apparent cell viability at some concentrations should be interpreted with caution. Although no significant reduction in viability was detected, future studies should include particle-only interference controls, characterization of particle stability and aggregation in complete culture medium, and complementary cytotoxicity assays based on independent endpoints, such as lactate dehydrogenase (LDH) release, trypan blue ex-

clusion, or live–dead fluorescence staining, to further confirm the biosafety of the volcanic rock particles.

In this study, a deep insight into the properties of the VR from the Cerro Blanco volcano is provided. In Table 8, the capacity for MB removal of the VR is compared with other adsorbents reported in the literature to validate its practical application in water remediation.

Table 8. Comparative analysis of methylene blue adsorption capacities across different carbonaceous and mineral materials.

Material	Source/ Composition Type	MB Adsorption (mg/g)	Initial Concentration (ppm)	Adsorbent Dose (g/L)	Initial pH	Contact Time (min)	Reference
	Natural zeolite modified by acid and alkaline treatments	Acid: 2.113 Alkaline: 1.089	5–20	6	11	120	[43]
	Natural zeolite (clinoptilolite)	1.8	20	10	4	60	[44]
	Sodalite octahydrate	3.5	40	5	7	150	[45]
	ZSM-5 zeolite	4.31	10	2	10	300	[46]
	Natural Chinese zeolite (clinoptilolite)	5.15	30	6	7.5	840	[47]
	Pumice powder from Anatolia and Turkey	Anatolia: 0.442 Turkey: 1.488	10–50	20–100	-	60	[48]
	Modified pumice stone	15.87	30–60	4	10	120	[49]
	Mixture of natural and nZVI pumice	Mixture: 4.27	100	in column	7	-	[50]
Volcanic rock	Mexico	10	50	5	9	30	This work

4. Conclusions

This study demonstrated that VR from the Cerro Blanco volcano, located in Divisaderos, Sonora, Mexico, can be used as a low-cost natural adsorbent, and this was demonstrated by using it for the removal of methylene blue (MB). The material characterization confirmed that the rock is composed of various minerals, including quartz, potassium feldspar, plagioclase, augite, and olivine, and it possesses a high surface porosity with an average pore diameter of 3.75 nm.

Compared to other adsorbent materials, this volcanic rock stands out because of its regional abundance, low cost, and ease of preparation, positioning it as a viable and sustainable alternative for wastewater treatment.

The adsorption tests revealed that the VR rock is capable of removing up to 99.99% of MB at an initial concentration of 50 mg·L^{−1} within just 30 min., indicating its strong potential for large-scale applications.

Overall, this work supports the development of eco-friendly and cost-effective solutions for water treatment, highlighting not only the high adsorption capacity of the material but also its non-toxic nature, as confirmed by cytotoxicity tests. These findings underscore the potential of natural materials to play a significant role in mitigating environmental pollution caused by industrial activities, while also ensuring safety for both humans and ecosystems.

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visualization, G.M.-C., B.I.B.-F., D.J.C.-J. and D.V.-H.; supervision, D.V.-H.; funding acquisition, G.M.-C., D.J.C.-J., D.L.V.-C., J.C.T.-C., A.D.M.-A. and D.V.-H. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

VR Volcanic rock
MB Methylene blue

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