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Utilizing Marble Wastewater in Cement Pastes and Mortars for Enhanced Physico-Mechanical and Microstructural Properties

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Abstract: This research explored the potential of marble wastewater (MWW) in cement paste and mortar production, addressing water scarcity, sustainable growth, and resource management. It investigated the physico-mechanical properties and microstructure of cement materials incorporated with varying amounts of MWW. In this study, we utilized tap water and MWW for mortar quality testing, focusing on parameters including setting times, water absorption, and mechanical strength. The viability of MWW in concrete formulations was confirmed by its acceptable total dissolved solids and alkalinity levels. A comprehensive experimental program determined that using marble wastewater in place of tap water reduced the quantity of water required for cement consistency and generated slightly higher compressive strengths (2, 3, 4, and 6%) after 28 days of curing. Analytical techniques, including Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray analysis, and X-ray diffraction (XRD), were employed for molecular and microstructural analyses, which revealed that MWW had a significant influence on portlandite development and CSH formation at higher replacement levels. In short, this research highlights the feasibility of using MWW in cement products, contributing to sustainable water resources, and industrial waste management and utilization.

Keywords: marble wastewater; wastewater analysis; compressive strength; cementitious composite; industrial waste management; analytical characterization

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1. Introduction

The urbanization trend and increased population, along with the rise of industry, have significantly raised the need for drinkable water [1,2]. Concrete has become the most important building material due to this quick expansion and development [3,4]. The concrete industry requires approximately 100 million gallons of water per year, not including water for washing and curing [2,5,6]. The scarcity of safe drinking water is one of the most critical issues facing the globe. Nevertheless, the global use of industrial water will increase to 1500 billion m^3 by 2030, from 800 billion m^3 in 2009 [7]. Concrete normally has a water–cement ratio of 0.45 to 0.60, i.e., the annual use of freshwater for concrete manufacturing is approximately 17 billion m^3 [8]. Increased concrete production will severely diminish these natural resources and pollute the environment [9,10]. Wastewater treatment and reuse is a crucial strategy in the emergence of water resource management under these circumstances and can perform a key role in addressing impending water shortage issues [11].

Recent studies have ascertained the usage of different types of water in the production of concrete and cement mortars and the utilization of hydrogen-rich water in the manufacture of cement paste and mortars [12–15]. Jo (2017a) discovered that the cement setting time was decreased, and the compressive and flexural strengths were enhanced with hydrogen-rich water [13]. Using electrolyzed water expedited the setting time, enhanced the stiffness and bulk densities (soaked and scorched), reduced the apparent porosity, lowered the water absorption, and improved the strength of the mortar in the initial curing stage [16]. Concrete was made using sludge water from a mixer derived from washout operations at a ready-mixed concrete facility. All the sludge water samples met the specifications for ready-mixed concrete mixing water criteria [17]. Increasing the amount of concrete sludge water in concrete mixes enhanced the dry shrinkage and weight loss due to acids while reducing the slump and strength. In another study, concrete samples were made with textile effluent, which maintained the samples' compressive strength within acceptable limits [18]. The strengths of concrete mixes prepared using wastewater (acquired from car washing units) and tap water were evaluated and found to be comparable [19]. Ismail and Al-Hashmi (2011) investigated the feasibility of making concrete with polyvinyl acetate wastewater and discovered that wastewater-mixed concrete was stronger than the control mix concrete [20]. In [21], concrete wash water was adequate for making fresh concrete samples. Many other studies have used concrete wash water [22], sewage water [23], and wash water from concrete plants [24] to study the compressive strengths of the formulated concrete, which were determined to be adequate [22]. The effects of alkaline water on cement mortar properties were researched, and it was determined that alkaline waters with a higher pH may be utilized as mixing fluids, boosting workability and strength [25]. The impact of electrolyzed water with a higher pH was investigated and shown to be advantageous in managing cement mortar possessing early-age qualities [16]. Utilizing hydrogen-rich water obtained by altering the pH level was suggested as an approach to improving cement properties [13]. Furthermore, previous studies have demonstrated the potential benefits of utilizing marble dust as a partial replacement for cement and as a fine aggregate, leading to increased compressive strength and durability of concrete [26,27].

The marble industry is prominent in many countries, including India, Iran, Pakistan, China, Turkey, Saudi Arabia, and Egypt [26,28,29]. In addition, the marble industry in Saudi Arabia has rapidly grown, and its market share is expected to increase by over 5.1% during the forecast period of 2020–2026 [28]. Meanwhile, Pakistan possesses 160 million tons of marble resources [30]. The marble and stone industry in Pakistan has grown rapidly, from 3 thousand tons in 1960 to over 450 thousand tons in 1990 [31]. Subsequently, this has expedited the amount of garbage produced. This garbage can harm the environment [30]. Marble cutting necessitates a considerable amount of water, which results in a huge volume of marble wastewater. This effluent is discharged into adjacent aquatic bodies, leading to their pollution. This pollution kills aquatic life as well as impacting agricultural growth [32]. Reducing the negative impacts of marble wastewater necessitates its long-term employment in sustainable solutions, such as in cement mortars and concrete. Its usage will safeguard water bodies from pollution and reduce the amount of fresh/drinking water consumed in cement mortar and concrete production. This research focuses on the feasibility of MWW utilization and addresses the problem of industrial wastewater disposal in water bodies. It also explores the feasibility of using marble wastewater (MWW) in the production of cement mortars and pastes.

2. Experimental Section

2.1. Materials and Solutions

In this study, four types of wastewater-based cement paste and mortar samples were produced by substituting various amounts of marble wastewater (i.e., 25%, 50%, 75%, and 100%) with tap water and compared with a control mix composed entirely of tap water.

Type-I Portland cement (Cherat Cement), possessing a specific gravity of 3.09 and conforming to the ASTM C 150 standards [33], was employed as a binder in this study.

Cement mortars were made with pit sand that met the gradation criteria (ASTM C-33) and a 2.36 mm average particle size with a specific gravity of 2.71 [34]. The fresh wastewater was collected from a local marble factory. Preliminary testing for pH, total dissolved solids (TDSs), chloride, hardness, alkalinity, and sulfates were performed before using the wastewater as an alternative to tap water. Figure 1 depicts the procedure for acquiring the MWW.

Figure 1. Photographic illustration of marble wastewater production. (**a**) Washing of marble rock. (**b**) Cutting of marble rock. (**c**) Marble wastewater effluence from industry. (**d**) Visual comparison of tap water and collected marble wastewater.

2.2. Mix Percentages and Sample Fabrication

This study investigated the utilization of two types of cement paste to evaluate the standard consistency and initial and final setting times of cement pastes derived from conventional sources and marble wastewater.

Five different mortar mix proportions were formulated using marble wastewater and fresh/tap water. These mortar mixtures were prepared to conform to the ASTM C305-12 standards [35]. Tables 1 and 2 provide a comprehensive summary of the formulations employed for the control and marble wastewater-based cement mortars. A water-to-cement ratio of 0.5 was used to fabricate cubic mortar samples measuring 50 mm on each side, with a sand-to-cement ratio of 2.75. Subsequently, these mortar mixtures were poured into cubic molds and covered with polyethylene sheets for one day to prevent water evaporation. After this initial period, the specimens were carefully removed from their molds and underwent a 7- and 28-day curing process, which involved immersion in water at room temperature.

Table 1. Mixture proportion for cement pastes.

Mixture ID	Cement (g)	Water (mL)	MWW (mL)
MWW 0	100	25.000	0.000
MWW 25	100	18.525	6.175
MWW 50	100	12.250	12.250
MWW 75	100	6.075	18.225
MWW 100	100	0.000	25.000

Table 2. Mixture proportion for cement mortars.

Mixture ID	Cement (g)	Sand (g)	Water (mL)	MWW (mL)
MWW 0	100	275	48.500	0.000
MWW 25	100	275	36.375	12.125
MWW 50	100	275	24.250	24.250
MWW 75	100	275	12.125	36.375
MWW 100	100	275	0.000	48.500

2.3. Testing Methods and Characterization

The water needed for the standard consistency and setting times were determined using the ASTM C187 [36] and ASTM C191 [37] standards, respectively. The normal consistency result revealed how much water was needed to make a cement paste of adequate consistency. After a day, the specimens were unmolded and cured in tap water for 7 and 28 days, respectively. The experiment was repeated thrice to obtain a definite conclusion.

The porosity and water absorption tests were performed on cubes with 50 mm sides as per the ASTM C642 standard [38]. The cubes were removed from the curing tank after 7 and 28 days and dried for 1 day. The percentage of water absorbed can be calculated using the following formula:

$$\text{Percentage of water absorbed} = \left(\frac{W_w - W_d}{W_d}\right) \times 100$$

where w_w and w_d refer to the mortar specimen's weight after immersion in water and oven-drying.

The compressive strength of the mortar mixes obtained using MWW was assessed using a universal testing machine (UTM). The tests were performed at two time points, specifically, 7 and 28 days after completing the curing process, following the parameters specified in ASTM C109 [39]. The specimens utilized in the testing process had dimensions of 50 mm on each side and were manufactured to ensure the absence of air voids. Following a 24-h molding period, the test specimens were removed from the molds and transferred to a curing tank. After the molds were removed, the surfaces of the specimens were treated to ensure they were even and free from irregularities. Compressive strength tests were performed for the designated curing durations of 7 and 28 days. Three sets of samples were tested for each mixture fraction, obtaining an average value.

The ultrasonic pulse velocity (UPV) values were determined following the ASTM C597 guidelines [40] for the MWW-based mortar samples and the control samples. A Portable Ultrasonic Non-Destructive Digital Indicating Tester (PUNDIT) was utilized to measure the ultrasonic pulse velocity (UPV) to determine the speed at which a pulse traveled through the cement mortar medium. Its primary function was to detect and locate air voids and cracks within the material.

The electrical resistivity (ER) test was performed on mortar samples prepared using MWW in the form of 50 mm cubic specimens using the Wenner technique. The experiment involved applying an electrical resistance measurement instrument equipped with two electrodes positioned on opposite sides of the sample, enclosing the specimen within this configuration. The electrical resistivity (ρ) can be calculated using the following formula:

$$\rho = \frac{RA}{L}$$

where ρ and R denote the resistivity in kΩι.cm and resistance in Ωι, respectively. The area and length were measured in cm^2 and cm.

Fourier-transform infrared spectroscopy (FTIR analysis) was employed to obtain the infrared absorption spectra, facilitating the determination of chemical bonds within the molecules. This technique is adept at detecting functional groups and covalent bonds within a molecule. FTIR analysis was applied to examine the control and MWW-based cement pastes following a 28-day hydration period. Before the spectral recording, FTIR pellets were prepared by combining 1 mg of the test material with 0.1 mg of KBr. The spectral data were obtained by averaging three readings within the wave number range of 400 cm^{-1} to 4000 cm^{-1}.

The microstructures of cement paste samples were investigated via chemical characterization combined with elemental microscopic analysis. Before the microstructural examination, the samples were dried and subsequently coated with a thin layer of platinum. To complement the SEM analysis, an EDX INCA 2000 analyzer (Oxford Instruments, Abingdon, UK) was employed to scrutinize the chemical compositions of the specimens.

The X-ray diffraction (XRD) analytical technique was employed to analyze the crystalline properties of the materials, including the average grain size, crystalline structure, microcracks, and strain. This chemical analysis was conducted for the X-ray diffraction patterns of the control and MWW-based pastes, which were recorded within the 2θ range of 5° to 90° at a scanning rate of 1 degree per minute.

3. Results and Discussion

3.1. Water Quality Analysis

The chemical analysis results for the marble wastewater and tap water are presented in Table 3. A higher difference in chemical components was observed between the marble wastewater and tap water. The marble wastewater exhibited a more acidic pH level. The chemical observation of the wastewater revealed its chemical contents complied with the ASTM standard limits for all contaminants The pH levels were within the standard range of 4.5 to 8. The highest total dissolved solids content was 433 ppm, which fell below the 50,000-ppm threshold and was thus acceptable. According to the specification, water with less than 2000 ppm of total dissolved solids may be satisfactorily utilized in concrete production. The maximum total alkalinity reading was 397 ppm, which was below the acceptable level (600 ppm).

Table 3. Qualitative comparison of marble wastewater and tap water.

Sr. No.	Test	Unit	Wastewater	Tap Water
1	pH	Scale	8.25	7.39
2	Elec. conductivity	micro-mhos/cm	529	479
3	Turbidity	NTU	432	1.07
4	Total dissolved solids	ppm	433	241
5	Total alkalinity	ppm	397	83
6	Total hardness	ppm	430	155
7	Calcium hardness	ppm	178	99
8	Magnesium hardness	ppm	252	57
9	Chloride	ppm	28.5	10.5
10	Calcium content	ppm	76.58	29.6
11	Magnesium content	ppm	66.25	35

Given these findings, marble wastewater can be employed in concrete formulations. However, the high chloride content may generate concerns about the risk of corrosion in reinforced concrete. Furthermore, high sulfate levels can lead to concrete cracking and sulfate attack. Therefore, durability tests must be conducted to check for the possibility of sulfate attack and corrosion induced by using marble company effluent in concrete.

3.2. Standard Consistency and Setting Time Analysis

A cement paste's consistency describes the condition of its fluidity and specifies the quantity of water required to prepare a fresh cement–plastic combination. The setting time indicates the duration required for the cement paste to transition from a plastic state to a stiff or solid state. The standard consistencies and setting times of MWW 0 (made with tap water) and the marble-wastewater-based cement paste are shown in Figure 2. The averages of the thrice-repeated experiment outcomes are shown in Table 2. Figure 2 shows that marble-wastewater-based cement pastes used less water than the control sample. The water requirement for MWW 0 is estimated to be 25%, while it was measured at 24.70, 24.50, 24.30, and 24.00% for MWW 25, MWW 50, MWW 75, and MWW 100, respectively. The additional tiny particles in wastewater diminish the resistance due to the sliding of cement particles, resulting in reduced uniformity. MWW 0, MWW 25, MWW 50, MWW 75, and MWW 100 had initial setting times of 152, 158, 166, 174, and 189 min, respectively. The final setup times were 272, 280, 289, 299, and 317 min, respectively. The tiny particles in wastewater may have caused the longer setting times because they cover the cement particles and restrict the amount of pore water available for appropriate hydration. Many studies have found that tiny marble particles have the same impact on cement setting and consistency. The water requirement for the marble powder–binder paste mixes was lower than that of the control cement paste. Furthermore, both the setting times of the binder mixtures were gradually increased [41]. Ma et al. [42] found that increasing the waste marble powder replacement ratio increased the fluidity and setting time [42]. A slight increase in the initial setting time for blended combinations can extend their period of usability. Marble wastewater appeared to hinder the cement-setting process, which may be due to the decelerated hydration process of cement paste [43,44]. Consequently, adding marble wastewater was projected to lower the quantity of water required to make a plastic cement mixture while simultaneously increasing the cement setting time.

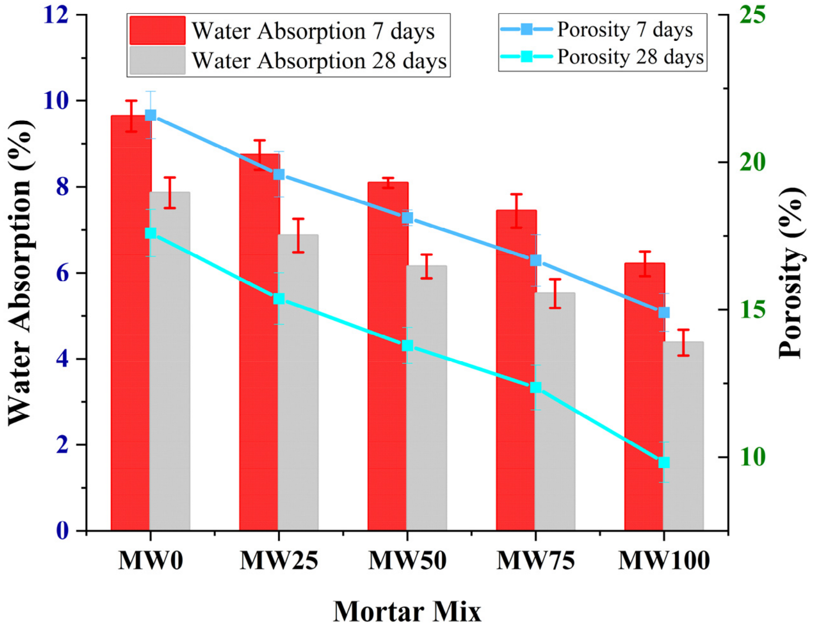

Figure 2. Standard consistency as well as initial and final setting times.

3.3. Effects of Marble Wastewater on Water Absorption and Porosity of Mortar

The water absorption was determined using the designated ratios of marble wastewater replacement with tap water. The water absorption of the mortar sample dropped as the amount of marble wastewater replaced with tap water increased. Figure 3 shows the water absorption and porosity percentages at curing ages of 7 and 28 days. The water absorption values of the hydrated samples were 9.64, 8.74, 8.09, 7.44% at 7 days and 6.21

and 7.86, 6.87, 6.15, 5.52, 4.38% at 28 days for MWW 0, MWW 25, MWW 50, MWW 75, and MWW 100, respectively. The filling of micropores by tiny suspended particles in marble wastewater decreases water absorption. The more voids in a mortar sample, the higher its susceptibility to chemicals. The porosities of the 7- and 28-day-hydrated mortar mixes decreased with an increasing marble wastewater incorporation percentage. The porosities of the mortar mixes were 21.6, 19.59, 18.12, 16.67, and 14.91% after 7 days and 17.6, 15.38, 13.79, 12.36, and 9.82% after 28 days of hydration for MWW 0, MWW 25, MWW 50, MWW 75, and MWW 100, respectively. These findings follow those of Li et al., who found that both the initial and secondary water absorption rates were lower for a given W/C ratio with an increased marble dust volume [45]. This may result from the effect of inert addition because ultrafine aggregates fill gaps [46]. The water absorption capacity was proportional to the degree of porosity [47]. This decrease in porosity might be attributable to the filler activity of marble dust [48]. Marble wastewater contains suspended particles that function as an inert filler, reducing porosity. Demirel [49] first showed the filler effect of marble dust. Consequently, marble wastewater may be completely substituted for tap/fresh water in mortar samples, resulting in lower water absorption and porosity.

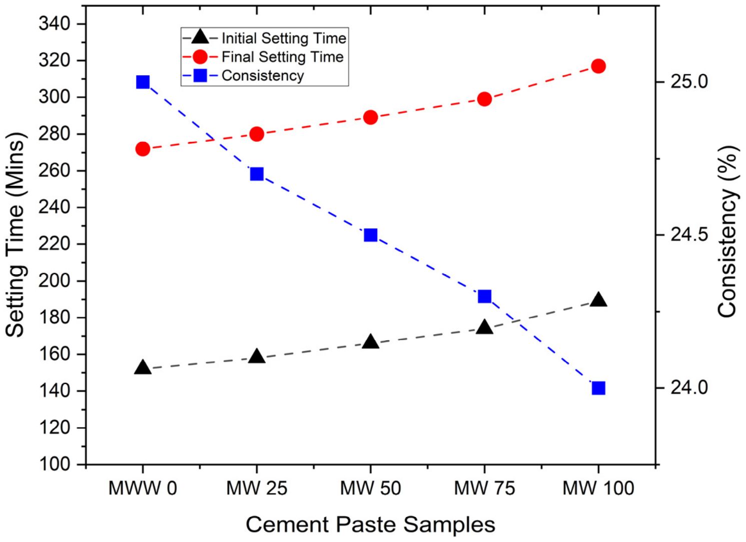

Figure 3. Effects on water absorption and porosity.

3.4. Effect of Marble Wastewater on Mechanical Properties of Mortar

The average cube compressive strengths of the mortar samples after 7 and 28 days are shown in Figure 4. The results demonstrate that the compressive strength values increased with higher percentages of fraction of tap water substituted with marble wastewater. The compressive strengths of the wastewater-based mortar mixes improved after 7 days of curing, at 12.5, 12.53, 12.58, 12.60, and 12.65 MPa for the MWW 0, MWW 25, MWW 50, MWW 75, and MWW 100 samples, respectively. The full replacement (100%) of marble wastewater provided a higher strength of 14.55 MPa at 28 days, which was 6% higher than the 13.72 MPa strength of the control sample. The compressive strengths of MWW 25, MWW 50, and MWW 75 were 13.99, 14.16, and 14.33 MPa, respectively, which were increased by 2%, 3%, and 4% compared with MWW 0. The pore-filling activity of the hydrated cement particles employed in mortar or concrete production is fundamental to increasing the materials' strength. The pore-filling of particles also improves the transition zone around aggregates [48]. A 10% utilization of marble powder as a cement substitute enhanced the strength at 7 and 28 days [41]. These findings follow those of Shekarchi et al., [50] who found that utilizing tertiary-processed wastewater as a tap water substitute increased the compressive strength by 6 and 15% after 7 and 28 days of curing due to the filling effect of the wastewater's suspended particles [50]. Likewise, Saxena et al. [51] deduced that the compressive strength was improved by incorporating a steel slag aggregate combined with wastewater [51]. Marble wastewater contains suspended small particles that fill the micropores, thereby increasing the compressive strength. The higher chloride content in wastewater might contribute to the improved early strength of concrete [52]. Marble wastewater is mostly composed of dolomite and calcite, alumina, and silica in minor amounts. The compressive strength increases when silica in marble powder reacts with calcium hydroxide [53].

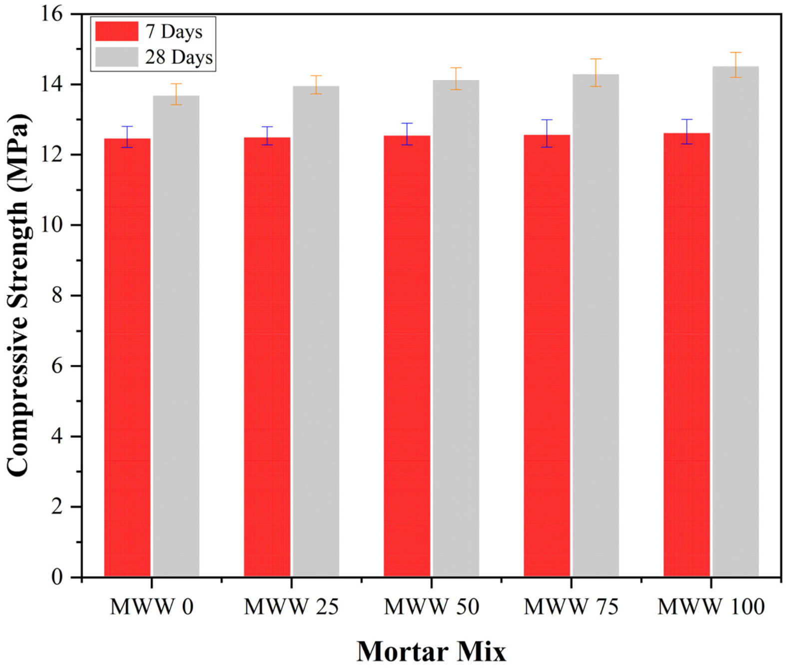

Figure 4. Compressive strength comparison of mortar cubes after 7 and 28 days of curing.

3.5. Ultrasonic Pulse Velocity (UPV)

By finding internal faults, such as inadequate compaction and voids or fractures in mortar, the UPV test can assess the mortar's homogeneity, crack presence, voids, and other issues without causing any destruction to the concrete. The presence of flaws delays the ultrasonic pulse in reaching the receiving transducer. Greater pulse velocities are created with a high concrete quality in terms of homogeneity, uniformity, and a lack of faults. In the current experiment, the generator and the receiving transducer were positioned on opposite sides of the specimens for the transmission of ultrasonic waves to execute the UPV test. The pulse velocity increased by 2–8% when utilizing marble wastewater instead of tap water. The ultrasonic pulse velocity increased from 2 to 6% at 7 days and 2 to 8% at 28 days for all wastewater replacements (Figure 5). The highest pulse velocity of the MW 100 mortar mix was 4745 m/s, which was 8% quicker than that of the control mortar mix. The pulse velocities for MWW 0, MWW 25, MWW 50, MWW 75, and MWW 100 were 3510, 3580, 3625, 3675, and 3730 m/s at 7 days, respectively. The UPVs reached 4410, 4475, 4545, 4655, and 4745 m/s after 28 days, respectively (Figure 5). These findings agree with those of Chawla et al., which showed that the ultrasonic pulse velocity increased as the proportion of marble dust replaced increased until reaching its maximum value [54]. The ultrasonic wave propagation time was shortened when utilizing fine marble dust instead of river sand [55]. The pore structure, material properties, mix proportions, and the interfacial zone between aggregates and cement paste are all key factors influencing the UPV values [56]. The use of marble wastewater is anticipated to enhance the interfacial zone by the precipitation of tiny marble particles, which in turn leads to the formation of a greater amount of cement hydrates, resulting in improved UPV values.

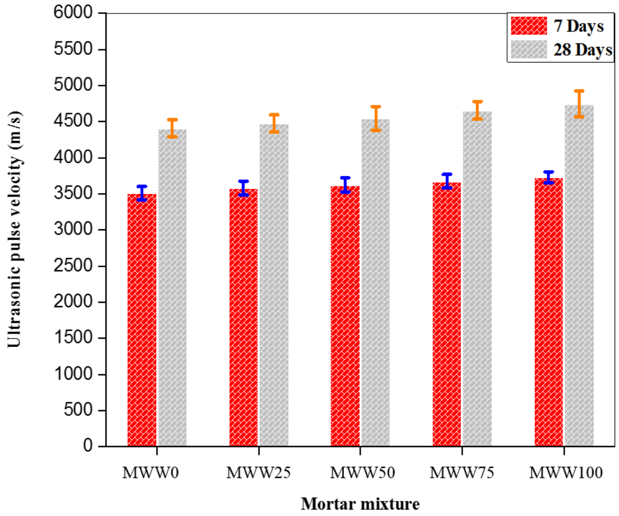

Figure 5. Marble wastewater's effects on UPV of mortar mixtures.

3.6. Electrical Resistivity (ER)

Figure 6 depicts the ER values of the mortar samples. The ER rose with increasing age in all the samples. After 28 days, however, the inclusion of wastewater substantially influenced the ER of the mortar mixes. The ER values continued to rise with the increase in the marble wastewater replacement. The mortar composed entirely of wastewater had the highest resistance among all samples. The ERs of all mortar combinations were in the range of 4.3–7.1 kΩ-cm after 7 days of curing, at 4.3, 4.8, 5.6, 6.4, and 7.1 kΩ-cm for MWW 0, MWW 25, MWW 50, MWW 75, and MWW 100, respectively. The ER values reached 6.2, 6.7, 7.4, 8.2, and 8.8 kΩ after 28 days, respectively. Corrosion is less likely to form when the ER value is equal to or greater than 10 kΩ-cm [57]. Asadollah et al. published similar findings [58], revealing that using treated wastewater rather than tap water increased the ER values of concrete samples by 7.7% on average. The microparticles in marble wastewater increase the density and reduce the permeability of the microstructure leading to an enhancement in ER values. Singh et al. (2017) reported analogous observations [59], wherein marble powder filled the gaps in the mixture, resulting in a denser product. Hence, it is anticipated that the utilization of marble wastewater leads to the forming of a denser and more compact microstructure with reduced interconnectivity between pores, which in turn leads to higher ER values.

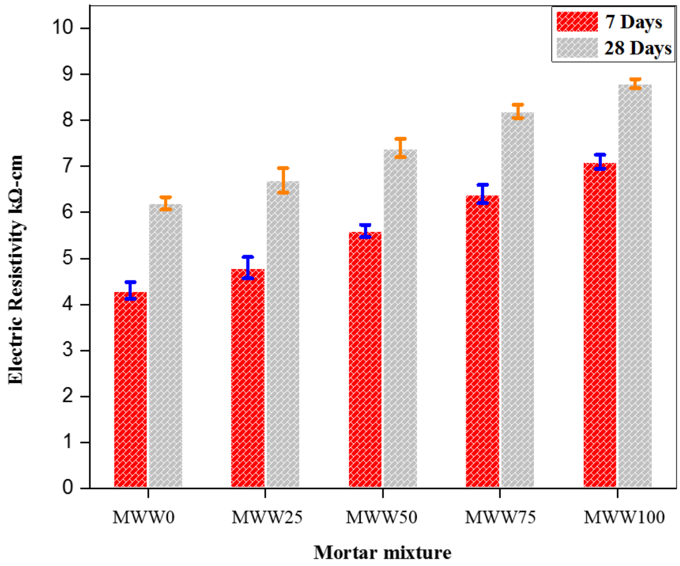

Figure 6. Marble wastewater's effects on ER of mortar mixtures.

3.7. Infrared Spectroscopy Analysis

The FTIR spectra of 28-day-hydrated control and marble wastewater-based cement pastes (MWW 50 and MWW 100) are shown in Figure 7. Many IR bands were observed in all the samples' IR spectra at various ranges of 3400–3100 cm^{-1}, 1640 cm^{-1}, 1420 cm^{-1}, 945 cm^{-1}, and 873 cm^{-1}, resulting from the v_1 and v_2 stretching of water molecules, v_2 bending of water molecules, v_3 carbonate stretching, the CSH vibrations, and v_2 carbonate stretching, respectively [60]. The intense band at 3642 cm^{-1} in the control sample was caused by the $Ca(OH)_2$ stretching of O-H [61]. The same band emerged with a higher intensity in MWW 50 and MWW 100. In addition, the band due to CSH vibrations at 945 cm^{-1}, appeared with greater intensity in MWW 50 and MWW 100, suggesting an excessive formation of CSH. Consequently, using marble wastewater increased the calcium hydroxide level as well as CSH content. Compared to the control mix, the bands due to carbonate stretching at 1420 cm^{-1} in MWW 50 and MWW 100 appeared less intense, suggesting a lower carbonation depth in the MWW 50 and MWW 100 samples [55]. According to Gupta [47], the strength characteristics of marble particles are controlled more by their physical properties and less by their chemical properties [47]. The same results were obtained for hydrogen-rich water and electrolyzed water, indicating that excessive formation of hydration products should occur [14,62,63].

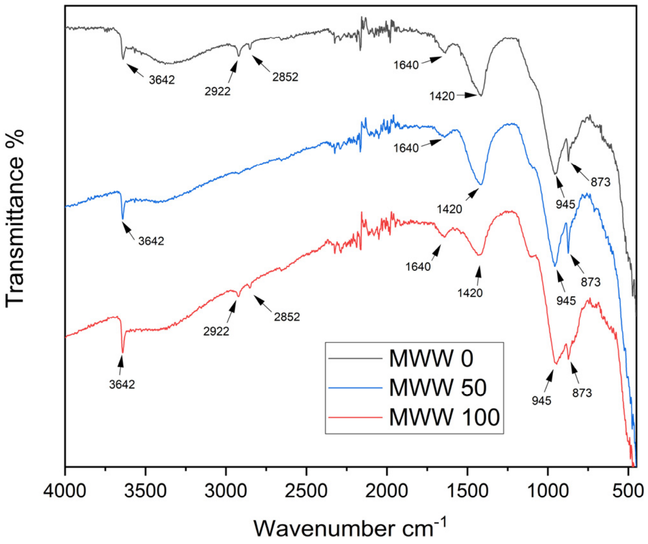

Figure 7. FTIR spectrums for cement pastes at 28 days of hydration.

3.8. SEM and EDX Analyses

SEM and EDX analyses were performed in conjunction to quantitatively predict the hydration products formed from hydrated cement pastes to derive a detailed interpretation of the chemical phases developed. Microstructural photographs of the 28-day hydrated control (MWW 0), MWW 50, and MWW 100 sample pastes collected at different magnification levels are shown in Figure 8.

Comparing the micrographs, the MWW 100 (Figure 8e,f) mix had a well-developed and compact microstructure with fewer voids than MWW 0 (Figure 8a,b) and MWW 50 (Figure 8c,d). The marble dust samples were denser and less porous than the control samples. Amorphous CSH particles and CH crystals generated dense layers in the microstructure [48]. Singh et al. observed the same results when using stone debris as a filler component in cementitious mixes, which helped to create a compact microstructure [64]. Electrolyzed water created a denser microstructure when employed in the production of cement mortars [16]. The appropriate proportioning and dispersion of the marble particles in wastewater with cement improved the mechanical performance of the marble wastewater-based cement pastes. The EDX and SEM investigations were carried out simultaneously (Figure 9). Table 4 indicates the weight percentages of the elements based on the samples'

EDX spectra. Figure 9 shows the EDX point analysis results for the representative MWW 0, MWW 50, and MWW 100 paste samples.

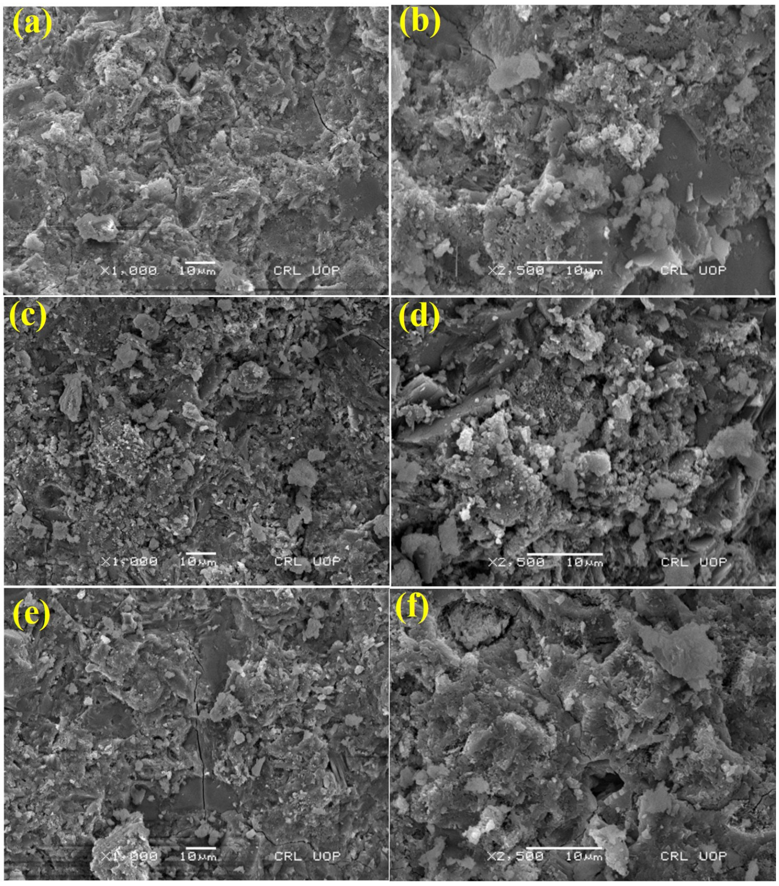

Figure 8. SEM images of 28-day-hydrated pastes: MWW 0 (**a**,**b**), MWW 50 (**c**,**d**), and MWW 100 (**e**,**f**).

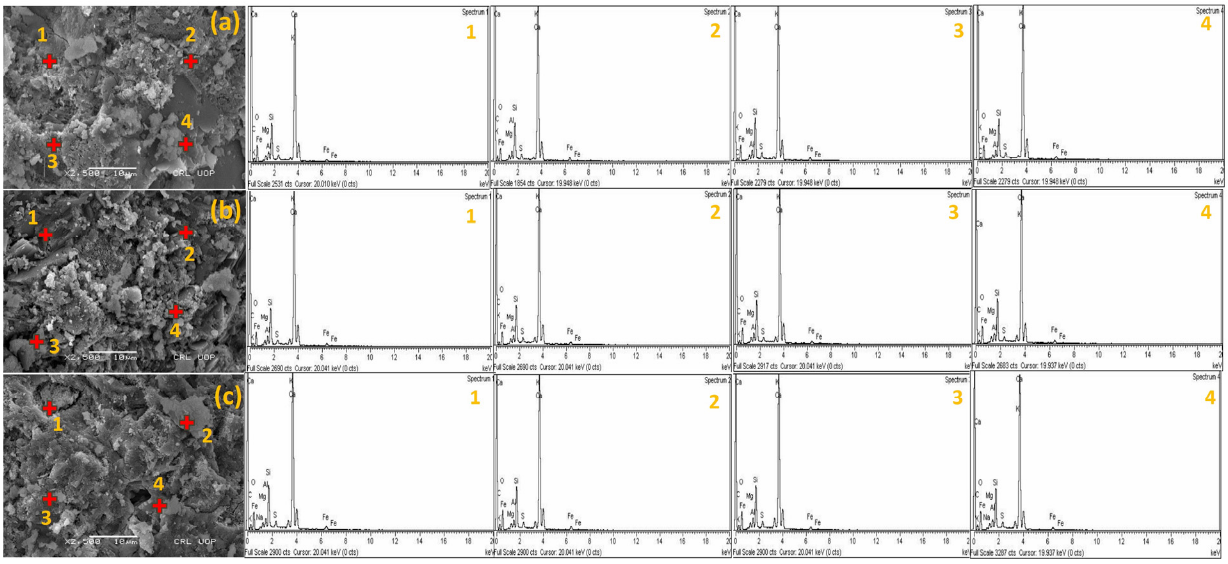

Figure 9. EDX spectra analysis of 28-day hydrated pastes: (**a**) SEM image of MWW 0 with EDX spectra recorded at four random points, (**b**) SEM image of MWW 50 with EDX spectra recorded at four random points, and (**c**) SEM Image of MWW 100 with EDX spectra recorded at four random points.

Table 4. EDX point analysis of 28-day hydrated control and MWW mixes (%wt).

Mix ID	Al	Ca	C	S	Si	Mg	O	Si/Ca
MWW 0	1.77	43.51	8.60	0.87	7.30	1.28	34.50	0.17
MWW 50	1.83	43.58	5.11	1.28	7.78	1.27	35.08	0.18
MWW 100	1.59	44.45	6.48	0.92	7.97	1.23	34.04	0.18

Table 4 presents the average weight percentages of the elements, as well as the Si/Ca ratios, for each point measured in the samples. The Si/Ca ratios of MWW 50 and MWW 100 were greater than that of the control sample due to the enhanced silica content in the marble wastewater-based cement pastes. Increasing the marble wastewater dosage in the cement pastes enhanced the Si and Ca contents. The higher Si/Ca ratio based on EDX point analysis for MWW 50 and MWW 100 demonstrates the formation of a greater amount of cement hydrates, such as CH and CSH, compared to MWW 0.

3.9. X-ray Diffraction Analysis

The MWW 50 and MWW 100 paste samples were differentiated from the control cement paste using qualitative X-ray diffraction analysis. The XRD patterns after 28 days of all three samples are shown in Figure 10. The MWW 100-based cement paste had more intense peaks than the control sample, whereas MWW 50 had less intense peaks. The portlandite phase (P) caused the intense peaks at 2θ values of 18.09°, 34.09°, and 47.12° [65]. Quartz (Q) accounted for the peak at a 2θ value of 68.13° in MWW 100 [66]. A peak occurred at 75.6° in the XRD pattern of MWW 100 due to magnesium oxide. The XRD pattern of MWW 100 showed prominent peaks for CH compared with mortars made with ordinary water, indicating a higher degree of hydration. For portlandite, the XRD patterns of hydrogen-rich water-based samples revealed a similar influence of strong peaks [14]. The phase composition did not qualitatively change when utilizing marble powder as a cement replacement in the mortar formulations; conversely, incorporating marble powder into a mortar caused a shift in the phase proportions. Hence, marble powder is a non-reactive material that does not significantly alter the phase composition of the final mix [41].

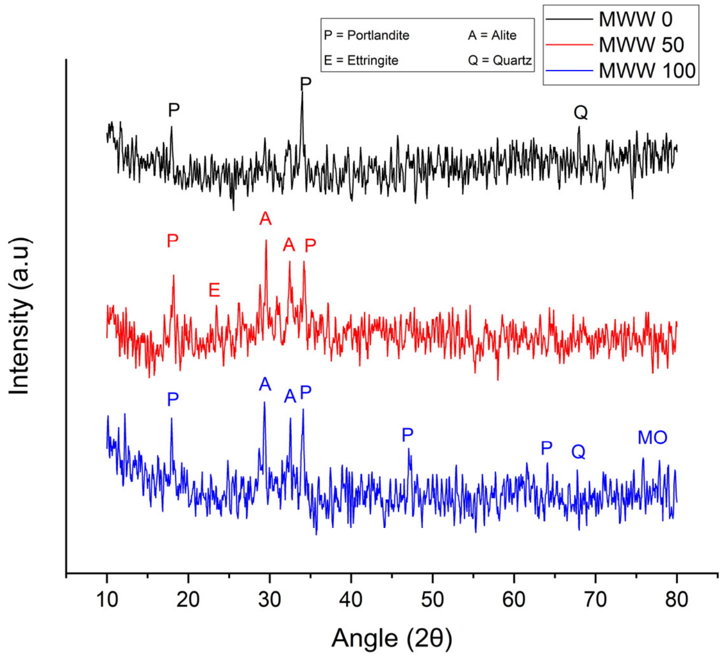

Figure 10. X-ray diffraction analysis of 28-day-hydrated cement pastes.

This study demonstrates the effectiveness of marble wastewater as a potential replacement for fresh water in the fabrication of cement composites. While the study showed improvements in the physico-chemical properties of cement composites across a wide range of experiments, its performance in controlling shrinkage, creep, chemical durability, and corrosion potential has yet to be adequately investigated. One possible drawback of using marble wastewater is the need for quality checks to ensure that the wastewater does not contain harmful chemical species that could deteriorate the quality of the cement composites.

4. Conclusions

This article demonstrates the potential application of marble wastewater (MWW) as a replacement for fresh water (tap water) in the fabrication of cement pastes and mortars. The major conclusions drawn from this study are as follows:

- The use of marble wastewater (MWW) slightly delays the setting of cement pastes, as shown by the setting time analysis. This retardation effect occurs because, in the initial stages, the cement particles are coated with tiny marble waste particles, requiring more time for the cement particles to fully hydrate.
- As the percentage of marble wastewater replacement increased, the water absorption and porosity of the mortar samples significantly decreased. This effect is due to the filler action of the tiny particles present in the marble wastewater.
- The compressive strength of cement mortar improved as the percentage of marble wastewater used in place of tap water increased. The 28-day compressive strength of the mortar increased by up to 6% with 100% replacement by marble wastewater. The pore-filling activity of the hydrated cement particles used in mortar or concrete production is essential for enhancing the material's strength.
- The UPV values increased with the use of marble wastewater, indicating the formation of cement mortar with fewer voids and flaws. Additionally, the ER values of the marble wastewater-based cement mortar increased compared to the control sample, indicating a lower risk of corrosion.
- According to the analytical characterization, marble wastewater significantly influenced portlandite development and CSH formation at higher replacement levels. SEM investigation revealed that the MWW-based mortar, with fewer capillary pores, had a more compact and denser microstructure compared to the control mortar, which had larger capillary pores.

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