Article

Preparation and Characterization of Plasters with Photodegradative Action

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Abstract: The aim of this project is to investigate the behaviour of several special types plasters specifically designed to degrade the most common pollutants which are present in the atmosphere. In particular, specific additives have been added to these plasters, in order to obtain a broad spectrum of active and synergic response, each of which have peculiar functions: - microporous materials, such as clinoptilolite, a natural zeolite, that promotes the adsorption of air pollutants thanks to its porous nature; - nano-fillers, such as carbon nanotubes, that behave both as reinforcing agents as well as adsorbent materials; - photochemical agents, such as titanium oxide, that degrade air pollutants, previously adsorbed on carbon nanotubes and zeolites, thanks to the action of light that activates photodegradation reactions. All the samples were also characterized in terms of mechanical properties, adhesion to supports and water absorption. Furthermore, photodegradation tests were carried out by exposing plaster surfaces, wetted with a Rodamine solution, to Ultraviolet rays (UV) for different times. Plasters photodegradative capacity was evaluated and the results highlighted the fact that the designed admixtures showed an important photodegradative action, strictly dependent on the types and specific ratios of the selected additives.

Keywords: photodegradative action; plaster; carbon nanotubes; clinoptilolite; titanium oxide; zeolite

1. Introduction

Even though construction in the past represented a sector with a high consumption of materials with a great impact on the environment, it is now becoming an increasingly sustainable and environmental friendly sector [1–4].

Environmental protection involves the adoption of policies that take into consideration many aspects such as the reduction of and impact of materials [5–9].

There are many different types of materials that are used in construction such as plasters, binders, insulating panels, paints etc. The preparation of which requires the use of components that often do not reconcile with respect and protection towards the environment, such as the use of adhesives and paints that in time may release harmful substances and thus creating a potentially dangerous environment health wise giving rise to the so-called Sick Building Syndrome [10–15]. This is why over the last years, many studies have turned towards the research of innovative materials that are, above all, prepared with possible natural and safe components [16–23].

Further studies were aimed towards the production of building materials using a variety of waste from civil to industrial with the dual advantage of offering a new location and value to waste and in order to be able to prepare innovative materials [24–27]. Therefore, one of the most significant aspects, of our present time, is to guarantee and preserve the link between innovation and the environment which reaches its maximum expression as in the case of multifunctional materials, i.e., those that add new functions to traditional ones thanks to the combination of other materials.

These materials, therefore can be intended as composite materials consisting of a matrix of traditional composition and of additives of different nature and with particular peculiarities.

The additives with photodegradative action make it possible to obtain materials that will guarantee a performance of self-cleaning and de-pollution in the presence of light [28–33] by activating a strong oxidation process that leads to the decomposition of certain pollutants, when these come into contact with the surface of a cement product. The pollutants present in the atmosphere may become even more dangerous in the presence of atmospheric particulate as they can impregnate onto it by depositing onto the surfaces more easily thus increasing their duration in the environment [34–38]. However, if this phenomenon occurs on surfaces that are photocatalyzed all this may improve degradation of pollutants. Amongst photodegradative agents we find titanium oxide [39–41] most commonly used together with other oxides [42–48].

In recent years, new photocatalytic species such as titano silicates given rise to much many interests. In particular, the Engelhard titanium silicate phases [49–56] have shown to have a photocatalytic activity which adds to their characteristics of being microporous materials, therefore also capable of acting as adsorbent materials [57–61].

The aim of our research was to find the optimal conditions in order to obtain special mortars to be used as finishing plasters which, in addition to their traditional functions, may also have the ability to adsorb and degrade any pollutants in the atmosphere. The presence of titanium oxide, as already extensively studied and reported in literature [39], allows the photodegradation of pollutants such as VOC's, improved in our case, from adsorption of the latter by the zeolite and carbon nanotubes that favor in this way the contact between titanium oxide and pollutants.

2. Materials and Methods

Three special additives were added to a mixture of traditional mortar, intended for use as plaster, each of which had different functions. These selected additives were: a photocatalytic agent, a microporous agent and a nano-fibro strengthening agent with adsorbent capacity.

The base mortar, i.e., without additives, was prepared with lime putty mixed together with sand previously washed in the proportion of 2/5 of lime and 3/5 of sand, and to which a quantity of white portland cement of 5% of the total weight obtained from the sum of lime plus sand was added. This mixture called base mortar was indicated with "S".

Particular importance has been given to the identification of the S/A ratio (S = base mortar, A = water) more suitable according to the quantity and nature of the additives added, since this depends on the characteristics of the hardened material and its workability for an efficient installation.

In particular, titanium oxide, TiO_2, was used as a photodegradative agent. in the form of anatase (Alfa-Aesar). The adsorbent agents used were a natural zeolite, clinoptilolite [62–66], and carbon nanotubes [67,68]. The latter were used both as adsorbents and as reinforcing nano-fibers [69–72]. The clinoptilolite used is a commercial zeolite.

The carbon nanotubes used are multi-walled nanotubes (MWCNTs) synthesized and characterized as already reported in our previous article [68].

Both systems were studied, those with only one additive, as well as those with mixed systems, in order to evaluate any synergistic action resulting from the simultaneous presence of more additives in the mortar. The range of variability of the percentages used of the additives has been provided by preliminary investigations with respect to the characteristic of the mortar obtained in the fresh state. Larger percentages of additives compared to those used were discarded because the mortars had poor

characteristics for their use. In fact, since it is a finishing mortar, which must be "spread" onto a wall surface, it should therefore be easily malleable, but at the same time it must not drip once applied.

The characterization of the systems was carried out through tests in order to determine: mechanical compressive strength, photodegradative activity, water absorption coefficient and tear resistance.

The compressive strength of the prepared mortars was carried out on pellets-shaped specimens. The preparation of the pellets was carried out using metal moulds (Figure 1a). Five specimens were prepared for each system. After a 10 days period of curing, at room temperature and environmental humidity level, the specimens were deformed thus obtaining a series of pellets of cylindrical form with a radius equal to 1.2 cm and a height of approx. 1.0 cm (Figure 1b). Subsequently compressive strength was measured on the pellets with a Vanderkamp Vk 200 tester (Figure 1c).
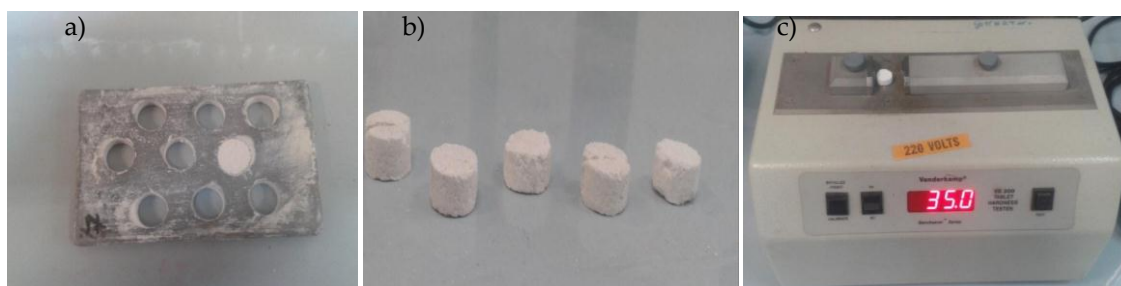

Figure 1. (**a**) Moulds; (**b**) Mortar pellets; (**c**) Hardness tester.

In order to determine the photodegradative activity, then specimens were prepared with the previously selected composition mortars, $1 \times 6 \times 9$ cm in size then left to mature for a period of 10 days. Subsequently a solution of Rodamine with a concentration of 0.2 g/L was brushed onto the surface of the specimens. Finally, the latter were subjected to UV irradiation by the use of a 100 W UV lamp and $\lambda = 365$ nm for a period of three hours (Figure 2a). Prior to irradiation, part of the surface was shielded from the radiation in order to be able to observe, at the end of these tests, the color variations between the irradiated and the screened surfaces (Figure 2b).
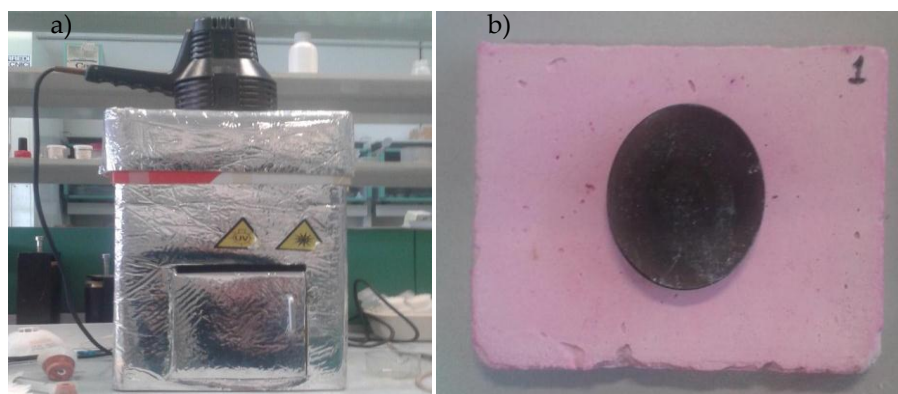

Figure 2. (**a**) Lamp Box UV 100 W $-$ $\lambda = 365$ nm; (**b**) Specimen brushed with a solution of Rodamine partially shielded.

In order to be able to determine the coefficient water absorption, a series of prismatic specimens were prepared. After a period of 28 days of maturation, in an environment with a constant temperature and humidity level, these were then dried in a ventilated oven at a temperature of 60 °C until reaching the constant mass. We may consider that constant mass has been reached when two consecutive weighing procedures, at distance of 24 h apart each, do not differ by more than 0.2%. Once the

constant mass is reached on the specimens, the coefficient of water absorption is calculated, following procedures reported in the standard [73].

European standards [74] was used for the "tearing-off" test. This test determined the adhesion between the mortar and a support, which in this case was a brick. Traction force was applied by a steel cylinder glued onto the surface of the specimen (Figure 3a) which was subsequently connected to the tear-off-adhesive tester (Figure 3b). Figure 3c,d show steel cylinders and sample after test respectively

Figure 3. (**a**) Sample with steel cylinders connected to the instrument for the measurement of adhesion strength; (**b**) tear-off-adhesive tester; (**c**) steel cylinders after test; (**d**)sample after test.

3. Results and Discussion

This project was carried out through consecutive phases as illustrated below:

- Identification of the S/A ratio optimal (S = base mortar, A = water) according to the different quantities of additives, through compression resistance tests.
- Characterization of systems with only one additive.
- Characterization of systems with multiple additives.

3.1. Identification of the S/A Ratio and the Quantity of Optimal Additives

Initially, different systems had been previously prepared in order to identify the S/A ratio and the quantity of optimal additive. Figure 4a–c show the compressive strength values of the mortars produced as a function of the S/A ratio and the quantity of the different additives added as, respectively for clinoptilolite, titanium oxide and carbon nanotubes.

As the values shown in Figure 4 demonstrate; we may note, as expected, that as the S/A ratio increases, so does the mechanical resistance. By using an equal S/A ratio, it is clear that the addition of clinoptilolite improves mechanical strength, up to a percentage of 10% (Figure 4a). Pozzolanic effect of zeolite, due to the reaction of soluble SiO_2 and Al_2O_3 with $Ca(OH)_2$ to produce C–S–H densified the plaster matrix, thus reducing porosity and improving mechanical properties.

We may observe that anything above this percentage causes a lowering of the resistance due to a more difficult cohesion of the mortar in the presence of an excessive quantity of zeolite. This trend is registered for all three values of S/A used. Analysis of the data shown in Figure 4b shows that for an S/A ratio of 2 and 3, the resistance value at compression increases up to a percentage of TiO_2 equal to 0.5% and then decreases. For a ratio S/A = 4, there is a gradual decrease in compressive strength as the percentage of TiO_2 increases. Most probably, the ratio S/A = 4 is too high and a further addition of TiO_2 makes the homogenization and hydration of the components even more difficult. The analysis of the data in Figure 4c shows that the compressive strength increases, only for a ratio S/A = 3 and a percentage of Carbon Nanotubes equal to 0.025%. As regards, all the other systems, however, the mechanical resistance was found to be lower than that of the basic mortar.
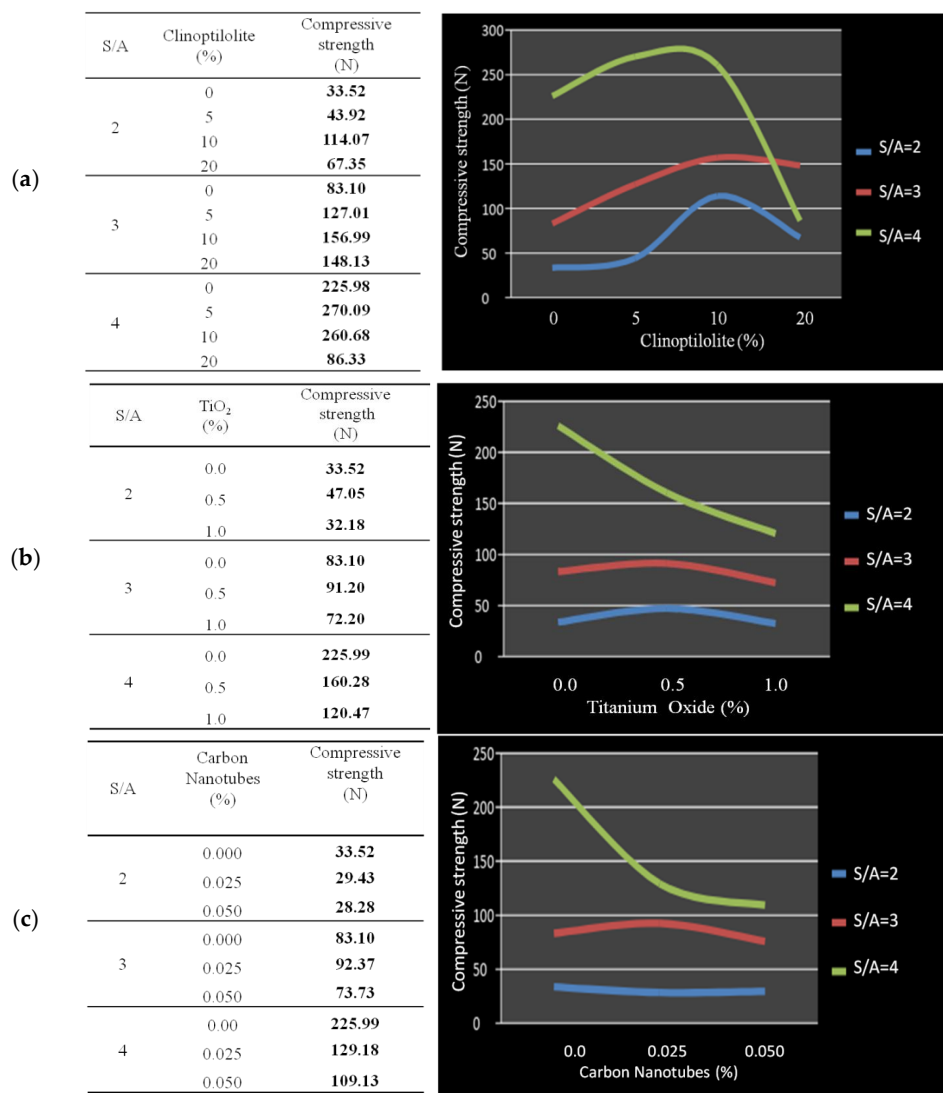
(a)

S/A	Clinoptilolite (%)	Compressive strength (N)
2	0	33.52
	5	43.92
	10	114.07
	20	67.35
3	0	83.10
	5	127.01
	10	156.99
	20	148.13
4	0	225.98
	5	270.09
	10	260.68
	20	86.33

(b)

S/A	TiO_2 (%)	Compressive strength (N)
2	0.0	33.52
	0.5	47.05
	1.0	32.18
3	0.0	83.10
	0.5	91.20
	1.0	72.20
4	0.0	225.99
	0.5	160.28
	1.0	120.47

(c)

S/A	Carbon Nanotubes (%)	Compressive strength (N)
2	0.000	33.52
	0.025	29.43
	0.050	28.28
3	0.000	83.10
	0.025	92.37
	0.050	73.73
4	0.00	225.99
	0.025	129.18
	0.050	109.13

Figure 4. Compressive strength of the mortars obtained by varying the S/A ratio and the amount of additive for (**a**) clinoptilolite, (**b**) titanium oxide, (**c**) carbon nanotubes, respectively.

3.2. Characterization of Systems with a Single Additive

Systems with a single additive have been formulated and characterized on the basis of data obtained, as above mentioned. A constant ratio S/A = 3 was chosen for these systems, which resulted in being the most optimal even from an applicative point of view. The following Table 1 shows the composition of the chosen systems, with only one additive, for the course of the characterization.
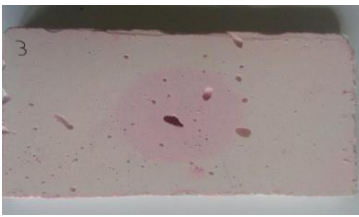
Table 1. Composition of the selected systems, for course of the characterization, with one additive only.

Systems	S/A	Clinoptilolite (%)	TiO_2 (%)	Carbon Nanotubes (%)
1	3	0	0.0	0.000
2	3	5	0.0	0.000
3	3	0	0.5	0.000
4	3	0	0.0	0.025

3.2.1. Colorimetric Tests of Photoactivity

The following Table 2 shows the images of the specimens before and after exposure to UV irradiation, regarding different systems containing only one additive.

Table 2. Images of specimens before and after UV irradiation for 3 h.

Systems	Before	After
1 (without additive)		
2 (with clinoptilolite)		
3 (with TiO$_2$)		
4 (with Carbon Nanotubes)		

The images show that the specimen relative to system 1, that is constituted solely by the base mortar without additives, does not present photodegradative activities, in fact following irradiation there are no chromatic variations nor formation of an imprint relative to the covered part.

System 2, which contains zeolite, presents an immediate discoloration, however without the formation of an imprint, which reveals an adsorbing action of the zeolite on the colorant rather than a photodegradation phenomenon. System 3, containing TiO$_2$, presents a marked imprint on the surface, showing, as we had expected, its photodegradative capacity. System 4, which contains carbon nanotubes, reveals a surprisingly photodegradative action; in fact the presence of an imprint on the specimen is evident, although less important than the titanium oxide system 3.

3.2.2. Water Absorption Coefficient

Table 3 shows the values of the water absorption coefficients applied to the specimens of mortar with variable composition.

Table 3. Water absorption coefficient.

Systems	$(kg/m^2 \ min^{0.5})$
1 (without additive)	0.4
2 (with clinoptilolite)	0.3
3 (with TiO$_2$)	0.4
4 (with Carbon Nanotubes)	0.5

The reported data show that the addition of titanium oxide (system 3) does not change the capacity of water absorption compared to the base mortar containing no additive (system 1).

As far as system 2 is concerned; which contains zeolite, there is a lowering of the coefficient probably due to the zeolite which has already reached its complete hydration during the specimens preparation. System 4, containing carbon nanotubes, shows an increase in the coefficient due to the excellent adsorbent capacities of the latter.

3.2.3. Determination of the Tear Adhesion Strength

Table 4 as follows, shows the data obtained after tear adherence tests carried out with the methods as previously reported in paragraph 2. The results show that system 2, containing zeolite, has a greater adhesion strength than the base mortar (system 1), whereas the presence of titanium oxide (system 3) lowers adhesion. In the case of system 4, in the presence of carbon nanotubes, adhesion is low therefore unable to be measured

Table 4. Adhesion strength of mortars with variable composition containing one additive only.

Systems	Adhesion Strength (N/mm^2)
1 (without additive)	0.498
2 (with clinoptilolite)	0.585
3 (with TiO$_2$)	0.241
4 (with Carbon nanotubes)	-

-: unable to be measured.

3.3. Characterization of Systems With Multiple Additives

The mortars were then subsequently prepared by adding more additives in order to evaluate their possible synergistic action. Table 5, as follows, shows the compositions of mixed systems prepared with more additives.

Table 5. Composition of mixed systems with multiple additives.

Systems	S/A	Clinoptilolite (%)	TiO$_2$ (%)	Carbon Nanotubes (%)
5	3	5	0.5	0.025
6	3	5	0.5	-
7	3	5	-	0.025
8	3	-	0.5	0.025

-: unable to be measured.

3.3.1. Compressive Strength

Table 6 shows the compressive strength values for specimens with two or three additives.

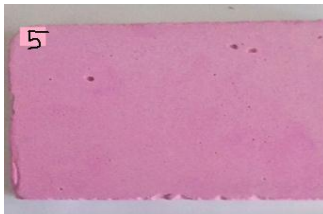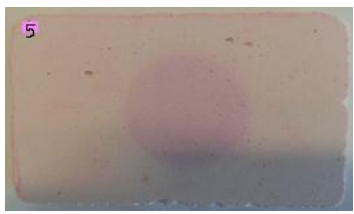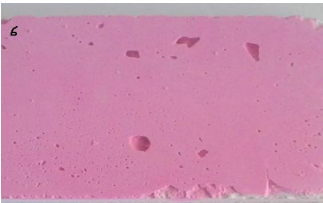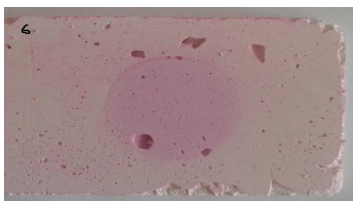**Table 6.** Resistance to compression of systems with more additives.
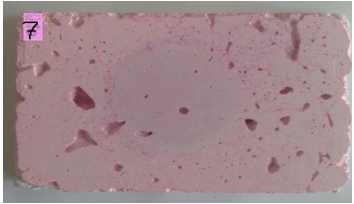
Systems	S/A	Clinoptilolite (%)	TiO$_2$ (%)	Carbon Nanotubes (%)	Compressive Strength (N)
1	3	0	0.0	0.000	83.10
5	3	5	0.5	0.025	66.68
6	3	5	0.5	0.000	72.39
7	3	5	0.0	0.025	87.31
8	3	0	0.5	0.025	78.02

The data show a slight lowering of compressive strength compared to the base mortar for systems 5, 6 and 8. The most significant lowering regards system 5 where all three additives are present, due to difficult homogenization and hydration of the components of the mortar; the value still remains acceptable. An increase in resistance is recorded for system 7 where clinoptilolite and carbon nanotubes are present.

3.3.2. Colorimetric Tests of Photoactivity

The photodegradation tests performed on "mixed" specimens revealed diverse results as shown below in Table 7.

Table 7. Images of specimens before and after UV irradiation for a 3 h period.

Systems	Before	After
5 (Clinoptilolite + TiO$_2$ + Carbon Nanotubes)		
6 (Clinoptilolite + TiO$_2$)		
7 (Clinoptilolite + Carbon Nanotubes)		
8 (TiO$_2$ + Carbon Nanotubes)		

We may observe from the images how the simultaneous presence of several additives, zeolite, carbon nanotubes and titanium oxide, enables us to set up a synergy between the components and

to improve the photodegradative action of the prepared mortar. The best results are obtained with system 5 where all three additives used are present. Furthermore, systems 6 and 7 show an important photocatalytic activity although slightly lower than system 5. Compared to other systems, system 8 presents the lowest photocatalytic activity.

As emerges from the results that the union of clinoptilolite and titanium oxide is the winning one whereas the first one, thanks to its nature, favors the adsorption of the rodamine thus facilitating contact with the titanium oxide which in turn exerts its photodegradative action.

System 8, titanium oxide and carbon nanotubes, also highlights a photodegradative action although the impression on the surface of the shielded part is only slightly visible probably due to the adsorbing action of the nanotubes on the rodamine as well.

Compared to systems with titanium oxide alone, there is a substantial improvement in photocatalytic activity when the latter is combined with clinoptilolite or with clinoptilolite and carbon nanotubes.

3.3.3. Water Absorption Coefficient

The results obtained concerning the water absorption of systems containing more additives are shown in the following Table 8.

Table 8. Water absorption coefficient.

Systems	Clinoptilolite (%)	TiO$_2$ (%)	Carbon Nanotubes (%)	Water Absorption Coefficient (kg/m^2 min$^{0.5}$)
1	0	0.0	0.000	0.4
5	5	0.5	0.025	0.7
6	5	0.5	0.000	0.2
7	5	0.0	0.025	0.3
8	0	0.5	0.025	0.5

The presence of zeolite tends to lower the coefficient water absorption (systems 6 and 7) most probably due to the mortar being in a saturated state of hydration. There is a significant increase in absorption coefficients where carbon nanotubes enhance their adsorbing capacity (system 8). System 5 shows the highest capacity which is characterized by the simultaneous presence of all three additives.

3.3.4. Determination of Tear Adhesion Force

Tear-off tests performed on systems with more additives, were carried out through procedures as previously shown in paragraph 2. As follows, Table 9 shows the values of adhesion strength obtained. Regarding systems 5 and 6, breakage of the specimens was of the adhesive type to the substrate, i.e., there were no detachments inside the mortar however a detachment from the surface of the brick occurred. As for systems 7 and 8 the adhesion strength was not measurable. By analyzing all the results, we may observe how the simultaneous presence of the three additives, clinoptilolite, titanium oxide and carbon nanotubes (system 5), creates a synergy thus increasing the adhesive force as compared to the mortar only (system 1). A negative role is played by carbon nanotubes when these are in the presence of zeolite only (system 7) or titanium oxide alone (system 8).

Table 9. Adhesion strength of mortars with a variable composition containing more additives.

Systems	Clinoptilolite (%)	TiO$_2$ (%)	Carbon Nanotubes (%)	Adhesion Strength (N/mm^2)
1	0	0.0	0.000	0.498
5	5	0.5	0.025	0.532
6	5	0.5	0.000	0.413
7	5	0.0	0.025	-
8	0	0.5	0.025	-

-: unable to be measured.

4. Conclusions

We may draw the following conclusions from results obtained as a whole, as in summary Table 10 below. It is necessary to underline that, from the evaluation of the 4 parameters considered, (compressive strength, absorption coefficient, adhesion strength and photoactivity), the best systems have been identified, among those that represented a fair compromise between the lowering of some characteristics, although always within acceptable limits, and the improvement of others. Particular importance was given to the improvement of the photocatalytic activity.

Table 10. Summary.

Systems	Clinoptil (%)	TiO$_2$ (%)	Carbon Nanotubes (%)	Compressive Strength (N)	Absorption Coefficient (kg/m^2 min $^{0.5}$)	Adhesion Strength (N/mm^2)	Photoactivity
1	-	-	-	83.1	0.4	0.498	
2	5	-	-	127.01	0.3	0.585	
3	-	0.5	-	91.20	0.4	0.241	
4	-	-	0.025	92.37	0.5	-	
5	5	0.5	0.025	66.68	0.7	0.532	
6	5	0.5	-	72.39	0.2	0.413	
7	5	-	0.025	87.31	0.3	-	
8	-	0.5	0.025	78.02	0.5	-	

Values with respect to system 1: greater lower equal

Clinoptilolite tends to increase compressive and adhesion strength, decreases water absorption and does not give photodegradative properties to the mortar, however neither is it compromised in systems where other additives are present (systems 5, 6 and 7).

As expected, titanium oxide gave good response as a photodegrading additive; in fact, for systems in which it is present (systems 3, 5, 6 and 8) response to the photodegradative tests has always been positive.

Carbon nanotubes, whether inserted individually into the mortar, or mixed with other additives, gave a good photodegradative response.

However they increased water absorption coefficient and limited the adhesion force of the mortar on the substrate. Furthermore, in the mixture containing all three additives (system 5) contemporaneously, adhesion force to the substrate was not compromised, on the contrary increased as compared to that of the base mortar.

The different additives used have played particular roles; it is possible to create systems in which these operate synergistically from their union and for their particular composition.

Amongst these systems that we studied No. 5 (which has all three additives) and No. 6 (which has both zeolite and titanium oxide additives, turn out to be the best compromise between the lowering, which still remains acceptable, and the recovery of some of the characteristics as regards to the basic mortar.

These identified systems, in particular allow the preparation of mortars which propose a greater photodegradation activity as against systems in which titanium oxide is individually used.

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References

1. Franzoni, E. Materials selection for green buildings: Which tools for engineers and architects? *Procedia Eng.* **2001**, *21*, 883–890. [CrossRef]
2. Scofield, J.H. Letters: Green building technology. *Environ. Sci. Technol.* **2000**, *34*, 448A. [CrossRef] [PubMed]
3. De Luca, P.; Carbone, I.; Nagy, B.J. Green building materials: A review of state of the art studies of innovative materials. *J. Green Build.* **2017**, *12*, 141–161. [CrossRef]
4. Warren, L.P.; Peter, A.T. A comparison of occupant comfort and satisfaction between a green building and a conventional building. *Build. Environ.* **2008**, *43*, 1858–1870.
5. Ljungberg, L.Y. Materials selection and design for development of sustainable products. *Mater. Des.* **2007**, *28*, 466–479. [CrossRef]
6. Govindan, K.; Madan Shankar, K.; Kannan, D. Sustainable material selection for construction industry—A hybrid multi criteria decision making approach. *Renew. Sustain. Energy Rev.* **2016**, *55*, 1274–1288. [CrossRef]
7. Magnone, G.; De Luca, P.; Salituro, A.; Cosenza, M.G. Assessment of reduction strategies for the mitigation of the environmental impact of the primary packaging within the large scale retail trade. *Procedia Environ. Sci. Eng. Manag.* **2014**, *1*, 93–97.
8. Jahan, A.; Ismail, M.Y.; Mustapha, F.; Sapuan, S.M. Material selection based on ordinal data. *Mater. Des.* **2010**, *31*, 3180–3187. [CrossRef]
9. Jahan, A.; Ismail, M.Y.; Sapuan, S.M.; Mustapha, F. Material screening and choosing methods—a review. *Mater. Des.* **2010**, *31*, 696–705. [CrossRef]
10. Norhidayah, A.; Lee, C.K.; Azhar, M.K.; Nurulwahida, S. Indoor air quality and sick building syndrome in three selected buildings. *Procedia Eng.* **2013**, *53*, 93–98. [CrossRef]
11. Stolwijsk, J.A.J. Sick building syndrome. *Environ. Health Perspect.* **1991**, *95*, 99–100.
12. Redlich, C.A.; Spare, J.; Cullen, M.R. Sick-building syndrome. *Lancet* **1997**, *349*, 1013–1016. [CrossRef]
13. Cooley, J.D.; Woong, W.C.; Jumper, C.A.; Straus, D.C. Correlation between the prevalence of certain fungi and sick building syndrome. *Occup. Environ. Med.* **1998**, *55*, 579–584. [CrossRef] [PubMed]
14. Apter, A.; Bracker, A.; Hodgson, M.; Sidman, J.; Wing-Yan Leung, B.S. Epidemiology of the sick building syndrome. *J. Allergy Clin. Immun.* **1998**, *94*, 277–288. [CrossRef]
15. Hodgson, M.; Levin, H.; Wolkoff, P. Volatile organic compounds and indoor air. *J. Allergy Clin. Immun.* **1994**, *94*, 296–303. [CrossRef] [PubMed]
16. Mathias, J.D.; Grédiac, M.; Michaud, P. Bio-based adhesives. In *Biopolymers and Biotech Admixtures for Eco-efficient Construction Materials*; Pacheco-Torgal, F., Ivanov, V., Karak, N., Jonkers, H., Eds.; Elsevier Science and Technology: Cambridge, UK, 19 February 2016; ISBN 978-0-08-100214-8.
17. De Luca, P.; Roberto, B.; Vuono, D.; Siciliano, C.; Nagy, J.B. Preparation and optimization of natural glues based on Laricio pine resin. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *374*, 012071. [CrossRef]
18. De Luca, P.; Pane, L.; Vuono, D.; Siciliano, C.; Candamano, S.; Nagy, J.B. Preparation and characterization of natural glues with carbon nanotubes. *Environ. Eng. Manag. J.* **2017**, *16*, 1659–1672. [CrossRef]
19. Packham, D.E. Adhesive technology and sustainability. *Int. J. Adhes. Adhes.* **2009**, *29*, 248–252. [CrossRef]
20. Ding, G.K.C. Sustainable construction—The role of environmental assessment tools. *J. Environ. Manag.* **2008**, *86*, 451–464. [CrossRef] [PubMed]
21. Venkatarama Reddy, B.V. Sustainable materials for low carbon buildings. *Int. J. Low-Carbon Technol.* **2009**, *4*, 175–181. [CrossRef]

22. Mohanty, A.K.; Misra, M.; Drzal, L.T. Sustainable bio-composites from renewable resources: Opportunities and challenges in the green materials world. *J. Polym. Environ.* **2002**, *10*, 19–26. [CrossRef]

23. Sudin, R.; Swamy, N. Bamboo and wood fibre cement composites for sustainable infrastructure regeneration. *J. Mater. Sci.* **2006**, *41*, 6917–6924. [CrossRef]

24. Nastro, V.; Vuono, D.; Guzzo, M.; Niceforo, G.; Bruno, I.; De Luca, P. Characterisation of raw materials for production of ceramics. *J. Therm. Anal. Calorim.* **2006**, *84*, 181–184. [CrossRef]

25. Chi-Liang, Y.; Dyi-Hwa, T.; Tung-Tsan, L. Characterization of eco-cement paste produced from waste sludges. *Chemosphere* **2011**, *84*, 220–226.

26. Yiming, L.; Shaoqi, Z.; Fuzhen, L.; Yixiao, L. Utilization of municipal sewage sludge as additives for the production of eco-cement. *J. Hazard. Mater.* **2012**, *30*, 457–465.

27. Kizinievič, O.; Žurauskienė, R.; Kizinievič, V.; Žurauskas, R. Utilisation of sludge waste from water treatment for ceramic products. *Constr. Build. Mater.* **2013**, *41*, 464–473. [CrossRef]

28. Han, B.; Zhang, L.; Ou, J. Light-Emitting Concrete. In *Smart and Multifunctional Concrete toward Sustainable Infrastructures*; Springer: Gateway East, Singapore, 12 June 2017.

29. De Luca, P.; Chiodo, A.; Nagy, J.B. Activated ceramic materials with deposition of photocatalytic titano-silicate micro-crystals. *Sustain. Chem.* **2011**, *154*, 155–165.

30. Husken, G.; Hunger, M.; Brouwers, H.J.H. Experimental study of photocatalytic concrete products for air purification. *Build. Environ.* **2009**, *44*, 2463–2474. [CrossRef]

31. Ballari, M.M.; Hunger, M.; Husken, G.; Brouwers, H.J.H. NOx photocatalytic degradation employing concrete pavement containing titanium dioxide. *Appl. Catal. B-Environ.* **2010**, *95*, 245–254. [CrossRef]

32. Chen, J.; Poon, C. Photocatalytic construction and building materials: From fundamentals to applications. *Build. Environ.* **2009**, *44*, 1899–1906. [CrossRef]

33. Boonen, E.; Beeldens, A.; Dirkx, I.; Bams, V. Durability of cementitious photocatalytic building materials. *Catal. Today* **2017**, *287*, 196–202. [CrossRef]

34. Chuck, W.F.Y.; Jeong, T.K. Building Pathology, Investigation of Sick Buildings—VOC Emissions. *Indoor Built Environ.* **2010**, *12*, 30–39.

35. Englert, N. Fine particles and human health—A review of epidemiological studies. *Toxicol. Lett.* **2004**, *149*, 235–242. [CrossRef] [PubMed]

36. Marcazzan, G.M.; Valli, G.; Vecchi, R. Factors influencing mass concentration and chemical composition of fine aerosols during a PM high pollution episode. *Sci. Total Environ.* **2002**, *298*, 65–79. [CrossRef]

37. Filice, M.; De Luca, P.; Guido, G.P. Particular matter pollution in university area: Traffic flow analysis. *Environ. Eng. Manag. J.* **2009**, *8*, 1407–1412. [CrossRef]

38. Pekkanen, J.; Timonen, K.L.; Ruuskanen, J.; Reponen, A.; Mirme, A. Effects of ultrafine and fine particles in urban air on peak expiratory flow among children with asthmatic symptoms. *Environ. Res.* **1997**, *74*, 24–33.

39. Fujishima, A.; Rao, T.N.; Tryk, D.A. Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C Photochem. Rev.* **2000**, *1*, 1–21. [CrossRef]

40. Di Paola, A.; Garcia-Lopez, E.; Marci, G.; Palmisano, L. A survey of photocatalytic materials for environmental remediation. *J. Hazard. Mater.* **2012**, *211*, 3–29. [CrossRef] [PubMed]

41. Liu, Q.; Zhu, Z.; Zhang, J.; Zhang, B. Application of TiO_2 photocatalyst to the stone conservation. *Mater. Res. Innov.* **2015**, *19*, 51–54. [CrossRef]

42. Reddy, V.R.; Hwang, D.W.; Lee, J.S. Photocatalytic water splitting over ZrO_2 prepared by precipitation method. *Korean J. Chem.* **2003**, *20*, 1026–1029. [CrossRef]

43. Pal, S.; Mondal, S.; Maity, J.; Mukherjee, R. Synthesis and characterization of ZnO nanoparticles using moringa oleifera leaf extract: Investigation of photocatalytic and antibacterial activity. *Int. J. Nanosci. Nanotechnol.* **2018**, *14*, 111–119.

44. Ghosh, M.; Biswas, K.; Sundaresan, A.; Rao, C.N.R. MnO and NiO nanoparticles: Synthesis and magnetic properties. *J. Mater Chem.* **2006**, *16*, 106–111. [CrossRef]

45. Comparelli, R.; Fanizza, E.; Curri, L.M.; Cozzoli, D.P.; Mascolo, G.; Agostiano, A. UV induced photocatalytic degradation of azo dyes by organic-capped ZnO nanocrystals immobilized onto substrates. *Appl. Catal. B Environ.* **2005**, *60*, 1–11. [CrossRef]

46. Zhai, J.; Tao, X.; Pu, Y.; Zeng, F.X.; Chen, F.X. Core/shell structured ZnO/SiO_2 nanoparticles: Preparation, characterization and photocatalytic property. *Appl. Surface Sci.* **2010**, *257*, 393–397. [CrossRef]

47. Ramirez, A.M.; Demeestere, K.; De Belie, N.; Mantyla, T.; Levanen, E. Titanium dioxide coated cementitious materials for air purifying purposes: Preparation, characterization and toluene removal potential. *Build. Environ.* **2010**, *45*, 832–838. [CrossRef]

48. Marwa, M.H.; Heather, D.; Louay, N.M.; Tyson, R. Evaluation of the durability of titanium dioxide photocatalyst coating for concrete pavement. *Constr. Build. Mater.* **2010**, *24*, 1456–1461.

49. Shough, A.M.; Douglas, J.; Doren, M.N.; Raul, F.L. Effects of vanadium substitution on the structure and photocatalytic behavior of ETS-10. *J. Phys. Chem. C* **2007**, *111*, 1776–1782. [CrossRef]

50. Ren, Y.; Gu, M.; Hu, Y.; Yue, B.; Jiang, L.; Kong, Z.; He, H. Preparation and photocatalytic activity of lanthanide loaded microporous titanosilicate ETS-10 catalysts. *Chin. J. Catal.* **2012**, *33*, 33,123–128. [CrossRef]

51. Labrés i Xamena, F.X.; Calza, P.; Lamberti, C.; Prestipino, C.; Damin, A.; Bordiga, S.; Pelizzetti, E.; Zecchina, A. Enhancement of the ETS-10 titanosilicate activity in the shape-selective photocatalytic degradation of large aromatic molecules by controlled defect production. *J. Am. Chem. Soc.* **2003**, *125*, 2264–2271. [CrossRef] [PubMed]

52. Krisnandi, Y.K.; Southon, P.D.; Adesina, A.A.; Howe, R.F. ETS-10 as a photocatalyst. *Int. J. Photoenergy* **2003**, *5*, 131–140. [CrossRef]

53. Turta, N.A.; De Luca, P.; Bilba, N.; Nagy, J.B. Synthesis of titanosilicate ETS-10 in presence of cetyltrimethylammonium bromide. *Microporous Mesoporous Mater.* **2008**, *112*, 425–431. [CrossRef]

54. De Luca, P.; Vuono, D.; Filice, M. Self bonded ETS-10 containing iron. *Environ. Eng. Manag. J.* **2009**, *8*, 1009–1015. [CrossRef]

55. Turta, N.A.; Veltri, M.; Vuono, D.; De Luca, P.; Bilba, N.; Nastro, A. Effect of crystallization temperature on the synthesis of ETS-4 and ETS-10 titanosilicates. *J. Porous Mater.* **2009**, *16*, 527–536. [CrossRef]

56. Vuono, D.; Guzzo, M.; De Luca, P.; Nagy, J.B. Physico-chemical characterization of zirconium-based self-bonded ETS-4 pellets. *J. Therm. Anal. Calorim.* **2014**, *116*, 169–182. [CrossRef]

57. De Raffele, G.; Aloise, A.; De Luca, P.; Vuono, D.; Tagarelli, A.; Nagy, J.B. Kinetic and thermodynamic effects during the adsorption of heavy metals on ETS-4 and ETS-10 microporous materials. *J. Porous Mater.* **2016**, *23*, 389–400. [CrossRef]

58. Anson, A.; Wang, Y.; Lin, C.C.H.; Kuznicki, T.M.; Kuznicki, S.M. Adsorption of ethane and ethylene on modified ETS-10. *Chem. Eng. Sci.* **2008**, *63*, 4171–4175. [CrossRef]

59. De Luca, P.; Poulsen, T.G.; Salituri, A.; Tedeschi, A.; Vuono, D.; Kònya, Z.; Madaràsz, D.; Nagy, J.B. Evaluation and comparison of the ammonia adsorption capacity of titanosilicates ETS-4 and ETS-10 and aluminotitanosilicates ETAS-4 and ETAS-10. *J. Therm. Anal. Calorim.* **2015**, *122*, 1257–1267. [CrossRef]

60. Canpolat, F.; Yılmaz, K.; Kose, M.M.; Sumer, M.; Yurdusev, M.A. Use of zeolite, coal bottom ash and fly ash as replacement materials in cement production. *Cem. Concr. Res.* **2004**, *34*, 731–735. [CrossRef]

61. De Luca, P.; Mastroianni, C.; Nagy, J.B. Synthesis of self-bonded pellets of ETS-4 phase by new methodology of preparation. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *374*, 012003. [CrossRef]

62. Nai-Qian, F.; Gai-Fei, P. Applications of natural zeolite to construction and building materials in China. *Constr. Build. Mater.* **2005**, *19*, 579–584.

63. Sabet, F.A.; Libre, N.A.; Shekarchi, M. Mechanical and durability properties of self consolidating high performance concrete incorporating natural zeolite, silica fume and fly ash. *Constr. Build. Mater.* **2013**, *44*, 175–184. [CrossRef]

64. Bhardwaj, D.; Sharma, M.; Sharma, P.; Tomar, R. Synthesis and surfactant modification of clinoptilolite and montmorillonite for the removal of nitrate and preparation of slow release nitrogen fertilizer. *J. Hazard. Mater.* **2012**, *15*, 292–300. [CrossRef] [PubMed]

65. Doula, M.K. Synthesis of a clinoptilolite–Fe system with high Cu sorption capacity Chemosphere. *Chemosphere* **2007**, *67*, 731–740. [CrossRef] [PubMed]

66. Koyama, K.; Takeuchi, Y. Clinoptilolite: The distribution of potassium atoms and its role in thermal stability. *Z. Krist.-Cryst. Mater.* **1977**, *145*, 216–239.

67. Li, Y.H.; Wang, S.; Luan, Z.; Ding, J.; Xu, C.; Wu, D. Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes. *Carbon* **2003**, *41*, 1057–1062. [CrossRef]

68. Policicchio, A.; Vuono, D.; Rugiero, T.; De Luca, P.; Nagy, J.B. Study of MWCNTs adsorption perfomances in gas processes. *J. CO2 Util.* **2015**, *10*, 30–39. [CrossRef]

69. Walraven, J.C. High performance fiber reinforced concrete: Progress in knowledge and design codes. *Mater. Struct.* **2009**, *42*, 1247. [CrossRef]

70. Wille, K.; Naaman, A.E.; El-Tawil, S.; Parra-Montesinos, G.J. Ultra-high performance concrete and fiber reinforced concrete: Achieving strength and ductility without heat curing. *Mater. Struct.* **2012**, *45*, 309–324. [CrossRef]

71. De Luca, P.; Nappo, G.; Siciliano, C.; Nagy, J.B. The role of carbon nanotubes and cobalt in the synthesis of pellets of titanium silicates. *J. Porous Mater.* **2018**, *25*, 283–296. [CrossRef]

72. Thostenson, E.T.; Ren, Z.; Chou, T.W. Advances in the science and technology of carbon nanotubes and their composites: A review. *Compos. Sci Technol.* **2001**, *16*, 1899–1912. [CrossRef]

73. *UNI ENI 1348:2000*; Italian National Unification: Milano, Italy, 2008.

74. *EN 1015-12*; British Standards Institution (BSI): London, UK, 2016.