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The effects of microorganisms on the plasticity and strength of clays

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The present study examines the effects of *microorganisms*, which are isolated from the clay used in roof tile making by storage, on the plasticity and strength of tile clay, kaolinitic clay and montmorillonitic clay. Following trials done by using live cells and their metabolites, it was observed that bacterial activity had an effect on the plasticity and strength values of clay in both cases. It was also determined that ripening could be accelerated by choosing appropriate bacterial isolates and it was possible to use bacteria in industrial aspects.

Key words: Bacteria, Clay, Plasticity, Bentonite, Kaolinite.

Introduction

When stored in silos and tankers for up to 48 h during clay product studies, clay normally becomes sour. The conditions of this environment are of great importance in shaping clay. After grounding and blending, a certain amount of water is added into the clay in storage silos. Many types of clay are identified with their plasticity [1-3]. This plasticity is determined by deformation tests that show the quality of the initial and end products [1, 4]. The existence of free alkali in clay must either be limited or prevented to stop souring. Before the plasticity increases, the alkali must be neutralised by an appropriate acid addition into clay.

Before any souring takes place in a clay, a predetermined amount of acetic acid addition is recommended into the clay which is performed by pottery makers using vinegar or wine additions [1, 5, 6]. It has been recorded that any change in the shape of the clay or bacteria have important effects during souring, but the extent of this effect is not known for sure [5]. The increase in the plasticity of many types of clay in souring is totally a physical matter [1, 3]. Cameselle *et al*. state that a fungus with Aspergillus niger filaments can produce a huge amount of organic acid, and that its use in decomposition of iron to achieve purity in kaolinite increases the amount of white color in kaolinite; and that this is a very important factor for industrial applications [7, 8].

Riis *et al*. demonstrated that separation of the *microorganisms* from solids is tested via different procedures. In their studies, they recommended a one-step decomposition by vibration or centrifuge of an amount smaller than 100 g or equal to this amount [9, 10]. Joel *et al*. have isolated bacteria from solids and demonstrated that bacteria can be isolated by a structural Fe (III) decrease from smectite clay minerals. They analysed the bacteria developments which can decrease Fe (III) in clay minerals and found that the bacteria culture that can decrease Fe (III) is MR1 from the Shewanella oneidendis link [11]. Datzkova *et al*. have compared the prior and post behaviors of Bacillus mucilaginosus and Bacillus circulans species silicate bacteria, Bulgar kaolinite and porcelain structures, and found that the microbial behaviors of ceramic raw materials and structures caused an increase in baking processes and mechanical resistance [12].

Groudeva and co-worker stated that positive effects have been gained from exopolysaccharides with mucilage during the development of silicate bacteria and other *microorganisms* in kaolinite; that they behave like resin during drying; and that heteropolysaccharides are generally more effective than homopolysaccharides. They have also pointed out that exopolysaccharides, in particular formed by bacteria, are the molecules that increase the plasticity of kaolinite [13-15].

The aim of this study is to isolate the *microorganisms* with a positive effect during the ripening of a clay by determining the effects of the *microorganisms* in a clay, decrease the duration of ripening, carry out ripening performance in the laboratory, and demonstrate the applicability of *microorganisms* in industry.

Materials and Methods

The raw materials (roof tile, kaolinite and bentonite) were provided as follows; the roof tile clay from Eskisehir (the clay used in roof tile production), kaolinite from Kutahya Porselen Inc. (kaolinite used in porcelain production), and bentonite which has the characteristics to bulge from Karakaya Inc.

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The isolation and identification of *microorganisms*

Microorganisms were isolated from clay samples collected from roof tile companies which especially use clay by performing "holding" (a process especially known as ageing, rotting and souring methods where holding is done in a moist environment) in Salihli, Eskisehir, Kutahya, which is known to be the area where roofing tiles are produced the most. The samples were picked among the ones which had been stored for the longest time (in a moist environment at least for a month). The isolation of bacterial strains from clay samples was carried out according to the "Pour Plate Method" using a nutrient agar medium which had 3.0 g meat extract, 5.0 g peptone and 15.0 g agar (Merck, Germany) in a litre [16]. The agar was left for incubation at 30 °C for 24-48 h. The colonies formed on plates were transferred to slants involving nutrient agar. And then, isolates were stored at 4 °C as pure culture samples. In this study, the cultures were activated before use. The ripe clay itself was used as a mixed culture and was kept at 4 °C all through the research. The bacterial isolates were identified at the genus level according to Bergey's Manual of Systematic Bacteriology [17].

The preparation of inoculum and treatment process

The *microorganisms* were grown in a modified Ashby nutrient medium (0.5 g of $(NH_4)_2SO_4$); 0.2 g of K_2HPO_4; 0.2 g of $MgSO_4$; 0.1 g of K_2SO_4 and 20 g of sucrose and 1000 ml of distilled water; pH of 7.5) at 30 °C for 24-48 h, at 150 1/s. These activated cultures were used to inoculate preliminary prepared clay samples. The clay samples were sterilized at 121 °C for 15 minute in an autoclave. Fifty grams of sterile clay sample were added to 140 ml of sterile Ashby medium. The experiments were conducted in 500 ml Erlenmeyer flasks agitated at 150 rpm on a rotary shaker. The resulting clay suspensions were dried by filtration and then put into a process to determine their properties. The clay was also exposed to distilled water so as to determine any effect due to the Ashby medium components.

The chemical and physical analysis of clay

The chemical analysis of the clay was done using a Perkin Elmer 1100B atomic absorption spectroscopy and the mineralogical analysis was carried out using a Rigaku Miniflex XRD equipment. The chemical and mineralogical analyses of the raw materials used in the experiments are presented in Table 1. The plastic limits of the clay which is 24 mm according to Pfefferkorn [4] and the physico-mechanical properties were analysed. Then the samples were added to water according to the 24 mm crushing height and after being held for 24 h, they were shaped in 7.5 cm × 1.25 cm × 0.75 cm plaster moulds. Afterwards, they were dried in a drying oven up to a constant weight. The dried samples were baked at 950 °C peak temperature. During the analysis of the effects of ripening bacteria on bentonite under laboratory conditions, their strength could not be observed due to cracks during drying.

Table 1. Chemical and mineralogical properties of the clay used in the experiments

Results of Chemical Analysis (wt.%)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	LOI
Clay	45.59	15.02	12.23	9.83	4.89	1.48	1.11	1.70	7.15
Kaolinite	45.65	37.63	0.73	0.30	0.27	0.62	2.40	0.13	11.91
Bentonite	58.98	18.64	4.79	2.91	2.73	2.12	1.90	0.09	7.14

Results of Mineralogical Analysis	
Clay	Hornblend, chlorite, albite, anorthite, biotite, quartz, montmorillonite, muscovite and microcline
Kaolinite	Kaolinite + klorite, muskovite + illite, quartz, feldspar
Bentonite	Sodium montmorillonite, anorthite, dolomite, quartz

Results and Discussion

Two bacteria genus coded as N11 and N17 were isolated from clay samples. As a result of microscopic observations and tests, it was determined that these two bacteria are Bacillus circulans, and their properties were presented comparatively in Table 2 [17]. However, in the mixed culture, it was not possible to determine the properties due to the existence of numerous bacteria.

The *microorganisms* were used to treat raw materials (roofing tile clay, kaolinite and bentonite) in two ways; by means of microbial cultures growing on an organic substrate (sucrose) in the presence of the raw materials being treated (direct method), and by means of microbial cultures grown, prior to the treatment, on sucrose in the absence of raw materials (indirect method). Thus, the reason for the change that occurred during ripening could be discussed.

According to the plasticity curves in Figs. 1(a)-(b), as the ripened bacteria in roofing tile clay decreases the plasticity, it becomes an advantage in shaping the clay with less water. In the clay samples involving a mixed culture when the indirect method was applied, a shift to the right in Pfefferkorn curves [18] and an increase in the value of plasticity were observed. After the indirect method, the plasticity limits of the clay samples, to which a mixed culture was applied, in the Pfefferkorn curves increased distinctly. Whether the direct or indirect method was applied, the plasticity of the samples which were treated with *microorganisms* was observed to change. This change may possibly be the result of the existence of materials which bacteria produced and which were generally in a polysaccharide structure.

In Figs. 2(a)-(b), in the plasticity curves of kaolinite, the curves shift to the right and plasticity increases as a result of the two applications. In kaolinite samples, the effect of bacterial activities on plasticity is more than that in the roof tile clay. Plasticity increases 2-4% more in the ripened kaolinite samples involving bacteria than those without bacteria. It was determined that plasticity increased in the sample to which the direct method had been applied.

Table 2. The identification results of the bacterial isolates isolated from clay

Characteristics	N11	N17	*B. circulans*
Cell diameter > 1.0 μm	-	-	-
Spores round	-	-	-
Sporangium swollen	+	+	+
Parasporal crystals	-	-	-
Catalase	+	+	+
Voges-Proskauer test	-	-	-
pH in V-P broth			
< 6	+	+	+
> 7	-	-	-
Acid from			
D-Glucose	+	+	+
L-Arabinose	+	+	+
D-Xylose	+	+	+
D- Mannitol	+	+	+
Hydrolysis of			
Casein	-	-	d
Gelatin	+	+	d
Starch	+	+	+
Utilization of citrate	+	+	d
Nitrat reduced to nitrite	+	+	d
Formation of indole	-	-	-
Growth at pH			
6.8, nutrient broth	+	+	+
5.7	+	+	d
Growth in NaCl			
2%	+	+	ND
5%	+	+	d
7%	+	+	d
10%	-	-	-
Growth at			
5 ºC	-	-	-
10 ºC	+	+	d
30 ºC	+	+	+
40 ºC	+	+	+
50 ºC	-	-	-
55 ºC	-	-	-
65 ºC	-	-	-

Symbols: -, 90% or more of strains are negative; +,90% or more of strains are positive; d, 11-89% of strains are positive; ND, no data available

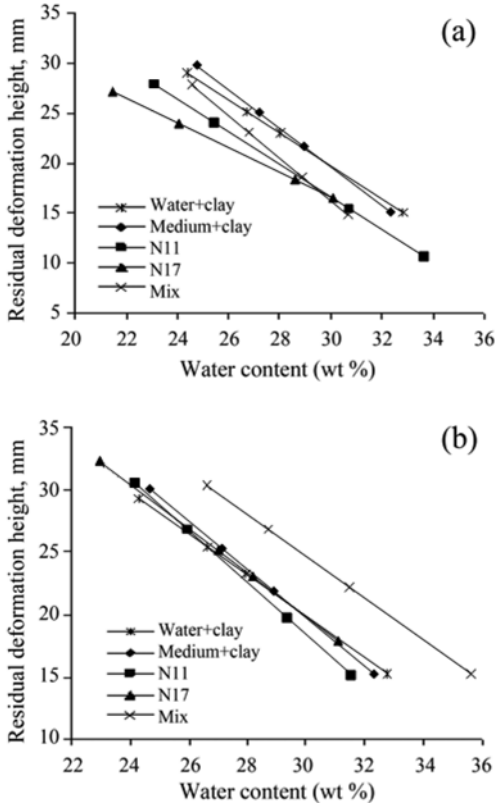

Fig. 1. The plasticity curves of the roofing tile clay samples to which the direct (a) and indirect method (b) have been applied.

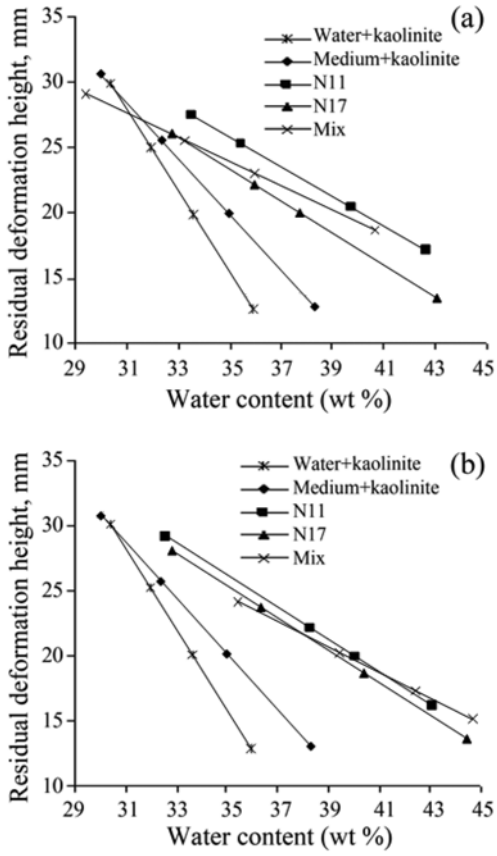

Fig. 2. The plasticity curves of the kaolinite samples to which the direct (a) and indirect method (b) have been applied.

However, it was observed that, as a result of the indirect method, the plasticity of kaolinite increased more than in the direct method and controlled applications. This supports the fact that, more than the direct effect of *microorganisms*, the metabolites they form have a role in the increase in plasticity.

According to Figs. 3(a)-(b), the medium decreased the plasticity of bentonite. The plasticity decreases in bentonites which were treated with active bacteria. The plasticity in samples, which were autoclaved and thus in which activation of the bacteria was ceased, increased more than that in samples involving B. circulans N11 and N17 active bacteria cultures.

The plasticity limit values of clay, kaolinite and bentonite in Figs. 4(a)-(b) were determined from Pfefferkorn plasticity curves according to 24 mm and their graphs were drawn. In the roof tile clay, in the samples with active bacteria, this limit was the lowest in B. circulans N17 strain with 23.94. The other bacterial strain, B. circulans N11 and the mixed culture, decreased the plasticity in comparison with the untreated material. In the bacteria samples which were autoclaved and thus inactivated, the highest plasticity was 30.34 in the mixed culture (Fig. 4(b)). It was also seen that the mixed culture which was applied to the clay after

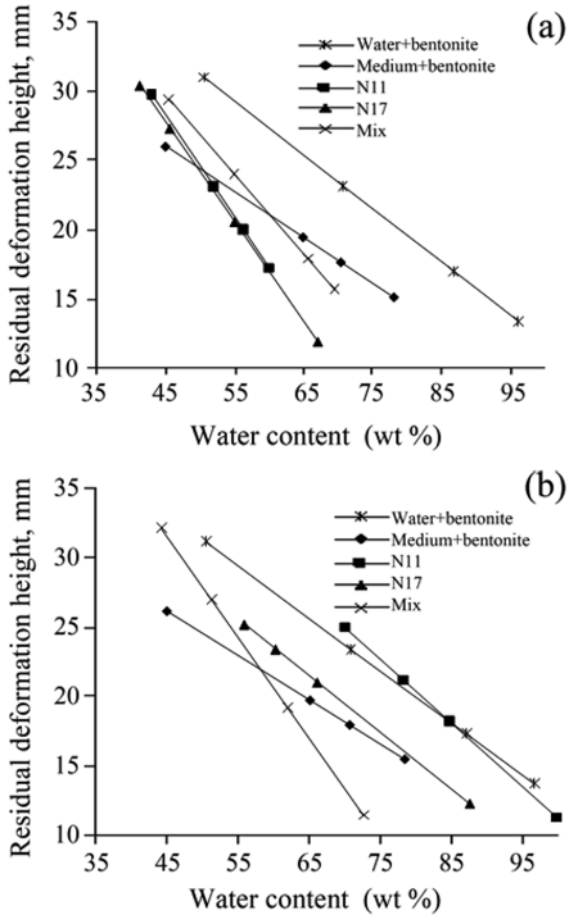

Fig. 3. The plasticity curves of the bentonite samples to which the direct (a) and indirect method (b) have been applied.

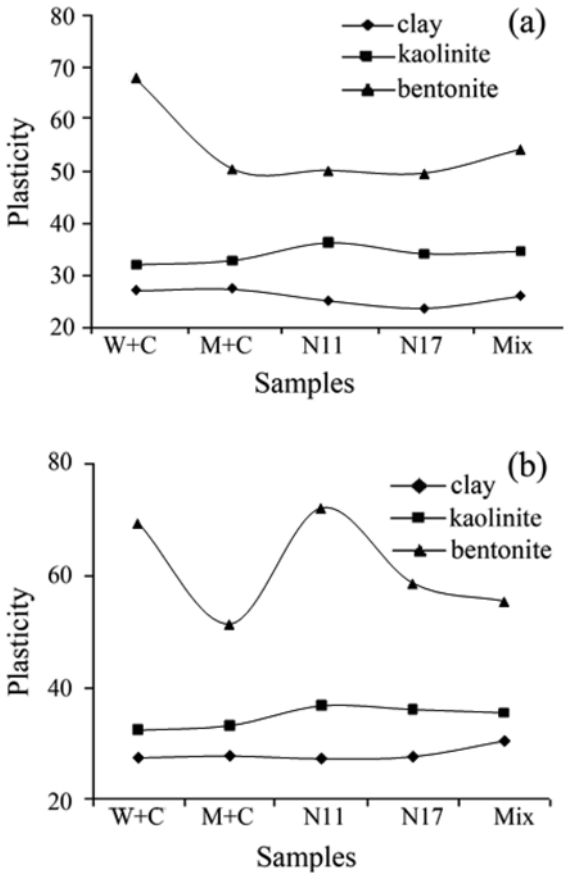

Fig. 4. The plasticity values of (a) activated and (b) inactivated bacteria according to 24 mm. W + C; water + clay (the roofing tile clay, kaolinite, bentonite), M + C; medium + clay (the roofing tile clay, kaolinite, bentonite).

being autoclaved and thus killed was more effective. This shows that bacterial activity has no direct effect on the ripening of the clay but the metabolites formed by the bacteria do. In the kaolinite samples, the plasticity values increased with bacteria. The highest value of plasticity was in B. circulans N11 coded study with 36.67, whereas the lowest was in B. circulans N17 with 34.51. In the kaolinites with active bacteria, the highest plasticity was 36.67 in N11, and the plasticity of the other B. circulans N17 and mixed culture increased more than the samples without bacteria. The highest plasticity increase in the kaolinite samples with inactivated bacteria was 36.63 in B. circulans N11.

The plasticity values of others B. circulans N17 and mixed samples, 35.98 and 35.41 respectively, increased more than the ones without bacteria. Although the plasticity value of bentonite that was treated with distilled water was 68.67, the plasticity of bentonite treated with the medium was 50.99. However, when compared with bentonite treated with the medium, the plasticity increased in the mixed coded study and became 54.83. The plasticity of autoclaved and unautoclaved samples in the mixed study did not change so much. In bentonite, especially with samples whose mixed culture had been ripened, plasticity

rose a little although its medium decreased the plasticity. In the samples with inactivated bacteria, B. circulans N11 increased the plasticity.

As can be seen from Figs. 5(a)-(b), according to the dry and fired strength values of the samples with active bacteria, in the active N11 coded culture applications, the dry strength value, 6.56 MPa, is lower than the strength value of pure clay. In the mixed and B. circulans N17 coded culture applications, the strength values increased; the highest was 9.17 MPa in N17. In the sample in which the lowest mixed culture was used, the baked strength of the samples with active bacteria was found to be 14.05 MPa. The effect of *microorganisms* on the dry strength value of kaolinite is very large. In particular in the mixed coded study, the highest strength value, 3.13 MPa, was obtained. The baked strength of kaolinite with active bacteria was decreased.

In Figs. 6(a)-(b), in the samples with bacteria inactivated by autoclave application, the dry strength of kaolinite increased by 34.26% with the highest mixed culture which reached 2.03 MPa. In the sample with a mixed culture, the dry strength values were found to be high, but the baked strength values were decreased to 6.25 MPa. The B. circulans N11 and N17 cultures, which were autoclaved, killed and applied to clay, showed effective results in the dry strength values of clay. The B. circulans N11 culture increased the dry strength of clay by 59.77% (10.89 MPa), whereas the B. circulans N17 coded culture led to be 62.47% (11.08 MPa) increase. The dry strength values of roof tile samples with inactivated bacteria appeared to be higher than those of the samples with active bacteria, which show that the bacteria metabolites are more effective on the dry strength. The B. circulans N11 and N17 samples of inactivated bacteria which were autoclaved in the kaolinite samples are more effective on the dry strength than those with active bacteria. In the autoclaved samples, the highest dry strength was 2.03 MPa in the mixed culture. The bacteria of the mixed culture were found to be effective on the dry strength of kaolinite.

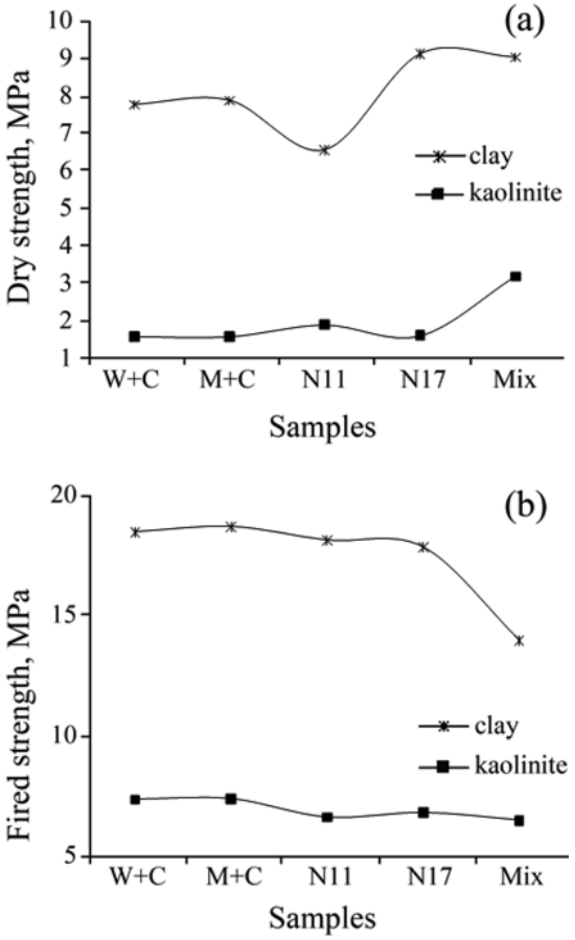

Fig. 5. (a) dry strength and (b) fired strength values of active bacteria samples. W + C; water + clay (the roofing tile clay, kaolinite), M + C; medium + clay (the roofing tile clay, kaolinite).

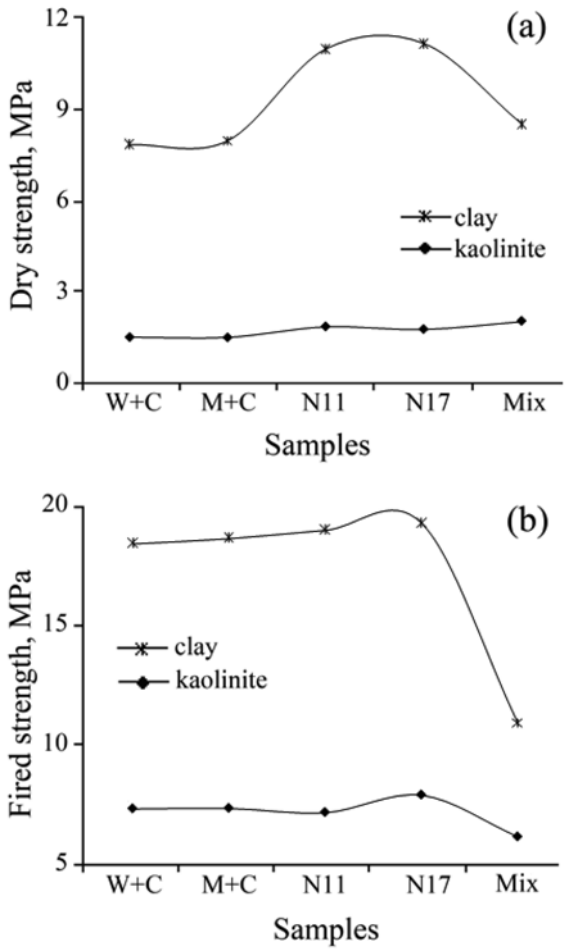

Fig. 6. (a) dry strength and (b) fired strength values of deactived bacteria samples. W + C; water + clay (the roofing tile clay, kaolinite), M + C; medium + clay (the roofing tile clay, kaolinite).

Conclusions

The effects of the active and inactivated-bacteria on different clays are given below.

1) The plasticity value of clay samples with bacterial

metabolites increased more than those with active bacteria.

2) Inactivated B. circulans N11 and N17 strains in clay were more effective on the plasticity, which increased strength. Active B. circulans N17 strain decreased the plasticity of clay, which made it easier to shape with less water and increased the strength. The mixed sample, both activated and inactivated, on the other hand, increased both the strength and dry plasticity more than the samples without active bacteria.

3) It is possible to use a mixed culture to increase the dry strength in clay and kaolinite. As such, bacterial activity was also observed to be beneficial because as a result of holding the roof tiles for a certain time, the mixed culture increased the plasticity and was effective on the strength.

4) The B. circulans N11 isolate increased both the plasticity and dry strength values of kaolinite. In terms of the increase in plasticity in kaolinite, the B. circulans N11 strain was more effective than B. circulans N17 and the mixed culture. When the activities of B. circulans N17 and mixed culture were stopped, the increase in plasticity was more than that of the samples with active bacteria.

5) Whereas the only process of treatment with components of the medium decreased the plasticity of bentonite, it increased the plasticity compared with the samples treated with the medium containing bacteria which was inactivated via autoclaving.

6) The mixed culture, activated and inactivated, in kaolinite had more influence on the strength than the other cultures.

7) In different types of clay, activated and inactivated bacteria affected the plasticity and strength values. The effect of the different bacterial cultures isolated from natural clay in different types of clay was due both to the bacteria directly itself and to the liquids the bacteria left behind after having been inactivated.

8) Choosing the appropriate *microorganisms* or consortiums would also yield the desired characteristics in addition to diminishing the ripening time.

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