

Algerian Montmorillonite as a Builder in a Detergent Powder

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ABSTRACT: Algerian montmorillonite treated with sodium chloride was used as a substitute for the builders sodium tripolyphosphate (STPP) and sodium sulfate in a detergent powder. The following performance parameters of the substituted composition powder were examined: pH, foaming, cleaning, sequestering, and ion exchange capacities. The latter factors remained the most important ones for effective detergency. Despite anticipated improvement in hard water ion removal, constant detergency results were observed with the treated montmorillonite-containing powder. This level of efficacy does not meet the cost-effectiveness of a standard detergent powder containing STPP.

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KEY WORDS: Detergent, foaming, montmorillonite, sequestering, sodium tripolyphosphate.

Synthetic detergent formulators have made tremendous inroads since the discovery of the surfactant sodium alkyl naphthalene sulfonate, the well-known German Nokal. The latter was actually the result of the embargo imposed on Germany during World War I (1,2). That synthetic detergent owed its low detergency to its short alkyl group, namely *n*-propyl and *n*-butyl. In contrast, the sodium salt of propylene tetramer benzene sulfonate, the American detergent developed in 1920, exhibited better detergency because of its longer alkyl group (C₁₂). Since 1965, linear dodecyl benzene sulfonate has been substituted for the branched version because of its relatively better biodegradation properties.

Despite these advances in surfactant technology, overall detergency of a formulation has remained highly dependent on the added builders in detergent powders. Among these additives, sodium tripolyphosphate (Na₃P₃O₉; STPP), introduced in 1947, and sodium sulfate (Na₂SO₄, used mainly as filler) have been indispensable for providing good cleaning performance, especially in hard water. Water always contains hardness, usually measured as the concentrations of Ca²⁺ and Mg²⁺. Moreover, the heavy metallic ions

present in water, such as Fe²⁺, Cu²⁺, Ni²⁺, and Mn²⁺, are potential catalysts for the decomposition of the perborates that are incorporated as bleaching agents in a detergent formulation. STPP is extremely effective in sequestering these metal ions and improving cleaning performance.

Although it is renowned for its sequestering, solubilizing, dispersing, peptizing, and emulsifying capacities, as well as for its alkalizing and electrolytic properties, STPP can adversely affect the environment because of eutrophication (1,2), a phenomenon linked to its limited biodegradability (1). Potential substitutes for STPP, such as nitrilotriacetic acid (NTA), ethylene diamine tetraacetic acid (EDTA) and zeolites, have other negative issues. For example, zeolites are less alkaline than STPP and therefore require the use of other builders such as the costly sodium citrate to compensate (3). In addition, NTA has proved to be quite toxic when contaminated with heavy metals in drinking water, and EDTA has poor biodegradability characteristics.

This paper presents experimental results on the partial substitution of both STPP and sodium sulfate by NaCl-treated Algerian montmorillonite in a heavy-duty household powder washing detergent. The objective of the present study was to determine whether appreciable quantities of Algerian montmorillonite can be used without appreciably altering the overall characteristics of the detergent product. The price of STPP on the world market is about three to four times that of the montmorillonite, so cost-effectiveness of the clay is a consideration. Currently, the best applications of this clay material have been in the catalysis of chemical reactions (hydrogenation, alkylation, etc.) (4) and for contaminant adsorption in water treatment processes (5).

EXPERIMENTAL PROCEDURES

The chemicals used in this work were provided by the ENAD firm (Entreprise Nationale des Détergents, Reghaïa, Algeria). These included sulfonate paste, sodium silicate solution, STPP, Na₂SO₄, EDTA, NaCl, chloroform, methylene blue, and benzethonium chloride. The crude montmorillonite was obtained from Mostaganem (Algeria). The following test equipment was used: (i) refractometer (Universal Me Benleit UME3), to estimate the powder whiteness; (ii) pH meter (Knick digital pH-meter 646), to determine the pH of the slurries; (iii) centrifuge (Gallenkamp); (iv)

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Abbreviations: AAM, anionic active matter; DDBS, sodium dodecyl benzenesulfonate; EDTA, ethylene diamine tetraacetic acid; *F*, formulation; NTA, nitrilotriacetic acid; STPP, sodium tripolyphosphate; TH, total hardness.

mechanical agitator; (v) washing drum, for cleaning studies; (vi) aerometer, for density measurement; and (vii) oven (Memmert, 30–120°C).

Treatment of montmorillonite with sodium chloride. In a 2-L beaker, a 200-g sample of crude montmorillonite was mixed with 1 L of 1 M sodium chloride solution. The heterogeneous mixture was stirred with a mechanical agitator for 3–4 h at room temperature. After the mixture was allowed to sit for 1.5 h, the top aqueous liquid was withdrawn and replaced by an equal volume of sodium chloride solution, and the stirring was restarted. This operation was replicated five times to maximize the gain in sodium ions by the material. After the fifth addition, distilled water was added to the treated material, and the system was stirred for 1 h. The latter operation was also repeated five times to wash off any extra chloride ions. Finally, the treated montmorillonite was dried at 50–60°C for 3–4 d.

Sequestering capacity. A slurry was prepared by adding an appropriate amount of the treated material to 200 mL of tap water (hard water). The slurry was then stirred at 60°C for 1 h. Finally, the filtrate was separated by gravity filtration using Whatman no. 40 filter paper and titrated with an EDTA solution at pH 10 in the presence of black Eriochrome as an indicator. The presence of noncomplexed Ca^{2+} and Mg^{2+} was indicated by the color change to violet. The total hardness (TH), expressed in mequiv/L is given by Equation 1:

$$\text{TH} = \frac{1000 \cdot V_b \cdot C \cdot n}{V_a} \quad [1]$$

where C is the concentration of EDTA solution (0.01 mol/L); V_a is the volume of the sample (50 mL); $n = 2$ is the ion charge (Ca^{2+} and Mg^{2+}); V_b is the volume of EDTA solution in mL required for titrating the noncomplexed ions Ca^{2+} and Mg^{2+} , and 1000 is the factor conversion from equiv/L to mequiv/L.

The sequestering or softening capacity of STPP and the exchange capacity of the montmorillonite are expressed as the difference between the initial hardness of the tap water, TH_i , and the hardness of the filtrate, TH_f , $\Delta\text{TH} = \text{TH}_i - \text{TH}_f$. TH_i was found to be 11.4 mequiv/L or 570 ppm as CaCO_3 ($V_b = 29.5$ mL); thus, according to Levitt hardness scale (1), the tap water used was very hard.

Formulations of detergent powders. The composition of the standard detergent formulation F_0 (in wt%) was as follows: sodium dodecylbenzenesulfonate (DDBS) (15), STPP (20), Na_2SO_4 (47), sodium silicate (10), H_2O (6.5), and other builders (1.45). The weights of sodium silicate solution, sulfonated paste, and water to be used in the formulations were determined in the following manner.

(i) *Weight determination of silicate solution.* The weight of sodium silicate solution corresponding to the required weight of silicate to be included in the formulations was determined by measuring the density of the solution in degrees Baumé using an aerometer. The density of this solution was found to be 52°Bé at 20°C. Its density ρ in g/mL was related to its Baumé density by the relationship shown in Equation 2 (1):

$$\rho = \frac{145}{145 - ^\circ\text{Be}'} \quad [2]$$

ρ was found to be 1.56 g/mL, which corresponds to 46.0 g of sodium silicate (Na_2SiO_3) in 100 g of solution (2). Therefore, for 10 g of silicate necessary for the basic formulation, F_0 , 21.7 g of the silicate solution was used.

(ii) *Weight estimation of sulfonated paste.* The DDBS surfactant had a molecular weight of 341 and was supplied as a paste. Therefore, it was necessary to determine the level of anionic active matter (AAM, of DDBS) in the sulfonated paste to calculate the exact weight of the paste required for the formulations. The AAM was determined experimentally by titrating the sulfonated paste with 0.003 mol/L aqueous solution of benzethonium chloride, a cationic surfactant, in the two-phase water/chloroform method described by Reid *et al.* (6) and Hummel (7). Methylene blue was used as the indicator for titration. An AAM level of 43% by weight was obtained. Therefore, to incorporate 15 g of DDBS into the basic formulation, F_0 , 34.9 g of the DDBS paste was used.

Preparation of the detergent powder. To make up the different experimental detergent formulations (F_i) given in Table 1, the amount of treated montmorillonite replacing STPP or Na_2SO_4 in F_0 was varied in the following manner: montmorillonite (%) for STPP: 1 (F_1), 2 (F_2), 3 (F_3), 4 (F_4), or 5 (F_5); montmorillonite (%) for Na_2SO_4 : 2 (F_6), 4 (F_7), or 5 (F_8). To prepare the detergent compositions, detergent paste was prepared by mixing the required amounts of inorganic and organic salts with 37.75 g of water. This quantity of water was determined on the basis of two conditions: (i) that the slurry should contain 40% water, and (ii) that the amounts of water should be adjusted based on the amount present in the sodium silicate solution and the sulfonated paste. Heat-sensitive additives (bleaching agent, perfume, and others) were added only at the end of the drying process. Stirring of the slurry was maintained for 1 h at 80°C for complete mixing of the system. Next, the slurry was dried in an oven at 100°C until a powder formed that contained about 6.5% by weight residual moisture, which is 30% by weight found in STPP (2).

Foaming capacity. The foaming capacity of a detergent was estimated according to the modified Ross–Miles method (ISO 696 1975). It was measured as the volume of foam produced after 500 mL of 5 g/L surfactant solution flowed

TABLE 1
Sequestering Capacity of STPP ($\text{TH}_i = 11.84$ mequiv/L)^a

Weight of STPP in the slurry (%)	V_b (mL)	TH_f (mequiv/L)	$\Delta\text{TH} = \text{TH}_i - \text{TH}_f$ (mequiv/L)
0.05	22.60	9.04	2.80
0.06	21.50	8.60	3.24
0.07	19.50	7.80	4.04
0.08	16.50	6.60	5.24
0.11	11.50	4.60	7.24
0.13	9.80	3.92	7.92
0.16	5.00	2.00	9.84

^aSTPP, sodium tripolyphosphate; TH_i , initial hardness of the tap water; TH_f , hardness of the filtrate; ΔTH , change in total hardness; V_b , volume of ethylene diamine tetraacetic acid solution used for titrating the Ca^{2+} and Mg^{2+} .

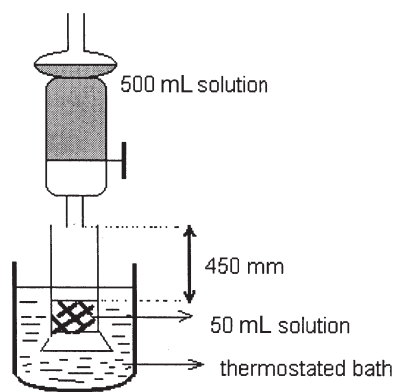


FIG. 1. Device used for the foaming measurement.

down from a height of 450 mm onto the liquid surface. Figure 1 shows the apparatus used for this technique.

Specifically, a 50-mL aliquot of a detergent solution was poured into the graduated cylinder along its wall to prevent foaming. The graduated cylinder was then placed in a water bath thermostated at $50 \pm 2^\circ\text{C}$. The position of the separatory funnel containing 500 mL of the detergent solution was adjusted in such a way as to make the axes of both the graduated cylinder and funnel coincide and to locate the lower tip of the funnel 450 mm from the surface of the 50 mL solution. The 500 mL of detergent solution was then added from the separatory funnel at a constant rate. The flow time of the added solution was noted, and the volumes of the foam present after 30 s, 3 min, and 5 min were recorded.

Sequestering capacities of the F_i . The sequestering capacities of the different F_i products were estimated using tap water. A 50-mL aliquot of 5 g/L detergent solution was titrated with 0.01 M EDTA in the presence of black Eriochrome. The results were calculated as the mean of three replicate test results.

Cleaning performance and powder appearance. The cleaning effectiveness of the different formulations using soiled white cotton fabrics (10×10 cm) was carried out in a stainless-steel drum (8.70 cm in diameter, 20.20 cm in height). The drum was fitted with an axle-arm by which it was rotated during washing. The soil placed on the fabric was an aqueous solution of tomato paste that was first concentrated in an edible oil. The white fabric was immersed into this solution for a few minutes and dried overnight in the drying oven. The fabric specimen was inserted inside the drum, containing 2 g of the detergent powder and 400 mL of water, and the washing cycle consisted of rotation of the drum for 15 min. The fabric was then taken out, rinsed with cold water, air-dried for 10 min, and finally dried in a drying oven. The whiteness was determined with a digital refractometer by using the refractive index of BaSO_4 at 100% as a reference. The whiteness of the powders and the cleaned fabrics was estimated against that of BaSO_4 .

RESULTS AND DISCUSSION

Good detergency is always the prime function of any new detergent formulation. In this regard, the surfactant is the

basic active ingredient necessary for soil removal. Yet the surface-active property of the latter may be somewhat altered when used in water containing metal ions such as Ca^{2+} and Mg^{2+} . Thus, the supremacy of STPP as a potential softening agent in detergent formulations is quite important, and it was imperative to study the factors affecting the initial detergency (F_0) when montmorillonite was substituted for STPP or Na_2SO_4 .

Knowing that STPP contributes to the detergency to a certain degree *via* its alkalinity, it was relevant to compare the alkalinity of the substituted montmorillonite to that of STPP. The pH of a 10% aqueous slurry of STPP was found to be 9.63, whereas that of the montmorillonite was 9.65. It was therefore clear that the montmorillonite would affect the detergency of a formulation in a manner similar to STPP with regard to alkalinity but be better than Na_2SO_4 , which exhibited a pH of only 6.98. It is worth noting that conventional zeolites do not provide levels of alkalinity comparable to those of STPP (2).

However, the whiteness of Na_2SO_4 and particularly that of STPP are far superior to that of montmorillonite. This low whiteness is considered a disadvantage because discoloration may arise when washing white textiles since montmorillonite deposits could result in the graying of articles. Also, the appearance of the detergent powder itself could be less attractive to the consumer.

The sequestering power of STPP and the exchange capacity of the montmorillonite remain important factors, as these illustrate their respective water-softening ability. The results of a complexometry study with EDTA are presented in Tables 1, 2, and 3 and illustrated in Figures 2 and 3. These results clearly illustrate the superiority of STPP over montmorillonite. Indeed, to reach the same efficacy as that of STPP, a 10-fold increase in concentration of the nontreated montmorillonite is required. For instance, 0.1% of STPP gives ΔTH of 7.24 mequiv/L, but a 1% montmorillonite slurry is needed to attain the same level of performance. A slight improvement in the treated material was noted, which was about 10% higher compared to the crude one.

Eight detergent formulations were prepared by substituting the treated montmorillonite for STPP (F_1 – F_5) or Na_2SO_4 (F_6 – F_8) as explained above. The detergent powders provided some alkalinity as revealed by their pH values, which were in the range of 10.38–10.80. The pH was not substantially affected by the degree of substitution, which

TABLE 2
Exchange Capacity of Crude Montmorillonite^a

Weight of montmorillonite in the slurry (%)	V_b (mL)	TH_f (mequiv/L)	$\Delta\text{TH} = \text{TH}_i - \text{TH}_f$ (mequiv/L)
1	11.10	4.44	7.40
2	7.30	2.92	8.92
3	5.50	2.20	9.64
4	4.50	1.80	10.04
5	3.00	1.20	10.64

^aFor abbreviations see Table 1.

TABLE 3
Exchange Capacity of Treated Montmorillonite^a

Weight of montmorillonite in the slurry (%)	V_b (mL)	TH_f (mequiv/L)	$\Delta TH = TH_i - TH_f$ (mequiv/L)	Increase relative to untreated (%)
1	9.30	3.72	8.12	9.73
2	4.50	1.80	10.04	12.55
3	3.00	1.20	10.64	10.40
4	2.00	0.80	11.04	9.96

^aFor abbreviations see Table 1.

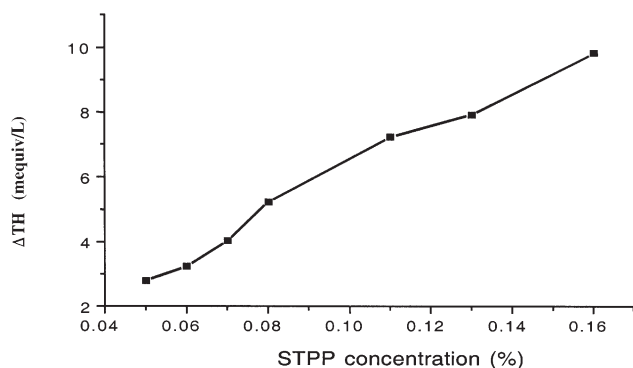


FIG. 2. Sequestering power of sodium tripolyphosphate (STPP). TH_i , total hardness of the tap water used.

suggests a buffering effect. Thus, the alkalinity provided by the treated montmorillonite should have a positive influence on detergency. For a formulated detergent, an alkaline pH of 9.5–10.5 is usually desirable (1).

Although foaming is not a direct requirement for detergency, it is important for a detergent powder intended for hand-washing applications. The results of the foaming power of different trials (F_i) are illustrated in Table 4. The best foaming power was observed for F_0 , F_3 , F_5 , F_7 , and F_8 as

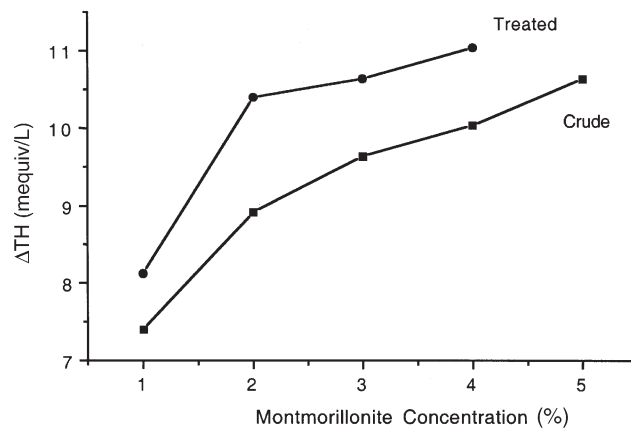


FIG. 3. Exchange capacity of the montmorillonite. For abbreviation see Figure 2.

revealed by their respective foam volumes after 5 min of 265, 250, 260, 265, and 270 mL, respectively. Because these values were not substantially different, however, one can conclude that the substitution of montmorillonite for STPP or Na_2SO_4 had little practical effect on foaming properties.

The sequestering power (ΔTH) of the different formulations varied from 9.30 to 10.50 mequiv/L as shown in Table 5

TABLE 4
Results of Foaming of Experimental Formulations (F_i)^a

F_i	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8
Flow time (s)	15	15.90	15.70	15.30	15.20	15.35	15.20	15.20	15.40
Volume of the foam produced (mL)									
30 s	360	352	390	365	300	385	370	355	330
3 min	310	305	290	270	270	330	295	295	330
5 min	265	207	250	225	230	260	240	265	270

^a F_0 , basic formulation; F_{1-5} , formulations with 1, 2, 3, 4, or 5% montmorillonite substituted for STPP; F_{6-8} , formulations with 2, 4, or 5% montmorillonite substituted for Na_2SO_4 ; for other abbreviation see Table 1.

TABLE 5
Sequestering Capacities of F_i ($TH_i = 11.70$ mequiv/L)^a

F_i	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8
Volume of EDTA solution (mL)	3.00	5.95	4.30	5.00	4.65	5.60	2.95	3.70	4.05
TH_f of solution (mequiv/L)	1.20	2.38	1.72	2.00	1.86	2.24	1.18	1.48	1.62
$\Delta TH = TH_i - TH_f$ (mequiv/L)	10.50	9.32	9.98	9.70	9.84	9.46	10.52	10.22	10.08

^aFor abbreviations see Tables 1 and 4.

TABLE 6
Results of Cleaning Performance of F_i^a

F_i	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8
Whiteness of the dirtied fabric (%)	30.22	31.97	34.32	32.30	29.92	32.60	32.17	30.80	31.55
Whiteness of the washed fabric (%)	57.62	56.47	59.15	58.65	59.92	59.50	59.50	59.67	59.67
Washing performance as an increase in whiteness (%)	27.40	24.50	24.83	26.35	30.00	26.90	27.33	28.87	28.12

^aFor abbreviations see Table 4.

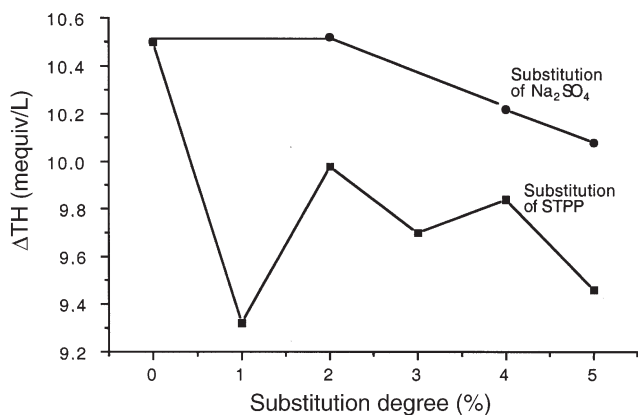


FIG. 4. Sequestering power of the experimental formulations (F_i). For other abbreviations see Figure 2.

and Figure 4. Overall, this softening capacity was somewhat reduced as the STPP was partially replaced by the treated montmorillonite. The ΔTH for F_1 – F_5 fluctuated and seemed to be independent of the amount of montmorillonite, probably owing to the architecture of montmorillonite. The structure of montmorillonite consists of layers of units made of two silica tetrahedral sheets (T) with a central alumina octahedral sheet (O), commonly called TOT layers (8). The softening sodium ions are inserted between the TOT layers, probably in unequal concentrations. These ions are embedded in such way that their entire release into the medium, and therefore their exchange with cations present in the medium, is not always rapid. This would also affect the rate of cation exchange, potentially resulting in an inconsistent substitution effect.

However, the substitution of montmorillonite for Na_2SO_4 (F_6 – F_8) provided better sequestration. These results are in a good agreement with the common knowledge that sodium sulfate is but a good diluent and filler with no detergency capacity (1,2). Interestingly, the ΔTH for F_7 and F_8 was lower than that for F_0 . This result may once again be due to an insufficient sequestration time or to the internal structure of montmorillonite as discussed above. These results indicate that a partial substitution of Na_2SO_4 could be a valid use for montmorillonite.

The whiteness of the montmorillonite-containing powders (in %) dropped monotonically relative to the standard

formulation (F_0) in the following manner: 88.40 (F_0), 85.30 (F_1), 84.60 (F_2), 81.70 (F_3), 80.0 (F_4), 77.70 (F_5), 85.10 (F_6), 79.80 (F_7), and 78.10 (F_8). As expected, the higher the degree of substitution, the lower the whiteness. It should be noted that a 1% substitution of STPP or 1% of Na_2SO_4 resulted in a whiteness rating only slightly lower than that of F_0 . Use of higher levels of montmorillonite could cause unacceptable powder appearance and graying of fabrics.

Undoubtedly, one key test of a detergent formulation is the extent of the whiteness of a dirtied white fabric after being washed. The results of the cleaning tests (F_i) presented in Table 6 suggest that most of the formulations produced cleaning results comparable to that of the standard formulation. The cleaning results, however, were limited to only one soiled-fabric combination. The reduced building capacity of the montmorillonite compared to STPP would likely cause deficiencies under different detergency conditions and with different soils and stains, even if only a partial substitution of STPP were attempted. As noted above, a more cost-effective option could be partial substitution of Na_2SO_4 to a degree where the drop in powder whiteness would not be noticeable.

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