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CHEMICAL TREATMENT OF URINE USING A SANITARY TABLET TO REDUCE WATER USAGE IN RESIDENTIAL TOILETS

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ABSTRAC

This study proposes an alternative to chemical treatment of urine to reduce water consumption in residential discharges, allowing a longer remaining time of the water to be discarded in the toilet bowl, before starting the discharge. The process consists of neutralizing the components responsible for the odor and color characteristic of urine with the development of a formulation whose main compound is sodium dichloroisocyanurate, NaDCC. The compound also presents a bactericidal action which can act for a given period of time. Moreover, there is the addition of a component indicating the medium saturation level to optimize the effect on health and aesthetics (odor, color, and bacteria). The proposed treatment should be inexpensive, stimulating a behavioral change by means of the awareness of water consumption reduction in homes. It is intended to follow the performance of the proposed process, with physico-chemical and microbiological complementary essays.

INTRODUCTION

Domestically, the use of water for hygienic and sanitary purposes, discharge after urination, as a specific example, is one of significant consumer situations and yet to be improved or streamlined. Some countries such as the United States, Mexico, Canada and Australia have encouraged people to replace old toilets and flow valves in-built in the wall by ecological discharge, attached box type.

The wall valve and other old equipment are large consumers of water. These valves can consume an average volume of 15 L of water per function, lpf: newer models consume on average 6 liters of water, as determined by ABNT NBR 15099:2004 [1].

The term *sanitary basin* is defined by ABNT NBR 8160:1999 [2]. Studies show that 35% of the water of a residence flows away the toilet by flushing. It is estimated that Brazil would have to change 100 million toilets, which waste an average of 30 to 40 liters of water each flush. However, the market has already been offering, for years, products that make latrines hygiene with 6-9 liters [3].

Human urine is mainly composed of water with an average of 96%, in volume. In its composition are also present: urea, uric acid, salts and other substances, mainly the body metabolic processes [4].
The urine volume eliminated by average people ranges between 1 and 2 L per day, depending on both dietary habits and hormonal balance. The urine eliminated by healthy people has a very characteristic odor, i.e., it is easily recognizable: the cause has not been well determined yet. With the passage of time, at rest, urine begins to show strong ammonia smell, resulting from bacterial hydrolysis of urea generating ammonia [4].

As a prospective case study, habits and customs of some citizens of the city of Jundiaí, SP, were informally evaluated. It was observed that, in an average family of five, where each adult ejects about 2 L of urine per day (four times on average), and each discharge, based on economic toilet models, consuming 6 L of water, each person uses, on average, 24 L of water per day.
Then, a family of five people will use 120 liters of water per day, L 3.600 per month, L 43.200 per year, only with discharges of urine. According to collection rates of the company responsible for the water and sewer service in Jundiaí, SP, in 2013, the cost of residential tariff is R$ 2.39 per cubic meter [5]. Data from the Brazilian Institute of Geography and Statistics, IBGE, indicate that the Brazilian family consisted of 3.1 people in 2009.

The reduction of a discharge (function) per person / per day in a family with 3 [6], would result in savings of about 24 L per day or 8.640 L of water per year. The impact would be very significant for a family, stimulating when addressing the Brazilian population and strategic for public planning. The use of NaDCC as a sanitizer becomes interesting due to its well-known effectiveness in reducing microbial population, as presented in the literature [7,8,9]. As a solution, a fraction of NaDCC will generate free chlorine, according to reactions presented. There is also the formation of mono or combined dichlorocanurate due to incomplete reactions of the remaining fraction. The reactions of chlorine are very favorable in the oxidation of micro-organisms, organic materials or nitrogenous and release the hypochlorous acid, which tends to stabilize the equilibrium to compensate for the loss of free chlorine consumption [8].

The active NaDCC principle, Figure 1 is acidic, therefore tends to lower the initial pH of the water, unlike hypochlorite, which is alkaline and tends to increase the water pH.

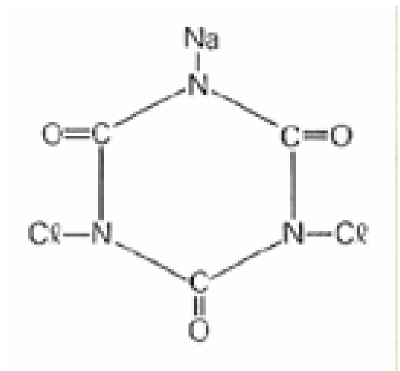


Figure 1: Sodium dichloroisocyanurate ($C_3Cl_2N_3NaO_3$)

In the NaDCC hydrolysis reaction, the cyanuric ring is shown in the reactions of CA as 1 - 4.

$$Cl_2CA^- + OH^- \leftrightarrow HClCA^- + OCl^- \quad (1)$$

Cl_2CA^- = dichlorocyanurate
OH^- = hidroxyl water
$HClCA^-$ = monochlorocyanurate
OCl^- = hypochlorite

$$HClCA^- + OH^- \leftrightarrow H_2CA^- + OCl^- \quad (2)$$

$HClCA^-$ = monoclorocianurato
OH^- = = hidroxyl water
H_2CA^- = cyanurate
OCl^- = hypochlorite

$$HOCl \leftrightarrow H^+ + OCl^- \quad (3)$$

$HOCl$ = hypochlorous acid
H^+ = hidrogen
OCl^- = hypochlorite

$$H_3CA \leftrightarrow H^+ + H_2CA^- \quad (4)$$

H_3CA = cyanuric acid
H^+ = hidrogen
H_2CA^- = cyanurate

As a solution, a fraction of NaDCC will generate free chlorine reactions, as presented. There is also the formation of mono or combined dichlorocanurate due to incomplete reactions of the remaining fraction. The reactions of chlorine are very favorable in the oxidation of micro-organisms or nitrogenous organic materials, releasing the hypochlorous acid, which tends to stabilize the equilibrium and compensate for the loss of free chlorine consumption [8]. The HClO and ClO^- are called free residual chlorine (CRL) [9].

Thus, from the perspective of treating urine with Sodium dichloroisocyanurate, NaDCC, the reaction of free residual chlorine (CRL) will, inevitably, occur with the fraction of ammonia derived from the hydrolysis of urea present in the urine. Chlorine in the form of hypochlorous acid reacts with the ammonia present in the water to form monochloramines, dichloramines and nitrogen trichloride.

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \text{ (monochloramine)} \quad (5)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \text{ (dichloramine)} \quad (6)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \text{ (trichloramine)} \quad (7)$$

On a scale of disinfecting power, there is, in descending order: chlorine dioxide (ClO_2), hypochlorous acid, hypochlorite ion, dichloramine, monochloramine and nitrogen trichloride, with a disinfecting power virtually nil.

As a whole, chloramines destruction may be represented by the excess of chlorine by the simplified reaction:

$$2NH_3 + 3Cl_2 \leftrightarrow N_2 + 6HCl \quad (8)$$

2. OBJECTIVE

This study objective is developing a chemical treatment of the urine, directly into the toilet bowl, with the elimination or minimization of the repulsive aspects of water after urination and, consequently reducing the consumption of water discharges, with the lowest possible impact on sewage treatment systems.

3. MATERIAL & METHOD

3.1. General characterization of the samples to be treated

The solution of urine that remains in the toilet after urination is the object of this work; therefore, it is necessary to know some of its physical and chemical characteristics. The tests presented in table 3, as a result, were performed in the laboratory of the company FOCO AMBIENTAL Ltda. Only color and COD parameters were carried out in an external laboratory (ACQUALAB Ltda - Jundiaí).

3.2. Statistical Data Treatment

The statistical analysis was applied in function of the process and phase of the work. In general, the development of the work consisted of:

1 - Using the NaDCC (sodium dichloro isocyanurate) as "active principle";
2 - Formulating a mixture of different secondary components, associated to NaDCC, based on bench tests performed;
3 - Applying it, initially, in the form of powder for subsequent compaction of a sanitizing tablet;
4 - Evaluating the efficiency of the product in relation to the most significant parameters, such as, general appearance (color, odor, foaming, presence of precipitate), physico-chemical, organic and microbiological results.
5 - Studying the behavior of the "active ingredient" as to its necessary function, i.e., eliminating or minimizing the repulsive aspects of urine in the toilet.

Thus, in the first four steps, a very interesting statistic tool to be applied is the Factorial Planning of Experiments [10,11,12] to optimize the product performance of. This tool improves the process comprehension, establishes the optimal conditions of work and defines safe limits (limits which allow the process to be conducted yielding the same or compatible results - Robustness) for the parameters studied.

This tool is based on the statistical variation of simultaneous multiple process parameters. For the present study, the following parameters for the development of the formulation may be exemplified : 1) NaDCC content, 2) Sodium Bicarbonate content, 3) Drying agent, 4) Essence, 5) Dye, 6) Antifoam; 7) Mass of product applied; 8) Volume of water in the toilet; 9) Overall volume of urine; 10) Urea concentration.

This tool can be applied more than once in sequence, considering both the fundamentals of multivariate statistical tools as the PDCA cycle.

For example, when there are 7 parameters to be studied, it is possible to perform simultaneous variation of all of them and combine them into a set of eight experiments (fractional saturated planning)

3.3. Optimization of the formulation - Planning Factorial (Factorial Design)

In this plan, we evaluated the importance of each component to eliminate the ammonia concentration in the solution. As previously mentioned, the main product is the Sodium Dichloroisocyanurate, NaDCC, but several substances were tested in combination with this compound, to improve the efficiency of the final product.

3.4. Production of sanitizing tablet

In order to evaluate the compression possibility of the principal component in association with other components of secondary action, the product NaDCC was pressed and mixed with various compounds with binding functions; among them, soluble starch presented the best answer.

The force applied to press the mixture of NaDCC 60% and starch 40% was 20 tons. The pellet obtained, illustrated in Figure 2, was easily demoulded and showed excellent compression, with consistency similar to the sparkling tablets available in the market.

Figure 2: Tablets produced with NaDCC in combination with adjuvant agents

4. RESULTS & DISCUSSION

1.1. General analysis of urine

To the knowledge of a possible difference in the values of the tests, samples (first urine of the day) of 4 healthy individuals and from different age groups were requested.

Table 1: Results of diluted urine solution analyses

General analyses of human diluted urine (4 times)				
Parameter	**Man**	**Woman**	**Child**	**Elderly**
pH	6.4	6.6	6.8	6.1
Color(mg/L Pt/Co)	850	750	820	910
Density (g/L)	1.002	1.000	1.002	1.004
Ammonia (mg/L NH_3)	272	184	197	296
N-Ammoniacal (mg/L N)	223	151	162	243
Turbidity (UNT)	45.5	22.5	35	52
DQO (mg/L O_2)	1795	998	1800	2105
Visual Aspect	Limpid	Limpid	Limpid	Limpid

The results in Table 1 show that there is not much discrepancy in relation to age. The differences are possibly due to habits or to each individual metabolism.

4.2. Evaluation of ammonia concentration

The ammonia content of the solution is an important parameter in this evaluation due to the urine characteristic odor, thus this result was initially chosen as an example in this paper.

	Factor	**(-1)** *Nominal*	**(+1)** *Variation*
1	**NaDCC, g**	**0.45**	**1**
2	**NaHCO3, g**	**0**	**0.5**
3	**Starch, g**	**0**	**0.5**
4	**Essence, g**	**0**	**0.25**
5	**Dye, g**	**0.005**	**0.009**
6	**Antifoam, g**	**0**	**0.12**
7	**Mass adition, g**	**0.025**	**0.05**

Combination of each assay

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1	1	1	1	1	-1	-1	-1	-1
2	1	1	-1	-1	1	1	-1	-1
3	1	-1	1	-1	1	-1	1	-1
4	1	1	-1	-1	-1	-1	1	1
5	1	-1	1	-1	-1	1	-1	1
6	1	-1	-1	1	1	-1	-1	1
7	1	-1	-1	1	-1	1	1	-1
Results	**114.05**	**109.24**	**114.03**	**119.53**	**123.50**	**111.10**	**122.07**	**121.29**

Results mean **117**

Standard deviation of Results **5**

Test for verifying effects significance

Reference: Vander Heyden. and coll.. *J. Pharm. Biomed. Anal.* 24(2001) 723-753.

Calculations to obtain ME and SME values are based on Dong algorithm

Factor	Effects	Orderings Effects	Effects Absolute	Planning Absolute	Square of the Ordenamento Absolute	Order					Rankit	Ordenamento Effects Absolute		
1	-5.28	-5.28	5.28	0.33	0.11	1	0.07143	-1.4652	0	0.54	0.09	0.33	5.973	9.43637
2	-4.76	-4.76	4.76	0.38	0.14	2	0.21429	-0.7916	0	0.61	0.27	0.38		
3	3.12	-3.47	3.7	3.12	9.75	3	0.35714	-0.3661	3	0.68	0.46	3.12		
4	-0.38	-0.38	0.38	3.47	12.02	4	0.5	0	3	0.75	0.67	3.47		
5	-3.47	-0.33	0.33	4.76	22.63	5	0.64286	0.36611	5	0.82	0.92	4.76		
6	5.48	3.12	3.12	5.28	27.85	6	0.78571	0.79164	5	0.89	1.24	5.28		
7	-0.33	5.48	5.48	5.48	30.06	7	0.92857	1.46523	5	0.96	1.80	5.48	5.973	9.43637
average	-0.80				102.57			median	3.4675					
								s_o	5.20	m	7	IC, %	95	
standard error	3.83							$2.5*s_o$	13.00	ME	5.97253	α	0,05	
								s_1	2.52579	SME	9.43637	?*	0.007	

Figure 3: Test for verifying effects significance. Results are the values of the measurement answers (ammonia concentration in mg/L).

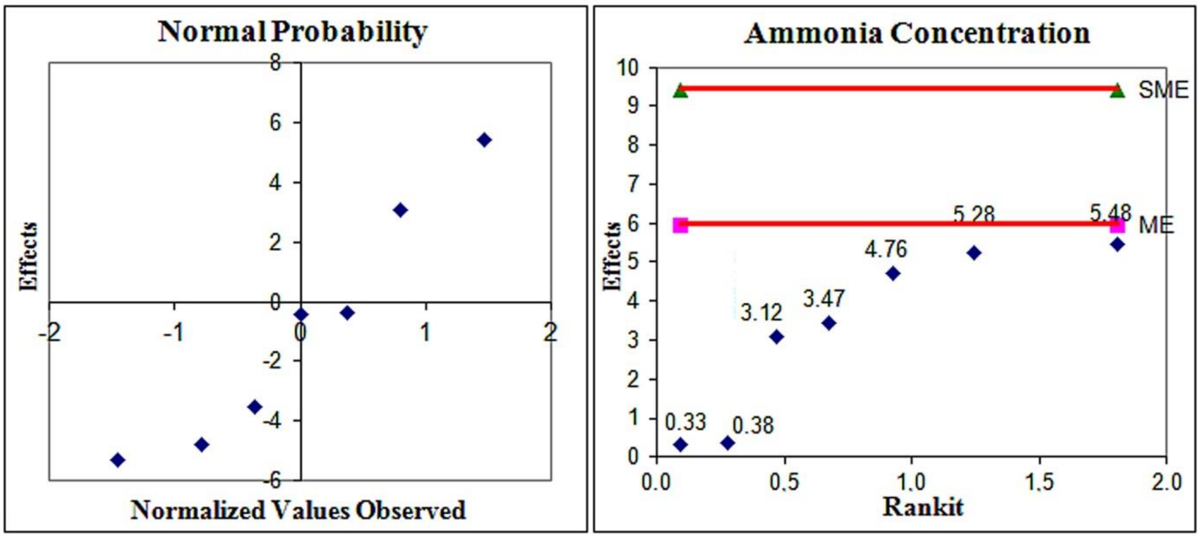


Figure 4: Graphs of normal probability and of Rankit for ammonia concentration.

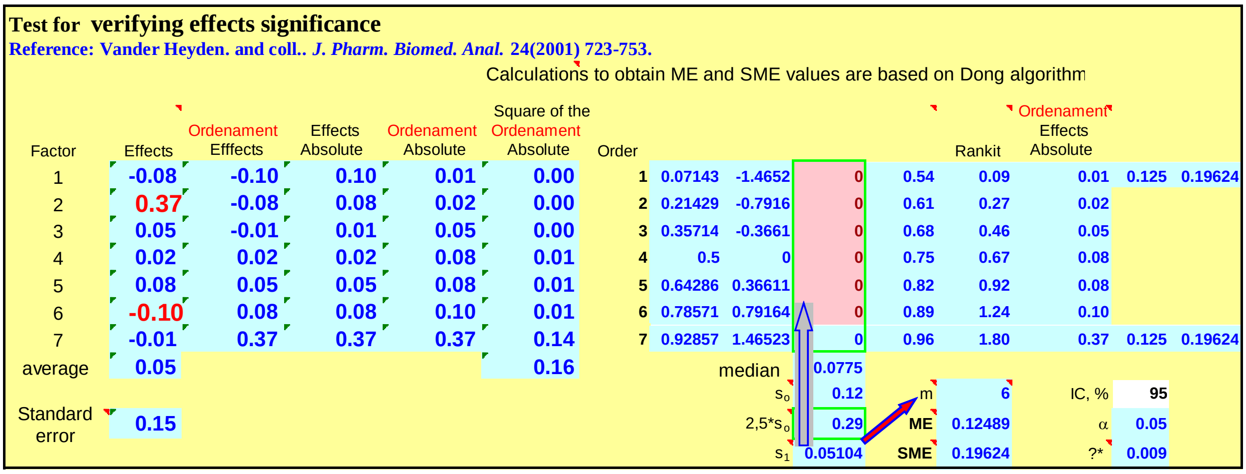
According figures 3 and 4, the parameters "NaDCC" and "Antifoam" are the most sensitive or significant in the process and the studied conditions are not optimized. By increasing the mass of NaDCC 0.45 to 1.0 g, the ammonia concentration decreases; the addition of antifoam agent contributes to the (non-) decreased concentration of ammonia.
The results of the characterization tests in Table 5 demonstrate the antifoam interference on the reduction of ammonia.

All other points are below this limit; the factor 1, referring to NaDCC, is the one with less effect (-5.28), then, it is the factor that decreases the concentration of ammonium; Thus, $NaHCO_3$ is also a factor that contributes to decrease the concentration of ammonium. Starch contributes to the lack of decrease in the concentration of ammonium, as well.

4.2.2. Evaluation of pH alteration

Using the same procedure, measuring the pH in each essay, the results were:

	Combination of each assay							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1	1	1	1	1	-1	-1	-1	-1
2	1	1	-1	-1	1	1	-1	-1
3	1	-1	1	-1	1	-1	1	-1
4	1	1	-1	-1	-1	-1	1	1
5	1	-1	1	-1	-1	1	-1	1
6	1	-1	-1	1	1	-1	-1	1
7	1	-1	-1	1	-1	1	1	-1
Result	**6.29**	**6.27**	**6.01**	**5.77**	**6.27**	**6.40**	**6.02**	**5.96**
Average of results			**6**					
Standard deviation of results			**0**					


Test for verifying effects significance

Reference: Vander Heyden. and coll.. *J. Pharm. Biomed. Anal.* 24(2001) 723-753.

Calculations to obtain ME and SME values are based on Dong algorithm

Factor	Effects	Ordenament Efffects	Effects Absolute	Ordenament Absolute	Square of the Ordenament Absolute	Order					Rankit	Ordenament Effects Absolute		
1	-0.08	-0.10	0.10	0.01	0.00	1	0.07143	-1.4652	0	0.54	0.09	0.01	0.125	0.19624
2	0.37	-0.08	0.08	0.02	0.00	2	0.21429	-0.7916	0	0.61	0.27	0.02		
3	0.05	-0.01	0.01	0.05	0.00	3	0.35714	-0.3661	0	0.68	0.46	0.05		
4	0.02	0.02	0.02	0.08	0.01	4	0.5	0	0	0.75	0.67	0.08		
5	0.08	0.05	0.05	0.08	0.01	5	0.64286	0.36611	0	0.82	0.92	0.08		
6	-0.10	0.08	0.08	0.10	0.01	6	0.78571	0.79164	0	0.89	1.24	0.10		
7	-0.01	0.37	0.37	0.37	0.14	7	0.92857	1.46523	0	0.96	1.80	0.37	0.125	0.19624
average	0.05				0.16			median	0.0775					
								s_o	0.12	m	6	IC, %	95	
Standard error	0.15							$2,5*s_o$	0.29	ME	0.12489	α	0.05	
								s_1	0.05104	SME	0.19624	?*	0.009	

Figure 5: Test to verify the significance of the effects for pH. Results are the answer values of the measurements (pH of means).

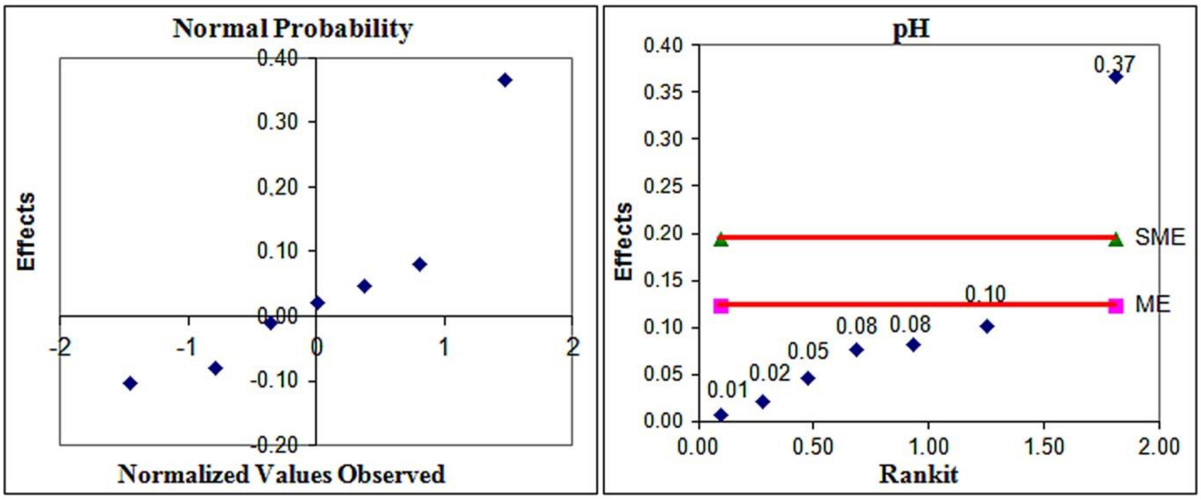


Figure 6: Graphs of normal probability and of Rankit for pH.

In the case of pH, the environmental legislation establishes the disposal of the effluent in a range between 6 and 9, so the combinations of factors should conduct the system to this range.

It was observed that factor 2 is more sensitive to this process and the $NaHCO_3$ mass is an agent with positive influence to increase the pH, since the point (0.37), related to this factor, is well above the ME limit (Figure 6).

The least significant factor in the change of pH is the addition mass (factor 7), for the point (0.1). The other factors did not have a significant role on the pH. Therefore, the pH adjustment may be performed only with the addition of $NaHCO_3$.
In Figure 7, the eight samples of urine solution, 5 minutes after addition of the products, can be observed.

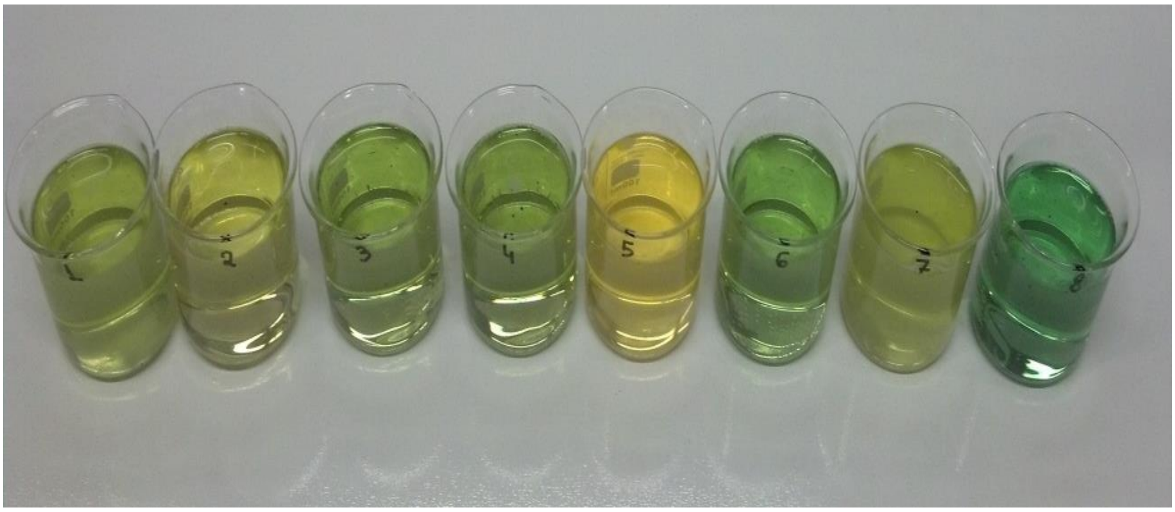


Figure 7: Evaluation after 5 minutes from addition of masses.

After 10 minutes, the contents of the beakers were transferred to Nesler tubes, for better observation, Figure 8. A pipe, identified with the letter C, refers to undiluted urine, in this case called: control.

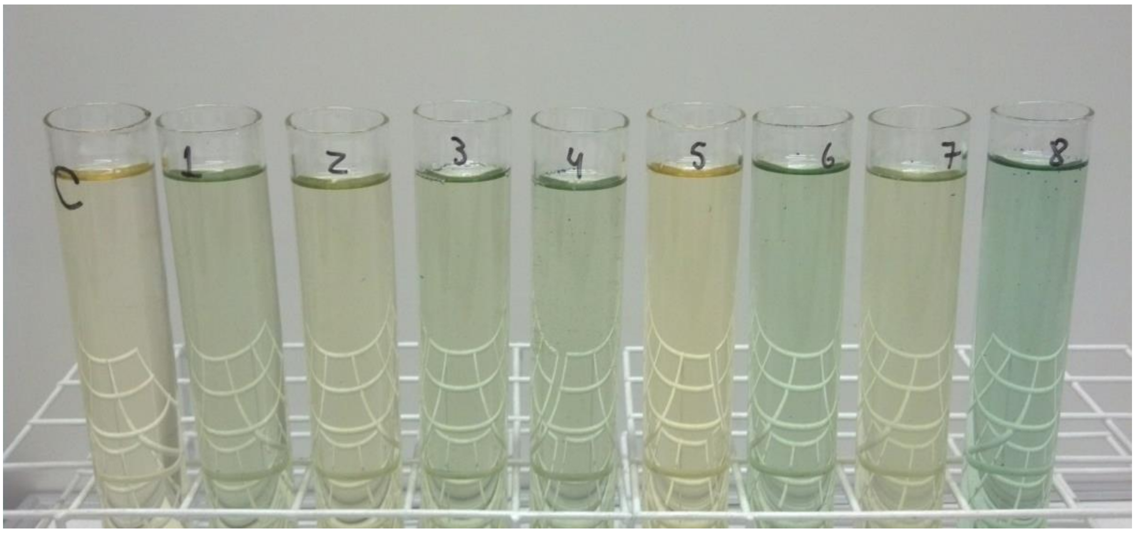


Figure 8: Evaluation in Nesler tubes, after addition of masses.

4.2.3. Development of formulation.

To evaluate the efficiency of the urine treatment method, some tests with 6 different formulations were performed, as shown in Table 2.

Table 2: Combinations of the main component, NaDCC, with adjuvant agents

Components	FM 1	FM 2	FM 3	FM 4	FM 5	FM6
NaDCC	1.00g	1.00g	0.50g	1.00g	1.0g	0.50g
$NaHCO_3$	-	0.50g	1.0g	-	0.50g	1.00g
Starch	-	-	-	0.60g	0.60g	0.60g
Essence	-	-	-	0.10g	0.10g	0.10g
Green Dye	0.01g	0.01g	0.01g	0.01g	0.01g	0.01g
Antifoam	-	-	-	0.10g	0.10g	0.10g
Total	1.01g	1.51g	1.51g	1.81g	2.31g	2.31g

In each combination, sensorial aspects (smell and color) and other important physical and chemical parameters were verified, Table 3.

Table 3: Test results for the 6 formulations and crude sample (diluted urine).

Parameter	Unity	Bruta	FM 1	FM 2	FM 3	FM 4	FM 5	FM 6
Ammonia	mg/L de NH_3	272.00	119.50	136.50	153.00	170.20	187.80	189.80
N-Ammoniacal	mg/L de N	223.04	97.99	111.93	125.46	139.56	154.00	155.64
Total chloramines	mg/L	< 0.1	7.40	1.40	0.30	1.50	0.60	0.10
Monochloroamine	mg/L de Cl	< 0.01	0.59	0.19	0.09	< 0.01	< 0.01	0.09
Color	mg/L de PtCo	850	304	325	303	506	401	418
Turbidity	UNT	45.5	2.8	3.0	2.9	68.7	41.7	43.0
pH	-	6.4	5.9	6.5	6.8	6.1	6.4	6.8
Free	mg/L de Cl	< 0.01	0.00	0.00	< 0.01	0.00	0.00	< 0.01
Total chorine	mg/L de Cl	< 0.01	7.4	1.4	0.30	1.50	0.60	0.10
Benzene	ug/L	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Toluene	ug/L	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Calcium	mg/L de Ca	71.37	51.67	66.81	77.67	74.59	76.33	83.51
Sodium	mg/L de Na	716.93	568.26	923.22	904.33	1172.77	997.52	1125.22
DQO	mg/L de O_2	1795	2035	1970	1950	2180	2020	2150

The figure 9 shows the evaluation in beakers immediately after addition of the masses.

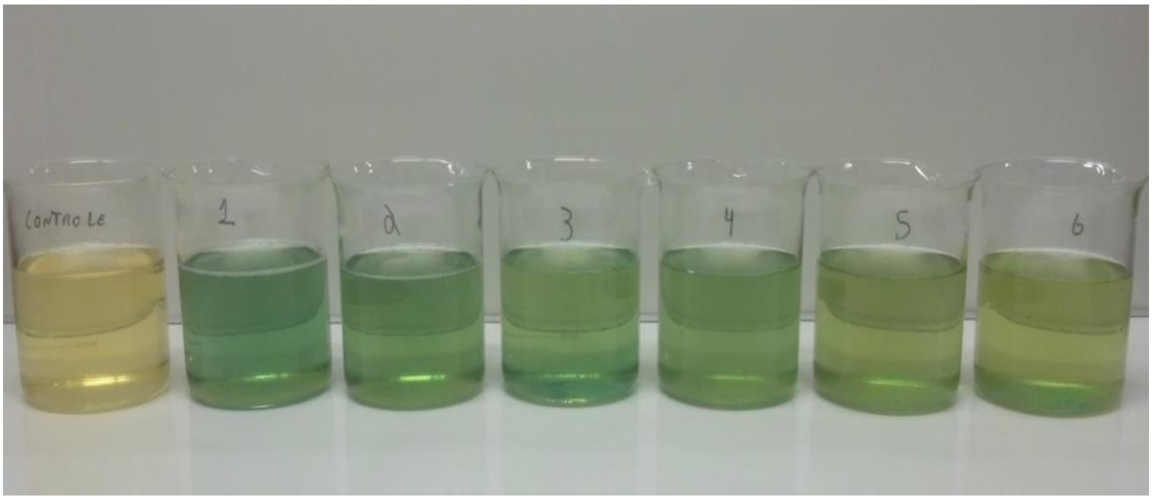


Figure 9: Evaluation of beakers immediately after addition of the masses.

5. CONCLUSION

The results show that Sodium Dichloroisocyanurate, NaDCC, is effective for the treatment of human urine in toilets.

The literature supports the findings that this substance can promote an improvement in the water quality, in a system containing pathogens: also, the same is approved by leading environmental agencies and health. Microbiological tests will be performed to prove this assertion.

The Factorial planning carried out indicated that the results of ammonia concentrations are greatly influenced by the presence of NaDCC, what was expected; however, it was observed that some adjuvant agents in the formula, such as defoamers, contribute to this concentration not to decrease, what is a downside to the process. Thus, an optimum combination of the formulation is important in order to have a composition with a lower presence of this component.

Likewise, it was observed in the pH test, that the presence of $NaHCO_3$ is the most significant component to change the pH of the medium, and some other factors represents insignificant influence this process. Under the perspective to frame the pH medium in the range between 6 and 9, indicated in Decreto Estadual Paulista (Art. 19A) [13], it is possible to optimize the formulation in order to adequate it to the final effluent.

Using this same planning, further tests may be performed to obtain other important results, such as: color, turbidity, residual chlorine, chloramines and Total monochloroamines, BOD, faecal coliform, benzene and toluene.

All tests were conducted with the product in powder form. In future theses, it will be considered, also, in a comparative way, analyzes of the product tablet- shaped product, similar to some products available in the market, with different uses.

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