

QUANTIFICATIONS OF SOME IONS IN NATURAL MUD AND IN ARTIFICIAL MINERAL MUD PRODUCED BY MINERAL WATER OF NINH HOA

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Abstract

Minerals play an important role in the human body and can be absorbed through the skin in the form of a mud soak. 2 batches of artificial mud are produced using mineral water and natural mud from Ninh Hoa. 1st Batch: natural mud dipped in mineral water. 2nd batch: soak natural mud dipped in mineral water, adding water cabbage (*pistia stratiotes*) above the surface. Time: 2 months in sunlight. Ratio of mud and mineral water: 1:1. Results: % (m/m) Cl⁻, SO₃, Fe₂O₃, loss of contents when increasing of the ignition, content (mg/kg) Arsenic (As) decrease from 1st Batch to 2nd batch of mud.

1. Background

Minerals have a very important role in the human body, especially in maintaining the development of teeth, bones, muscles and the functions of the nervous system, minerals can supplement the body in the form of minerals. Absorbed through the skin from mineral water and mineral mud by soaking, bathing. In recent years, a number of hot mineral centers have launched mineral mud therapies in the treatment and rehabilitation of some chronic bone and joint diseases, osteoarthritis, especially knee joints. In a study Clinical statistics in

Key words: mineral mud, artificial mud, *Pistia stratiote*.

Italy have shown that mud bath therapy at Chianciano Spa improves the condition and reduces the severity of osteoarthritis patients[1]. From the benefits brought to patients in bathing in mud and mineral water, we have produced artificial mineral mud from Ninh Hoa mineral water source, Khanh Hoa province, thereby applying therapeutic support to people with how to soak in mineral mud.

2. Materials and Artificial mineral Mud Productions

2.1 Materials

Mineral water and natural mud are taken in Ninh Da Ward, Ninh Hoa Town, Khanh Hoa Province.

2.2 Artificial mineral Mud Productions

Natural mud is dried in the sun, then finely ground and sieved through a sieve with a hole diameter of 1mm to remove grit, stones and other components with irritation greater than 1mm. Divided into 2 batches, proceed to soak natural mud and mineral water into a rectangular tank with a volume of 20 litres, the ratio of natural mud and mineral water 1:1 [1], mark the water line, add mineral water to the mark when the water is evaporated during immersion as follows:

1st Batch: 5 kg of natural mud are soaked in 5 liters of mineral water, soaking time for 60 days, in the sunlight.

2nd Batch: procedure is same the 1st batch but adding 10 g of water cabbage (scientific name: *Pistia stratiotes*) to reduce the amount of heavy metals in mud and mineral water such as Arsenic, Hg, Cd [10].

The artificial mud in 1st batch and 2nd batch are drained, the changes of the ions mass of the artificial mud are checked and compared with the natural mud.

2.2.1 Determination of chloride content (Cl-) [3]

Principle

Method of Charpentier Volhard. Calculation

$$\%Cl = \frac{(V_0 - V_1) \times 0,0008865}{m} \times 100$$

V_0 (ml): the volume of 0.025 N ammonium sulfocyanide standard solution (the blank).

V_1 (ml): the volume of 0.025 N ammonium sulfocyanide standard solution (test sample).

m (g): weight of test sample
 0.0008865 (g): mass of Cl⁻ corresponds to 1ml of 0.025 N NH₄SCN solution.
 the difference between two parallel determination results is not more than 0.05%.

2.2.2. Determination of sulfur trioxide content (SO₃) [3]

Principle

Melt the test sample with a mixture of alkaline carbonate and then dissolve in dilute HCl solution, all the sulfate present in the test sample will dissolve into the solution, determine the content of sulfate in this solution.

Separation of the influencing elements present in the solution. Then proceed to precipitate sulfate in the form of BaSO₄ in acidic medium. Heat the precipitate at 850 °C from which to calculate the SO₃ content in the test sample.

Calculation

$$\%SO_3 = \frac{0,343(m_2 - m_1)}{m} \times 100$$

m_2 (g): the mass of the crucible and precipitate.

m_1 (g): the mass of the crucible.

m (g): the weight of the test sample 0.343: the conversion factor from BaSO₄ to SO₃.

2.2.3. Determination of loss on ignition [3]

Principle

The test sample is heated at 1000 °C ± 50 °C to constant mass. From the decrease in mass of the test piece, calculate the loss on heating.

Calculation

Determination of loss on ignition (LOI), expressed as a percentage using the formula

$$\%LOI = \frac{m_1 - m_2}{m} \times 100$$

m_1 (g) is the mass of the crucible and sample before heating.

m_2 (g) is the mass of the crucible and sample after heating.

m (g) is the weight of the test sample.

2.2.4. - Determination of silicon dioxide content (SiO₂) [3]

Principle

Evaporate the sample solution to dehydrate the silicic acid. Heat the precipitate at 1000 °C ± 50°C. Then treat the precipitate with hydrofluoric acid solution to separate silicon in the form of silicon tetrafluoride, thereby determining the amount of silicon dioxide (mainly) present in the test sample.

2.2.5 - Determination of iron oxide content (Fe₂O₃) [3]

Principle

Titrate iron(III) with EDTA solution at pH = 1.5 to 2 with sulfosalisilic acid indicator.

At the end of the titration, the color of the solution changed from purple-red to straw yellow.

Calculation

$$\%Fe_2O_3 = \frac{(0.0007985 \times V \times K_1) \times 500}{(m \times 25)} \times 100$$

0.0007985 (g) is the mass of Fe_2O_3 corresponding to 1 ml of 0.01 M EDTA solution.

V (ml) is the volume, of the 0.01 M EDTA standard solution consumed during the titration

K_1 is the concentration coefficient of 0.01 M EDTA solution;

m (g) is the weight of the test sample.

The difference between two parallel determination results is not more than 0,20 %.

2.2.6 - Determination of arsenic [4]

Principle

Arsenic, antimony and selenium are extracted from soil samples with aqua regia.

Arsenic is determined by the hydride-generation technique (HGAAS). Arsenic and antimony are first pre-reduced in the aqua regia extract by a mixture of ascorbic acid and potassium iodide. After that, the hydride formation occurs by reaction with a sodium borohydride solution. The hydrides are carried from the solution by an argon stream into a heated quartz cell and decomposed at 900 °C and then the atom concentration for arsenic is measured by atomic absorption spectrometry.

Calculation

$$w(E) = \frac{(p_1 - p_0)}{m} f \frac{V}{1000} C$$

$w(E)$ (mg/kg): the mass fraction of the element in the sample, dry matter.

p_1 ($\mu g/l$): the arsenic concentration corresponding to the absorbance of the test portion.

p_0 ($\mu g/l$): the concentration of arsenic corresponding to the absorbance of the blank;

f : the dilution factor of the test portion (if the test portion is diluted);

V (ml): the volume of the test portion used for analysis;

M (g): the mass of the sample taken;

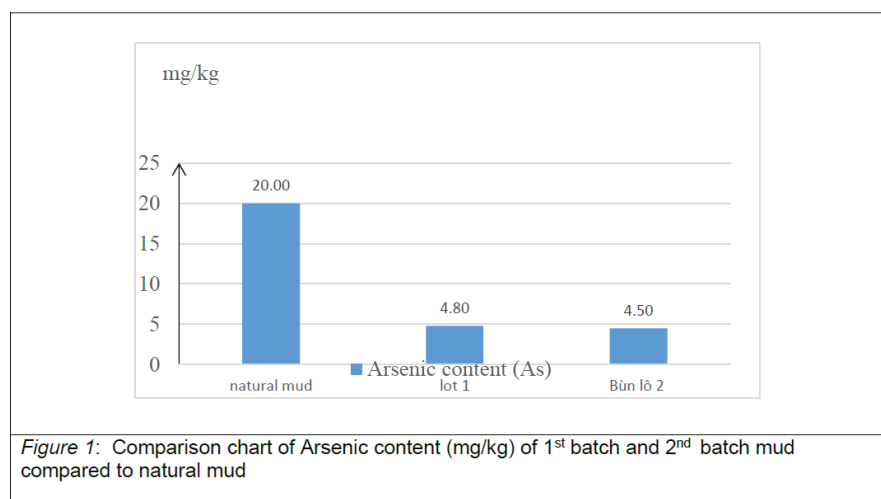
C : the correction factor for dry soil samples: $C = 100/Wdm$;

Wdm is the dry matter content of the soil, expressed as a percentage.

3. Results

Table 1. Parameters of natural and artificial mud measured at quality assurance and testing center 3 (Quatest 3)

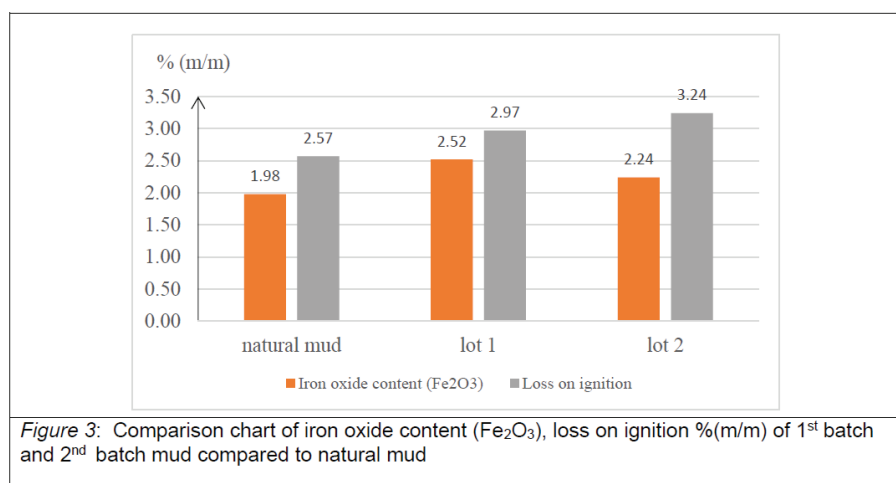
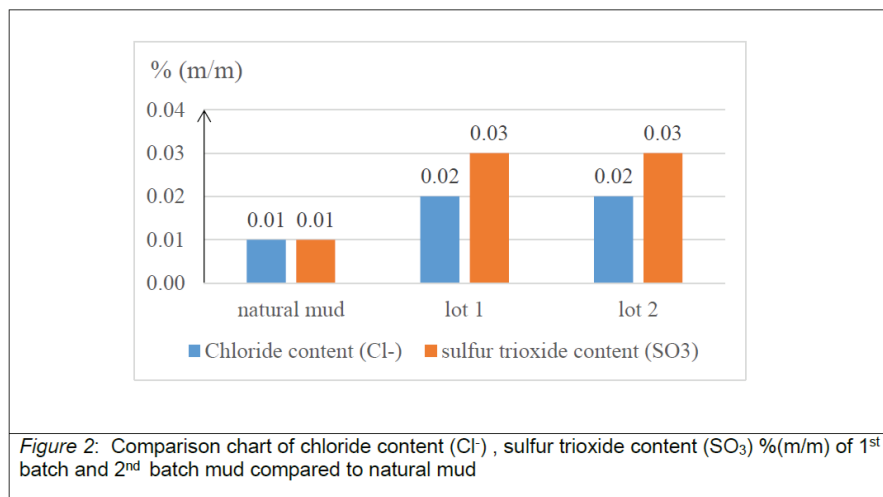
No.	Characteristic	Unit	Test method	Test result natural mud	Test result of 1 st batch	Test result of 2 nd batch
1	Arsenic content (As)	mg/ kg	HG-AAS	20,00	4,80	4,50
2	Chloride content (Cl ⁻)	% (m/m)	TCVN 7131: 2002	0,01	0,02	0,02
3	sulfur trioxide content (SO ₃)	% (m/m)	TCVN 7131: 2002	0,01	0,03	0,03
4	Iron oxide content (Fe ₂ O ₃)	% (m/m)	TCVN 7131: 2002	1,98	2,52	2,24
5	Loss on ignition	% (m/m)	TCVN 7131: 2002	2,57	2,97	3,24
6	Silicon dioxide content (SiO ₂)	% (m/m)	TCVN 7131: 2002	70,9	66,1	66,2



4. Discussion

Arsenic content (As).

Arsenic is a neurotoxic metal, causing adverse effects on brain development [5], can be absorbed through the skin during mud soaking, so the artificial mud in 1st batch and 2nd batch is significantly reduced arsenic content is an advantage, in which the amount of Arsenic mud in 2nd batch decreases better



	1 st batch mud	2 nd batch mud
Arsenic content	reduced: 15.2 (mg/kg).	reduced: 15.25 (mg/kg).
Cl⁻, SO₃, Fe₂O₃, Loss on ignition content	increased: 0.01; 0.02; 0.54; 0.4 % (m/m).	increased: 0.01; 0.02; 0.26; 0.67 %(m/m).
SiO₂ content	1 st batch decreased	2 nd batch decreased

than that 1st batch because there is a water cabbage to help absorb heavy metals [2].

Cl⁻, SO₃, Fe₂O₃, Loss on ignition content.

Cl⁻, SO₃ in the 1st batch and the 2nd batch increased equally, Fe₂O₃ in the 1st batch increased more than the 2nd batch, loss on ignition in the 1st batch increased less than that of the 2nd batch.

S²⁺ : is a component of antioxidant molecules in the body such as glutathione, thioredoxin, glutathione reductase. [6]

Cl⁻ : role in regulating body fluids, balancing electrolytes, maintaining electrical neutrality. [7]

Fe³⁺ : Necessary for hemoglobin synthesis and oxygen transport, cognitive development, immune system and working ability [8].

Loss on ignition: Estimated organic matter, CaCO₃ content in mud.

SiO₂ content

Compared with natural sludge, the SiO₂ content of the 1st batch and the 2nd batch decreased, due to the exchange of components in the mud with mineral water.

SiO₂: The highest concentration of silicon is found in skin, hair, and nails. Silicon is part of collagen (the main protein of connective tissue in the human body), ensuring the alignment of collagen and elastin fibers, thus giving strength, strength and elasticity of connective tissue.[9]

In Iceland in 1992, a study on 27 psoriasis patients bathed at Blue Lagoon three times a day for one hour at a time for three weeks with the main chemical composition SiO₂, Cl⁻, Na⁺, Ca²⁺, K⁺ resulted in reduced erythema and infiltrates in patients with psoriasis [10]. Another study in patients with osteoarthritis of the knee showed that bathing in hot sulfuric water was effective in reducing pain and improving function in patients [11].

Thereby, we see that compared with natural mud, with high SiO₂ content and increasing Cl⁻ content in mud 1st batch and 2nd batch, there are many prospects for human therapy.

5. Conclusion

After selecting natural mud and mineral water in Ninh Hoa town, Khanh Hoa province for trial production of 2 batches of artificial mineral mud by the method of immersing the mud in mineral water with additional water cabbage, the results show that:

- Arsenic content decreased in artificial mud batches: these heavy metals are not good for human health, in which the mud in the 2nd batch with additional water cabbage decreased more than in batch 1 without water cabbage.

- The content of Cl⁻, SO₃, Fe₂O₃ both increased, due to the change in ion exchange of mineral water and mud, in which the increased content of Fe₂O₃ in 2nd batch was lower than that of 1st batch because water cabbage reduces metal heavy species in water such as Fe [2].

- Loss on ignition increased in both 1st batch and 2nd batch, due to the change in the composition of the slurry during immersion with mineral water.

- SiO₂ content in 2 batches of artificial mineral compensation decreased compared to natural mud.

Therefore, the topic has many prospects for development on a larger scale in order to create a mineral supply for human health.

References

- [1] A Traioli, A Serio, G Mennuni, F Ceccarelli, L petraccia, J Campanella, M Fontana, S Nocchi, G Tanzi, M Grasi, G Valesini, (2009), *Efficacy of mud - bath therapy with mineral water from the sillene spring at Italy's Chianciano Spa for osteoarthritis of the knee a clinical statistical study*, *Laclinica terapeutica*, 160(6): e63-74.
- [2] Kenrick Berend, Leonard Hendrikvan Hulsteijn, Rijk O B gans, (2012), *Chloride: the queen of electrolytes*, *European journal of internal medicine*, **23**(3), 203-11.
- [3] P. Tripathi, R.Kumar, Ak sharma, A. Mishra, R. Gupta, (2010), *Pistia stratiotes (Talkumbhi)*, *Pharmacognosy review* 4(8):153-160.
- [4] TCVN 7131 : 2002,(2002), *Clays - methods of chemical analysis*.
- [5] TCVN 8467 : 2010,(2010), *Chất lượng đất - xác định asen, antimon và selen trong dịch chiết đất cứng thủy bằng phương pháp phổ hấp thụ nguyên tử theo kỹ thuật nhiệt điện hoặc tạo tủa hyrua*.
- [6] Meng Wang, Farhana Hossain, Rosalind Sulaiman Xuefeng Ren, (2019), *Exposure to inorganic arsenic and lead and autism spectrum disorder in children*, *A systematic review and meta - analysis*, **32** (10): 1904 - 1919.
- [7] Emmanuel mukwevho, Zane Ferreira, Ademola Ayeleso, (2014), *Potential role of sulfur - containing antioxidant systems in highly oxidative environments*, *Molecules*, **19**(12), 19376 - 19389.
- [8] Katrin Kbatchz, wobbeke Weistenhofer, Frauke Neff, (2017), *The health effects of aluminum exposure*, *Deutsches Arzteblatt International*, 114: 653 - 659.
- [9] Nazanin Abbaspour, Richard Hurrell, Yoya Kelishadi, (2014), *Review on iron and its importance for human health*, *Journal of research in medical sciences*, **19**, 164 - 74.
- [10] L. Churadze, V. Chagelishvili, M. Kakhetelidze, P. Iavich, L. Mskhiladze, (2021), *Study of the possibility of using silicon dioxide, obtained from metal mananese production waste, in the production of cosmetic creams and ointments*, *Georgian medical News*, 314 : 166 - 171.

- [11] Sara Cacciapuoti, Maria A Luciano, Matteo Megna, Maria C Annunziata, Maddalena Napolitano, Cataldo Patruno, Emanuele Scala, Roberta Colicchio, Chiara Pagliuca, Paola Salvatore, Gabriella Fabbrocini, (2020), *The role of thermal water in chronic skin diseases management: A review of the literature*, Journal of clinical medicine,9,3047.
- [12] Marcelo Branco, Neiva N Reego, Paulo H Silva, Ingrid F Trevisani, (2016), *Bath thermal waters in the treatment of knee osteoarthritis a randomized controlled clinical trial*, European J. of physical and rehabilitation medicine, **52**(4):422-30.