

DETERMINATION OF MINERAL ELEMENTS AND TRACES PRESENT IN THE FRACTIONS OF THE HUMIC SUBSTANCES OF PERUÍBE BLACK MUD

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ABSTRACT

Peruíbe Black Mud (PBM) found in the city of Perúibe in state of São Paulo, is known for its curative and anti-inflammatory properties. Considered as a material with high cation exchange capacity, microbiological analyzes revealed a large amount of sulfate reducing bacteria and high content of organic material from the biological-metabolic process. In order to provide data that may be useful to understand its therapeutic effects and secondly to certify its quality for use in medical treatments it is necessary to determine the presence of trace elements and minerals present in the different fractions of humic substances and, for this, the technique of neutron activation analysis (INAA) associated with gamma spectrometry was used. Results demonstrate that elements such as Cr and Zn may be concentrated in the humic fraction over the mineral fraction of the mud.

1. INTRODUCTION

The use of minerals with therapeutic proposals is a millenarian practice, particularly with respect to mineral clays [1]. For a long time, clays have been used in wound healing, to relieve skin irritations, anti-inflammatory purpose and to treat gastrointestinal disorders. Currently, its use in the pharmaceutical industry as an active principle has been highlighted, due to its high adsorption capacity, as an excipient, as it promotes the disintegration of drugs, influencing the drug release processes when administered orally. In addition, it can be used as a cosmetic because of its characteristic of absorbing substances such as fats and toxins [2]. The high number of applications of this material is due to its great mineral variety in its composition, frequency of occurrence and properties [3]. In this context, therapeutic treatments using clays have acquired great economic importance.

In Southeast Brazil, Perúibe Black Mud (PBM), found in the city of Perúibe, a municipality on the South coast of São Paulo state, has been extensively used for therapeutic treatments. The material occurs in the plain of the city of Perúibe, accumulating in the dikes adjacent to Rio Preto, during events of overflows, originating a deposit containing approximately 83 thousand tons of the material in a depth of 75 meters. This brings to the city the largest continuous natural resource in the world [4].

PBM is commonly used for the treatment of psoriasis, peripheral dermatitis, acne and seborrhea, myalgia, arthritis and non-articular rheumatic processes.

A chemical and mineralogical characterization of PBM was made which determined the following composition: clay-silt material (22% clay and 39% silt) and sand (33% total fine and fine sand), with the remainder (6%) probably composed of organic matter; approximately neutral pH for *in natura* and mature samples; the swelling test performed with water and hexane showed that PBM has little interaction with both polar and non-polar solvent, characteristic of the presence of silica. As for the mineralogical composition, it was determined that PBM presents quartz with small amounts of illite, gypso, kaolinite, feldspar and halite; the cation exchange capacity, an important parameter for medicinal sludge, was 26 to 36 meq/100g; as for the chemical composition, it was verified that the mature PBM presents slightly higher contents of Ca, Cl, Fe, K, Mg, P and Ti, relative to the mud. As regards the trace elements, it was verified that the PBM is enriched in As, Br, Cr, Sb, Se and Zn and depleted in the elements Ca, Rb and Ta when compared with the values of the upper continental crust. It was also verified the availability of the chemical elements present in the PBM that can eventually be exchanged and absorbed by the skin during its application, through sequential extraction and simple extraction with artificial sweat. It was verified that among the analyzed elements, Ca, Mg, Mn and Na are more available in the most easily exchangeable fraction of the sequential extraction. In the extraction with artificial sweat it was verified that the elements extracted in greater quantity were Ca, K, Mg and Na [5].

In the other study, a chemical and radiological characterization of the PBM was performed, where it was found that the organic matter content varies from 5.2% to 20% for samples after the maturation process. It has been determined that PBM is a type of material mainly composed of clay and particles of fine grain size. Quartz is the main mineral constituent, presenting small amounts of muscovite, feldspar, gypsum, kaolinite, pyrite, halite and smectite: this material is characterized by its low carbonate content. The mature PBM, after treatment with sea water, shows enrichment in gypsum and halite. Results report that most of the silica present is inert. These elements are probably associated with the mineral structure by means of the electrostatic interaction, linked to the iron and manganese oxyhydroxides, amorphous or organic matter. Considering the amount of potentially toxic elements that can be exchanged with the skin during treatment, any damage that could occur to the patient is highly unlikely. The concentration of radionuclide activity was determined indicating that the PBM samples generally have lower decay series member values for ^{238}U and ^{232}Th . The highest effective annual dose measured was in the order of $4\mu\text{Sv}$, considering a scenario of conservative exposure, indicating that the therapeutic use of PBM does not pose a risk for individuals who are being treated [6].

In short, this material is characterized by a large amount of fine particles (especially colloidal), high organic matter content, high sulfate reducing bacteria content and, consequently, ion reduction potential [7]. The amount of organic matter, of oceanic and continental origin, differentiates the product from the common materials, like clays. It also has bacteria and microalgae that give rise to biochemical processes, resulting in an increase in organic matter content in Peruíbe Black Mud.

However, when used with therapeutic proposals, PBM is not, at first, exempt from the possibility of causing adverse health effects [8]. This situation highlights the need to evaluate

the chemical composition of organic matter, strongly influenced by microbial activity and the availability of organic components [9], in order to provide some fundamental data that are useful to understand its effects therapies.

Organic matter consists of a mixture of compounds in various stages of decomposition that result from the biological degradation of plant and animal waste and the synthetic activity of microorganisms. It can be grouped into humic and non-humic substances. Non-humic substances are composed of substances with defined chemical characteristics, such as polysaccharides, amino acids, sugars, proteins and low molecular weight organic acids. Humic substances do not have well-defined chemical and physical characteristics and are divided into humic acid, fulvic acid and humin, based on their solubility characteristics. Because they are negatively charged, these acids are strong cation-fixing agents, so molecules or cations that are adsorbed become unavailable for the biological assimilation process [10].

The humic substances are divided based on their solubilities in aqueous media: fulvic acid, the fraction soluble in any pH condition, humic acid, the fraction soluble in the alkaline medium and insoluble in acidic pH, $\text{pH} < 2$, and humin, the fraction insoluble in any pH condition.

The presence of the distinct groups in the humic substances, such as carboxylic acids, phenolic hydroxyls and carbonyls, causes the humic substances to behave like polyelectrolytic and act as complexing agents of various metal ions [11]. Thus, one of the main properties of humic organic matter is the ability to form complexes and chelates with metals [12], due to its great capacity for complexing with these elements, especially the trace ones. This property is attributed to the different groups that can have oxygen, such as the carboxylic, phenolic and carbonyl groups, which can solubilize the metallic ions of the sediments and, therefore, affect their mobilization [11].

In the organism, humic acids may stimulate the macrophage defense reaction, promote nerve tissue regeneration, stimulate a tissue effect and may have an anti-inflammatory effect on tissue burns and corneal diseases [13].

2. EXPERIMENTAL

2.1. Sample identification

Mature PBM samples were collected directly from the maturation pools of the "Lamário" located in the Thermal Complex of the Peruíbe Black Mud. For the preparation of the sample, about 10 grams of the mature PBM was oven dried at $40\text{ }^{\circ}\text{C}$ for 48 hours. It was then crushed in mortars and passed in 2 mm sieves previously. After the process, it was ground until passing through the 115 mesh ($125\mu\text{m}$) sieve in order to obtain a homogeneous powder of low grain size.

2.1. Extraction of humic substances

The extraction of fulvic and humic acid was done according to the conventional methodology suggested by the International Humic Substances Society [14]. A mass of 100g of PBM was added to 1000 mL of 0.1 mol.L⁻¹ HCl solution. After 12 hours of gentle stirring, the material remained for 24 hours at room temperature. The supernatant was separated from the solid residue by siphoning and reserved.

To the solid residue, 1000 mL of 0.1 mol.l⁻¹ NaOH was added; this mixture was stirred gently for 4 hours under N₂ atmosphere, followed by 12 hours of standing at room temperature. In the sequence the mixture was centrifuged at 1200 rpm for 20 minutes. The supernatant was separated from the residue by siphoning and reserved.

The supernatant was acidified to pH = 1.0 by dropping a 6 mol.L⁻¹ aqueous HCl solution and allowed to flocculate the humic acid.

After 18 hours of rest, the excess supernatant was aspirated by siphoning and reserved. The remainder of the precipitated material was centrifuged at 1200 rpm for 20 minutes, with the remaining supernatant remaining.

The precipitated humic acid was resolubilized in 1000 mL of 0.1 mol L⁻¹ NaOH solution under N₂ atmosphere for the removal of clays and humins. This mixture was stirred gently for 4 hours, followed by 12 hours standing at room temperature. The mixture was then centrifuged at 1200 rpm for 20 minutes. The supernatant from the mixture was acidified to pH = 1.0 by dropping a 6 mol.L⁻¹ aqueous HCl solution and allowed to re-incubate the humic acid.

To solidify the fulvic acid dissolved in aqueous solution, the evaporation technique was used. This was done using a hot plate at 40 ° C for 48 hours. Then, the resulting solid residue (fulvic acid) was kept in a desiccator.

2.2 Instrumental Neutron Activation Analysis associated with gamma spectrometry

Instrumental neutron activation analysis (INAA) is one of the simplest techniques for trace element analysis. In recent decades, INAA has been widely used in the determination of elements at lower levels and trace in various types of matrices, being a non-destructive multielemental analysis method. This technique presents high sensitivity for concentration levels of the order of µg.g⁻¹ and mg.g⁻¹, high specificity and high selectivity [15] [16] [17]

The INAA consists of neutron bombardment of a given material, followed by the measurement of induced radioactivity. The method is based on a nuclear reaction resulting from the interaction of a neutron with a target nucleus producing an excited state composite nucleus, which will decay according to half life and releasing gamma-specific energy rays. radioisotope formed (table 1).

Table 1: Elements determined by neutron activation, radioisotope formed on activation, gamma ray energy used in gamma spectrometry, half-lives and decay time.

Element	Radioisotope	E (keV)	Half-life	Decay Time
As	⁷⁶ As	559	26,32 hours	7 days
Ba	¹³¹ Ba	496	11,8 days	15 days
Br	⁸² Br	554 e 776	35,3 hours	7 days
Ca	⁴⁷ Sc	158	3,35 days	15 days
Ce	¹⁴¹ Ce	145	32,5 days	15 days
Co	⁶⁰ Co	1173 a 1332	5,72 years	15 days
Cr	⁵⁷ Cr	320	27,7 days	15 days
Cs	¹³⁴ Cs	795,85	2,06 years	15 days
Eu	¹⁵² Eu	121 e 1408	13,33 years	15 days
Fe	⁵⁹ Fe	1009 e 1291,6	44,5 days	15 days
Hf	¹⁸¹ Hf	482,18	742,39 days	15 days
K	⁴² K	1524,58	12,36 hours	7 days
La	¹⁴⁰ La	328 e 1596,21	40,27 hours	7 days
Lu	¹⁷⁷ Lu	208,26	6,71 days	15 days
Na	²⁴ Na	1368,68	14,96 hours	7 days
Nd	¹⁷⁴ Nd	91,1 e 531,01	10,98 days	15 days
Rb	⁸⁶ Rb	1076	18,66 days	15 days
Sb	¹²² Sb	564	2,7 days	7 days
Sc	⁴⁵ Sc	889	83,81 days	15 days
Se	⁷⁵ Se	264	119,77 days	15 days
Sm	¹⁵³ Sm	103,18	46,27 hours	7 days
Ta	¹⁸² Ta	1221 e 1231	114,5 days	15 days
Tb	¹⁶⁰ Tb	879,38	72,3 days	7 days
Th	²³³ Pa	312,01	27 days	15 days
U	²³⁹ Np	228,18 e 277,6	2,36 days	7 days
Yb	¹⁶⁹ Yb	177,21 e 197,98	32,02 days	7 days
Zn	⁶⁵ Zn	1115,6	243,9 days	15 days
Zr	⁹⁵ Zr	724,2 e 756,7	64,02 days	15 days

Approximately 150 mg of sample were packaged in polyethylene wrappings. Then, samples and certified reference materials, were enclosed in aluminum (rabbit) capsules that were completely sealed and sent for irradiation in a nuclear reactor for periods of 8 hours.

The certified reference materials used were: Estuarine Sediment, SRM 1646a (ES) from the National Institute of Standards and Technology (NIST), Syenite, Table Mountain, STM-2 from United States Geological Survey (USGS), and standard solutions (SPEX Certiprep) pipetted on filter paper sheets and synthetic patterns

In the long irradiation 2 counting series are performed. The first one is made after 7 days and the second one is done after 15 days of decay.

The counting of the gamma activity induced in the samples and reference materials was done using a germanium detector, Ortec EG & G with resolution of 0.88 keV and 1.90 keV for the peaks of 122 keV and 1332 keV for the ⁵⁷Co and ⁶⁰Co, respectively, and associated electronic equipment. The counting time for samples and reference materials was 2 hours. The calculations for the determination of the concentrations of the analyzed elements were done

in spreadsheet. All samples were irradiated in the IEA-R1 research reactor at IPEN, under a neutron flux of 10^{12} n cm⁻².s⁻¹.

Table 2: INAA detection limit values ($\mu\text{g}\cdot\text{g}^{-1}$)

Element	Detection Limit ($\mu\text{g}\cdot\text{g}^{-1}$)
As	0,4
Ba	33
Br	0,3
Ce	0,5
Co	0,11
Cr	0,9
Cs	0,23
Eu	0,03
Fe	80
Hf	0,11
K	3200
La	0,11
Lu	0,007
Na	32
Nd	3,1
Rb	4
Sb	0,04
Sc	0,02
Se	0,26
Sm	0,01
Ta	0,19
Tb	0,11
Th	0,11
U	0,26
Yb	0,2
Zn	3,8

3. RESULTS

The determination of the elemental concentrations in the three fractions of humic substances (humic acid, fulvic acid and humin with clay) of the PBM was done through the Instrumental Neutron Activation Analysis associated with gamma spectrometry. The results obtained are shown in tables 3, 4 and 5.

Table 3: Trace elements found in HUMINA in $\mu\text{g}\cdot\text{g}^{-1}$ and associated uncertainty

	HUM-1	HUM-2	HUM-3	HUM-4	HUM-5	Minimum	Maximum
As	6.4±0.3	4.0±0.2	4.2±0.2	4.1±0.2	4.9±0.2	4.0	6.6
Ba	413±35	405±29	418±23	402±28	428±30	402	428
Br	42.1±0.4	93.0±0.7	90±1	101±1	107±1	42.1	107
Ca	7000±1100	6200±400	6000±500	7100±4000	6600±600	6000	7100
Ce	32±1.1	29±1	30±1	32±1	34±1	29	34
Co	7.2±0.1	4.7±0.1	4.95±0.09	5.4±0.1	5.47±0.09	4.66	7.20
Cr	47±2	35±1	36±1	39±1	41±2	35	47
Cs	4.4±0.2	3.0±0.1	2.9±0.1	3.0±0.2	3.3±0.2	2.9	4.4
Eu	0.55±0.02	0.50±0.02	0.52±0.02	0.60±0.02	0.62±0.03	0.50	0.62
Fe	22900±200	21000±300	22200±300	23200±300	24500±400	21000	24500
Hf	5.55±0.07	5.3±0.1	5.07±0.05	5.64±0.06	5.39±0.06	5.07	5.64
K	900±270	2000±700	2000±800	1000±800	4000±1600	1000	9000
La	21.3±0.5	18.2±0.3	19.0±0.4	20.2±0.4	20.6±0.4	18.2	21.3
Lu	0.17±0.01	0.16±0.01	0.18±0.01	0.17±0.01	0.15±0.01	0.15	0.18
Na	1.48±0.04	1.27±0.03	1.28±0.03	1.40±0.03	1.43±0.03	1.27	1.48
Nd	21.6±0.8	20±1	20±2	13±3	23.8±2.5	12.6	23.8
Rb	67±3	74±3	76±3	77±3	88±4	67	88
Sb	0.7±0.1	0.55±0.1	0.65±0.15	0.7±0.2	0.47±0.1	0.47	0.68
Sc	7.10±0.04	6.78±0.04	7.04±0.04	7.33±0.04	7.64±0.04	6.78	7.64
Se	<LD	<LD	0.6±0.1	<LD	0.66±0.2	<LD	0.66
Sm	2.7±0.1	2.4±0.1	2.4±0.1	2.6±0.1	2.7±0.1	2.4	2.7
Ta	0.60±0.04	0.53±0.04	0.54±0.04	0.73±0.03	0.49±0.04	0.49	0.73
Tb	0.2±0.2	0.31±0.02	0.38±0.08	0.38±0.03	<LD	<LD	0.38
Th	7.2±0.6	6.6±0.3	7.1±0.4	6.9±0.4	7.3±0.4	6.6	7.3
U	3.1±0.3	2.2±0.2	2.6±0.2	2.7±0.2	2.5±0.2	2.2	3.1
Yb	0.8±0.1	0.94±0.08	1.0±0.1	0.92±0.09	0.89±0.07	0.83	1.03
Zn	44±2	39±2	45±3	43±3	50±4	39	50
Zr	<LD	128±20	223±10	207±23	157±12	<LD	223

Table 4: Trace elements found in FULVIC ACID, in $\mu\text{g.g}^{-1}$ and associated uncertainty

	FA-1	FA-2	FA-3	FA-4	Minimum	Maximum
As	12±2	<LD	<LD	<LD	<LD	12
Ba	<LD	17±9	127±28	<LD	<LD	127
Br	819±5	1338±8	1274±9	928±6	819	1338
Ca	19000±1000	1300±3000	9000±1700	<LD	<LD	19000
Ce	65±2	<LD	59±3	31±2	<LD	65
Co	14.7±0.2	9.1±0.3	8.4±0.3	6.3±0.2	6.3	14.7
Cr	16±1	21±1	19±1	23±1	16	23
Cs	<LD	<LD	<LD	0.4±0.06	<LD	0.4
Eu	1.01±0.03	0.62±0.03	0.74±0.04	0.39±0.02	0.39	1.01
Fe	10900±100	9300±100	8700±100	6500±100	6500	10900
Hf	<LD	<LD	<LD	<LD	<LD	<LD
K	<LD	<LD	<LD	<LD	<LD	<LD
La	20.4±0.4	18.2±0.4	20.6±0.5	11.4±0.3	11.4	20.6
Lu	0.15±0.01	0.12±0.01	0.14±0.01	0.09±0.01	0.09	0.15
Na	<LD	1570000±30000	1660000±40000	1930000±400000	<LD	1930000
Nd	22.9±0.7	13.0±1.3	15.4±1.8	12.4±1.4	12.4	22.9
Rb	1.9±0.6	<LD	<LD	<LD	<LD	1.9
Sb	0.10±0.07		0.17±0.08	<LD	<LD	0.17
Sc	0.19±0.01	0.17±0.01	0.16±0.01	0.07±0.02	0.07	0.19
Se	<LD	<LD	<LD	<LD	<LD	<LD
Sm	3.8±0.2	2.5±0.1	2.9±0.1	1.8±0.1	1.8	3.80
Ta	0.22±0.05	<LD	<LD	<LD	<LD	0.22
Tb	0.7±0.10	0.2±0.06	0.4±0.07	0.10±0.05	0.1	0.7
Th	0.18±0.7	<LD	<LD	<LD	<LD	0.18
U	5.6±0.4	<LD	5.6±0.7	2.2±0.4	<LD	5.6
Yb	1.00±0.10	0.68±0.08	0.58±0.07	0.34±0.07	0.34	1.00
Zn	85±3	69±4	74±4	47±2	47	85
Zr	131±10	<LD	<LD	205±22	<LD	205

Table 5: Trace elements found in HUMIC ACID, in $\mu\text{g}\cdot\text{g}^{-1}$ and associated uncertainty

	HA-1	HA-2	HA-3	HA-4	HA-5	Minimum	Maximum
As	13.8±0.5	6.4±0.2	5.9±0.2	7.5±0.2	7.5±0.3	5.9	13.8
Ba	107±28	49±18	<LD	21±18	<LD	<LD	107
Br	195±1	157±1	162±1	173±1	175±1	157	195
Ca	8000±800	2500±700	10000±1300	5000±400	3000±300	10000	80000
Ce	30±1	31±2	29±1	30±1	32±2	29	32
Co	8.9±0.1	7.3±0.2	7.4±0.2	7.1±0.2	7.8±0.2	7.1	8.9
Cr	101±3	70±3	71±3	69±2	77±3	69	101
Cs	5.6±0.2	3.5±0.7	3.1±0.6	3.2±0.6	3.3±0.7	3.1	5.6
Eu	0.62±0.04	0.120±0.005	0.120±0.005	0.12±0.004	0.13±0.01	0.12	0.62
Fe	16200±200	14200±200	15000±200	14900±200	15100±200	14200	16200
Hf	2.00±0.04	0.98±0.03	0.87±0.02	0.91±0.03	0.99±0.03	0.87	2.00
K	<LD	3400±2000	4400±2000	<LD	<LD	<LD	4400
La	12.8±0.3	10.5±0.3	10.5±0.2	11.3±0.3	12.1±0.3	10.5	12.8
Lu	0.080±0.004	0.08±0.01	0.07±0.01	0.07±0.01	0.07±0.005	0.07	0.08
Na	46700±1000	41300±1000	35000±1000	40700±1000	42900±1000	35000	46700
Nd	24±1	4.8±0.8	<LD	1.0±0.3	5.8±0.3	<LD	24.4
Rb	45±2	33±2	34±2	35±2	33±2	33	45
Sb	<LD	0.53±0.07	0.60±0.08	0.52±0.07	0.46±0.06	0.34	0.60
Sc	12.6±0.1	12.9±0.1	13.8±0.1	13.4±0.1	13.9±0.1	12.6	13.9
Se	<LD	0.4±0.2	<LD	<LD	0.4±0.1	<LD	0.4
Sm	3.3±0.1	2.9±0.1	2.8±0.1	3.0±0.1	3.2±0.1	2.8	3.3
Ta	<LD	0.18±0.03	0.20±0.02	0.37±0.04	0.17±0.02	<LD	0.37
Tb	0.2±0.2	0.30±0.1	0.30±0.1	0.21±0.04	0.16±0.1	0.16	0.30
Th	17±1	15±1	15±1	15±1	16±1	14.7	17.0
U	7.5±0.5	6.1±0.3	6.8±0.3	6.0±0.3	6.6±0.2	6.0	7.5
Yb	0.6±0.1	0.70±0.1	0.65±0.1	0.71±0.2	0.76±0.2	0.65	0.76
Zn	48±2	51±3	<LD	<LD	50±2	<LD	51
Zr	224±53	<LD	193±21	<LD	53±50	<LD	224

Figure 1 expresses the elemental composition of each analyzed fraction, based on the maximum values found, which makes it possible to verify the predominance of each element in each fraction and figure 2 shows the distribution of the sodium, potassium, heat and iron elements (elements found in greater abundance) present in each fraction of organic matter of PBM, based on the maximum values found.

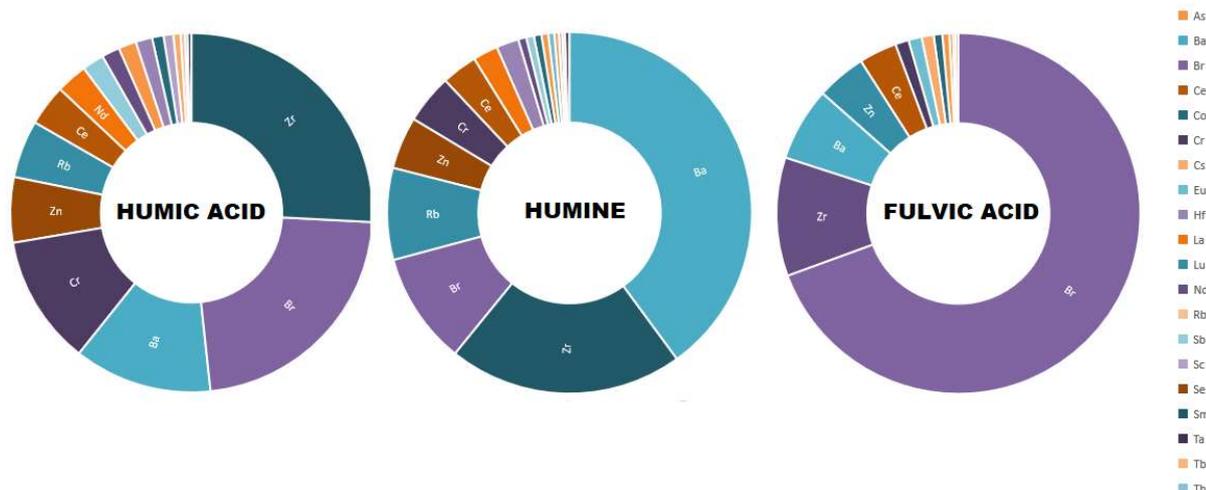


Figure 1: Elementary composition of fractions of humic substances present in PBM

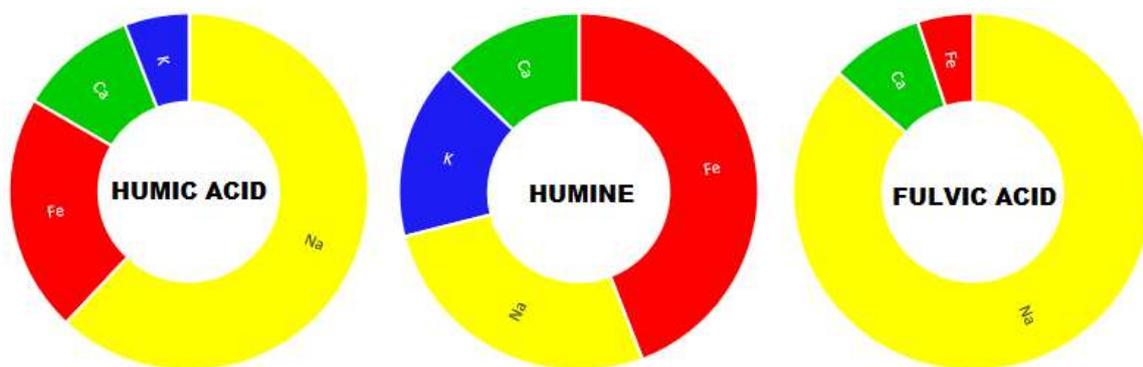


Figure 2: Distribution of sodium, potassium, calcium and iron elements in the PBM humic substance fractions

The elements As, Sb, and Ba are potentially toxic, whereas Rb, Cr, Zr, and rare earth elements can be considered hazardous [18]. However, there is no regulation for these elements in clays used for therapeutic purposes. According to European regulations, elements such as As, Sb, and Se must be absent in cosmetics due to their respective toxicities [19] and therefore it is important that the concentrations of these elements are known in muds used for medical purposes [18].

It was observed that the arsenic present in PBM is associated mainly with the structure of humic and fulvic acids. This element is ubiquitous in our environment and is very dangerous in large quantities and has been declared carcinogenic to humans by the International Agency for Research on Cancer (IARC) in 1980. Excessive exposure to arsenic can lead to serious health problems such as various cancers, cardiovascular diseases, diabetes and neurological diseases [18].

The bromine present in PBM is mainly concentrated in fulvic acid. However, bromine only causes damage to people when inhaled or ingested [18] [20], in this way, the high concentration of this element may not be a problem.

The study of "rare earth" elements is important to understand how these elements are incorporated into the mud. They are generally divided into two groups: "light rare earth", which is represented by La, Ce, Nd, Sm and Eu, and "heavy rare earth", which include Tb, Yb and Lu [18]. Lanthanum is mainly distributed in the structure of fulvic acid and humina that is combined with clay as it was not possible to separate them. Cerium and europium are concentrated mainly in fulvic acid. Neodymium and samarium were evenly distributed among the three analyzed fractions. Terbium is predominantly found in fulvic acid, Ytterbium is uniformly distributed among the three fractions, and finally, as regards lutetium, it is found mainly in fulvic acid and humina.

4. CONCLUSIONS

This study aimed to determine trace element concentrations through INAA present in PBM organic matter, which was separated based on their solubility in different pH ranges.

The most common elements present in the PBM's organic matter are: calcium, iron, bromine, zirconium, barium, zinc, cerium for the three humic substances fractions (humic acid, fulvic acid and humine) and potassium and rubidium present with greater predominance in the fraction of humic acids and humine. However, we can observe the presence of the other elements analyzed, but in smaller quantity.

Thus, it was possible to confirm the polyelectrolytic behavior assumed by humic substances which act as complexing agents of various metallic ions, showing that one of the main properties of PBM's organic matter is the ability to form complexes and chelates with metallic elements to different oxygen groups, such as carboxylic, phenolic and carbonyl groups, which can solubilize the metal ion present in any inorganic sediment material. This feature may be a possible way to incorporate these elements into the human body during PBM application through skin absorption.

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