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A COMPARATIVE MINERALOGICAL AND PHYSICO-CHEMICAL STUDY OF SOME CRUDE MEXICAN AND PHARMACEUTICAL GRADE MONTMORILLONITES

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ABSTRACT

All bentonites samples including those used as reference were characterized by x-ray diffraction minerological study, whole chemial analysis (total oxides), ion exchange capacity and physical-chemical properties tests. The x-ray diffraction analysis reveal only slight differences among mexican bentonites raw material. Either Mexican bentonite or the reference material show very similar impurity content. Chemical analysis of bentonites show wide variability in oxide content but results are in close accordance with those reported in the

literature (2). The results obtained for reference compared to those of raw bentonites are in good agreement.

I. INTRODUCTION

Bentonites are clay minerals which belong to the smectite mineralogical group (1). Most commercial bentonites are dioctahedric magnesium smectites or montmorillonites (1), although saponite, a trioctahedric smectites, is present as the main component of some commercial bentonites.

The smectites are phillosilicates with a crystal structure similar to that of the micas (1,2,3,4). The different smectites species could be differentiated from each other attending mainly to the composition of the octahedrical layer. Thus, montmorillonites have 2/3 of their octahedrical lattice occupied by Mg^{2+} and Al^{3+} (dioctahedric) and owing to the fact that these ions are loosely bound to the crystal layer some substitutions can occur and it has been found that a substitution of Mg^{2+} for each sixth Al^{3+} is possible leasing the dioctahedric sheet unbalanced in charge resulting in this way a net positive charge on the crystalline lattice.

The deficiency in positive charges mentioned above is neutralized by solvated Na^{+} and or Ca^{2+} entering in the interlayer space. The different smectites species and subspecies are, besides other properties, characterized by their different net charges; therefore, existing smectities of low and high charges respectively. The differences in charges contributes to a great variability in the physicochemical behavior of smectites. For example, the ability for reversible water sorption, energy retention of the sorbed water, expansibility or change in the volume over different degree of water content, gel forming ability, etc. All the above properties are directly or indirectly related to the nature or the crystal lattice of these minerials, primarily to the relative magnitude of their net charge and also to the site in the lattice where that charge is produced.

The cations filling the interlayer in smectites are also important in determing their physicochemical properties. Thus bentonites bearing Na^+ as the primarily interlayer cation present more expansitivity power and high gelification ability. Any smectite clay is able to be transformed into a Na^+-smectite by means of a simple cation exchange process. However, this treatment is by no means so simple as could be seen at first sight and there is no warranty that a clay treated by the simple procedure will reach the desirable behavior (i.e. gel forming power, colloid stability, etc.) In addition to the interlayer cation specificity there exist other reasons why certain clay minerals do not reach some physicochemical properties or specifications completely. Therefore, a characterization study and some physicochemical test have to be performed as the only means for selecting proper bentonites that are to be used in specific applications.

On the other hand, when dealing with crude materials or weakly processed ones, a comparison with other fully or highly purified minerals could obviously not be made. However, by careful examination of the results of the characterization study and physicochemistry tests on bentonites raw materials some guidelines could be drawn to assists us in selecting the proper way in the purification process that conducts to the pure product having the desired properties.

The present work was undertaken to establish some guidelines that might be observed in the planning of a purification process for bentonites raw materials attending both characterization studies and physicochemical tests to obtain a product conforming the quality standards for pharmaceutical or other uses of mexican bentonites clay minerals.

II. EXPERIMENTAL

The sample of bentonites raw materials were of different origin principally due to the widespread of clay mineral ores in the country. Bentonites 1, 3, 4 and 8 were from Puebla state, samples 2 and 7 from Durango state, No. 5 and 6 samples were from Yucatan and bentonites sample 9 were from Queretaro. Four bentonites of Pharmaceutical grade were used as reference standards and were bindly supplied from Pharmaceutical Laboratories. Bentonites UPN and UP from Upjohn, Bentonite K from Knoll, and Bentonite N from Norwich Laboratories. All bentonites samples including those used as reference were characterized by the following tests:

- X-ray diffraction mineralogical study
- Whole chemical analysis (total oxides)
- Ion exchange capacity and total bases
- Physico-chemical properties

The mineralogical study performed on samples includes x-ray diffraction patterns obtained following the technique reported by

Ford (4), and was carried out in an x-ray Diffraction Spectrometer (Philips, pw 1130/00, NC:9430, 011 30001 made in Holland No. Dy 848). Several treatments were applied according to Thorez (6).

A fully chemical analysis (total oxides) was performed following the procedures recommended by Perez Obregon (8) and the content of SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O and H_2O at 100°C and 1200°C was determined.

Cation exchange capacity was evaluated using the NH_4Ac 1N, pH 7 method described by U.S.D.A. (8). The exchangeable bases extracted by de ammonium acetate method were examined by the following techniques: Na^+ and K^+ by flame analysis using the 650 C & C Technicon Autoanalyzer, Ca^{2+} was determined by the EDTA murexyde method described in (8) and Mg^{2+} by the formation of magnesium blue in the Technicon Autoanalyzer 650 C & C.

The physicochemical test performed were those described in the following pharmacopeias: USP (9), BP (10), FNEUM (11), pH (12) PF (13) and includes: swelling power, gel forming ability, pH, loss on drying, and alcalinity.

III. RESULTS

The x-ray diffraction analysis reveal only slight differences among mexican bentonites raw material. And only in samples 5 and 6 Yucatan bentonites the chacteristique spacing of sodic montmorillonite was found (first raw, Table 1). In all other benonites the basal spacing of the air dryed sample laid about 15Å showing in addition a similar intensity pattern in the diffraction peaks.

TABLE 1

X-ray Diffraction Analysis of Montmorillonites. (001) Reflections in Å

	Air Dryed	500°C 1 hr	K IN	E Glycol	K^+ + Glycerol
1 UPN	14.71	9.71	12.16	16.97	13.39/14.24
2 K	12.16	9.84	12.66	16.97	14.23
3 N	12.61	9.71	12.16	18.01	14.01/18.78
4 UP	18.01/12.62	9.71	12.26	17.66	17.66/14.01
1 AZC	15.23/10.24	9.71	12.26	16.97	14.01
2 S-Na	15.5	9.60	12.26	16.66	13.80
3 AZB	15.23	9.71	12.26	16.96	14.01
4 MPC	14.96/14.47	9.71	12.26	16.97	14.01
5 Y-2	12.61	9.84	12.26	16.97	14.01
6 Y-3					
7 VT	18.01/14.97	9.60	12.26	17.31	13.80
8 DC	14.47	9.71	12.26	16.97	14.23
9 BS	14.47/14.71	9.60	12.26	18.01	14.01

In another way, either mexican bentonite raw materials or the reference material analyzed shows a vary similar impurity content. Thus, in reference bentonites quartz is present in 3 of 4 studied (i.e. UP, N and UPN) as well as in all bentonite raw materials as a constant component in the fraction size of clay. Bentonite 1 shows in addition a reflection at 10.04Å indicating the presence of a mixed illite or hyromica.

Several diffractograms obtained after applying the treatments already mention (6) do not show any clear differences between reference and bentonites raw material as could be seen from Table 1. However, a slightly basal spacing following K^+ + glycerol treatment resulted slightly greater in reference than in bentonite raw material and as a consequence of this a smaller charge in the former could be postulated.

Chemical analysis of the bentonites studied are presented in Table 2 and a wide variability in oxide content can be observed, but results are in close accordance with those reported in the literature (2). The dispersion in the result could be seen as a consequence of the mineralogical impurities present in samples as well as errors inherent to the application of the analytical technique. However, the results obtained fo reference compared to that of raw bentonites are in good accordance. Specially the iron content which are similar in both bentonites precludes that their use as pharmaceutical material is not limited by this element.

Table 3 shows cation exchange capacity and base extracted by pH 7 ammonium acetate. CEC values determined are in agreement with those reported in the literature (2) for clays.

The data shown in Table 4 are very illustrative in relation to the state of the absorption complex of the clay mineral studied. The Ca/Na ratio in raw bentonites is generally higher than in reference one. However, some raw bentonites studied such as 3, 5 and 6 present ratio values slightly lower than reference material.

TABLE 2

Chemical Analysis (Total Oxides) of Montmorillonites (g%)

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	$H_2O(+)$	$H_2O(-)$	Total
Limits	45.7-	15.9-	0.06-	2.3-	0.5-	0.04	-0.11-	7.4-	14.7-	100 %
	57.5	28.2	4.13	6.5	3.28	2.75	0.59	8.5	15.7	
1 UPN	56.1	15.77	4.03	2.6	2.1	4.36	1.56	17.8	10.95	93.37%
2 K	56.1	23.19	4.03	2.9	2.8	9.94	0.09	18.1	11.6	106.05%
3 N	69.1	13.59	2.01	1.9	2.1	6.37	0.376	15.1	8.85	101.7%
4 UP	57.6	20.77	4.03	1.7	2.1	5.68	0.68	15.1	8.0	99.66%
1 AZ-C	67.4	10.45	3.35	1.5	2.8	5.74	2.24	12.0	5.65	99.83%
2 S-Na	57.3	11.32	2.68	3.1	2.1	4.38	1.02	18.35	10.5	89.75%
3 AZ-B	67.5	8.25	3.35	1.6	1.4	5.38	2.05	14.1	8.05	95.58%
4 MPC	65.8	8.52	2.68	1.9	1.4	5.30	2.02	13.65	7.65	93.52%
5 Y-2	57.4	16.5	2.01	3.3	4.2	7.44	2.97	16.05	10.1	99.77%
6 Y-3	63.1	16.12	2.68	1.8	2.1	5.17	1.43	15.8	10.85	97.35%
7 VT	66.5	10.65	3.35	1.8	2.1	5.06	2.88	12.05	6.1	98.29%
8 DC	67.7	17.52	2.68	1.9	1.4	4.54	1.77	12.9	7.0	103.41%
9 BS	57.4	19.17	4.7	3.6	2.8	8.19	1.56	17.6	12.05	102.97%

TABLE 3

Ion Exchange Capacity and Total Bases of Montmorillonites (Meq/100 g)

	C.E.C.	K	Ca	Mg	Na	Total Bases
1 UPN	88	0.6	18.1	23	30.0	71.7
2 K	86.5	0.4	26.9	12.8	75	115.1
3 N	69	0.6	25	3.1	40	68.7
4 UP	95	1.0	21.9	7.1	34.8	64.8
1 AZ-C	59.5	2.6	31.3	14.7	22.8	71.4
2 S-Na	93	0.5	31.9	6.7	30.5	69.6
3 AZ-B	82.5	5.9	25.6	12.9	35.7	80.1
4 MPC	94	4.9	27.5	12.9	32.5	77.8
5 Y-2	63.3	2.0	29.7	10.3	44.4	85.4
6 Y-3	67.5	0.8	23.4	7.5	29.2	60.9
7 VT	65.5	2.7	31.3	11.9	25.6	71.5
8 DC	72.5	5.3	18.8	11.5	33.1	68.7
9 BS	85.0	0.3	30.6	2.2	61.9	95

From the point of view of the probable use of these clays for purification purpose the one which improves the Ca/Na relation must be the option.

Table 5 also includes figures for Na saturation % of the CEC and % of Na respect to the total base. By inspection it is readily

TABLE 4

Some Characteristics of Cation Exchange Capacity of Montmorillonites

	Ca/Na	$\frac{Na}{C.E.C.}\%$	$\frac{Na}{T.B.}\%$
1 UPN	0.603	34.1	41.8
2 K	0.358	86.7	65.2
3 N	0.625	58.0	58.2
4 UP	0.337	36.6	53.7
1 AZ-C	1.372	38.3	31.9
2 S-Na	1.046	32.8	43.8
3 AZ-B	0.717	43.3	44.6
4 MPC	0.846	34.6	41.8
5 Y - 2	0.668	70.1	52.0
6 Y - 3	0.801	43.2	47.9
7 VT	1.222	39.0	35.8
8 DC	0.568	45.6	48.2
9 BS	0.494	72.8	65

TABLE 5

Physicochemical Analysis of Montmorillonites According to the U.S.P.

	pH	Alcalinity ml 0.1 N	Gel Forming*	Swelling P.	H_2O (-)
Limits	9.5-10.5	0.1 ml	No more than 2 ml	More than 24 ml	5-8%
1 UPN	9.9	0.05	0 ml $^{+++}$	23.6	8.46
2 K	10.2	0.05	0 ml $^{++}$	28	6.82
3 N	9.5	0.1	0 ml $^{+}$	22	6.85
4 UP	9.6	0.1	0 ml $^{+}$	30	
1 AZ-C	10.2	0.05	35 ml $^{+}$	7.4	6.09
2 S-Na	9.8	0.05	9 ml $^{+}$	12.4	11.69
3 AZ-B	9.8	0.05	8 ml $^{+}$	8.8	8.66
4 MPC	10.0	0.1	9 ml $^{+}$	9	8.10
5 Y - 2	10.1	0.05	8 ml $^{+}$	14	7.66
6 Y - 3	9.7	0.05	35 ml $^{+}$	14	7.16
7 VT	10.2	0.05	91 ml $^{+}$	6	7.94
8 DC	7	0.05	1 ml $^{+}$	7	6.55
9 BS	10.3	0.05	26 ml $^{+}$	18	12.18

*, + Very fluid; $^{++}$ Poor gelification; $^{+++}$ Completely gelificated.

seen that the higher Na% of CEC is presented by 5 and 6 raw bentonites and their values are also comparable to the reference clays.

Data obtained from various physicochemical test as specified by the principal pharmacopeias (9,10,11,12,13) are shown in Table 5. The tests were performed in reference as well as in raw materials and the data thus obtained are by no means comparable, but some insight on which properties must be modified by the purification process could be drawn from these data. The raw bentonites much alike to the reference material studied were samples 6,7,8 and 13 as they approach very close to the quality requested for material intended for pharmacuetical use, specially those concerning with the gel forming ability and swelling power.

IV. CONCLUSIONS

1. The mexican bentonites studied are of calcic origin and attending to their mineralogical and physicochemical characteristic properties are not to be used by the pharmaceutical industries directly.
2. Owing to the similar mineralogical and physicochemical properties of Mexican bentonites compared to those of foreign origin lead us to presume that a proper management of the purification process could yield bentonites that conform quality standards for pharmaceutical applications starting from bentonite mineral crudes.
3. From the results obtain in chemical analysis, the most easily purification processed bentonites could be the samples labeled as 6,7,8 and 10.

4. The purification process must include fine particle separation and a sodium saturation treatment.

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