EFFICIENCY OF MODIFIED CLAYS IN WATER SOFTENING

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INTRODUCTION

The scenario of water scarcity, present in various parts of the world, implies on the need for searching alternatives to obtain drinking water. In Northeastern Brazil, for instance, wells are indispensable for survival of the inhabitants of the areas affected by droughts. In general, this water contain components that, when in very high concentrations, are harmful (WHO, 2011).

Two components are calcium ions (Ca^{2+}) and magnesium (Mg^{2+}), whose added quantities result in a water quality parameter called hardness. Given this reality, there is need to create methods meeting the treatment purposes of this natural resource. Therefore, the application of Green Chemistry principles becomes essential to defend sustainable, environmental and social guidelines (Royal Society of Chemistry, 2007).

Highlighting the need to develop low cost processes, and taking advantage of local raw materials to facilitate logistics, this paper aims to study the efficiency of using clays in water softening and their application in column filtration. Parallel analysis of methodologies for the modification of clays (bentonite and vermiculite) and tracking of fundamental physicochemical parameters – conductivity, total dissolved solids and pH – were performed.

Through extensive specialized literature – represented by scientific articles focused on chemical and structural properties of the clays, as well as their modification processes – chemical methods were selected in order to obtain a variety of materials to be tested for the ability to adsorb components that, when in excess, can alter water quality.

METHODS/MATERIALS

The methodology consisted of treating the selected adsorbent materials for the tests, studying parameters to control water quality and testing the procedure using a laboratory-produced calcium standard solution.

Natural vermiculite and bentonite clay samples were used on the experiments without previous treatments.

Chemical modifications of the clays used acidic, alkaline and salt solutions, applying methods described in literature (Morales-Carrera, 2009; França; Arruda, 2006; Quartarone *et al.*, 2012; Bertella *et al.*, 2010).

X-ray diffraction tests were performed with a Bruker-D2PHASER equipment to verify the characteristic structural order of the clays and their subsequent chemical modifications. Graphs were compared to those obtained from literature, in order to confirm clay natures.

Two procedures were established to measure the adsorptive capacity of the modified clays, in order to prove their water treatment efficiency. First, a magnetic stirrer was used, as seen in literature (França; Arruda, 2006). In this case, 1g of each clay was put in contact with 100 mL of a 1000 ppm calcium standard solution. After stirred with a magnetic stirrer for 1h, the mixtures were filtered and then collected for further analysis.

In the second procedure, the calcium standard solution passed through a column at constant flow, fed by a peristaltic pump, where the clays with best previous results were deposited, supported on a porous tissue.

At the end of this procedure, the clay with best results was applied on successive column filtration tests, until no further substantial reductions on hardness could be observed, aiming to obtain the maximum amount of calcium ions adsorbed per 1g of clay.

The solutions obtained from the filtration processes described were measured according to the following parameters: hardness (complexometric titration), salinity, total dissolved solids, conductivity and pH (HANNA equipment). These measurements were compared with the physicochemical properties of the calcium standard solution, which specified the effectiveness of each clay.

RESULTS AND DISCUSSION

According to specialized literature, the interlayer distance for natural vermiculite (NV) revolves around 14 Å (Albers *et al.*, 2002; Santos *et al.*, 2002).

Regardless of that, the diffraction patterns obtained indicate that sodium chloride modification (NaCl-V) generated an increase on that distance, reaching 14.7 Å (Fig. 1). Although not seeming very expressive, this finding is in agreement with Avelino *et al.* (2009) for sodium vermiculite. The modification with sodium hydroxide (NaOH-V) generated a similar increase in the interlayer spacing, shifting the characteristic peak to 14.6 Å, which can identify the beginning of deep changes on the structural order. Despite these changes, it was noted that a certain structural order did not cease to exist.

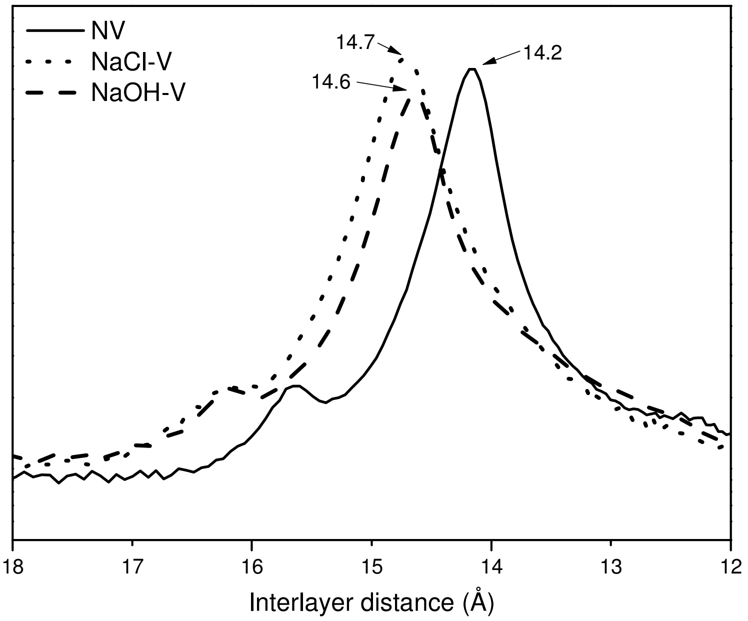

Fig. 1 – Increase on interlayer distance after sodium chloride (NaCl-V) and sodium hydroxide (NaOH-V) treatments.

Treatment with hydrochloric acid (Fig. 2), on the other hand, led to a profound loss of vermiculite structural order. This, however, did not extinguish the adsorption capacity of the material, as observed on both stirring and column tests. An explanation for this fact is the increase on adsorbent surface area and porosity.

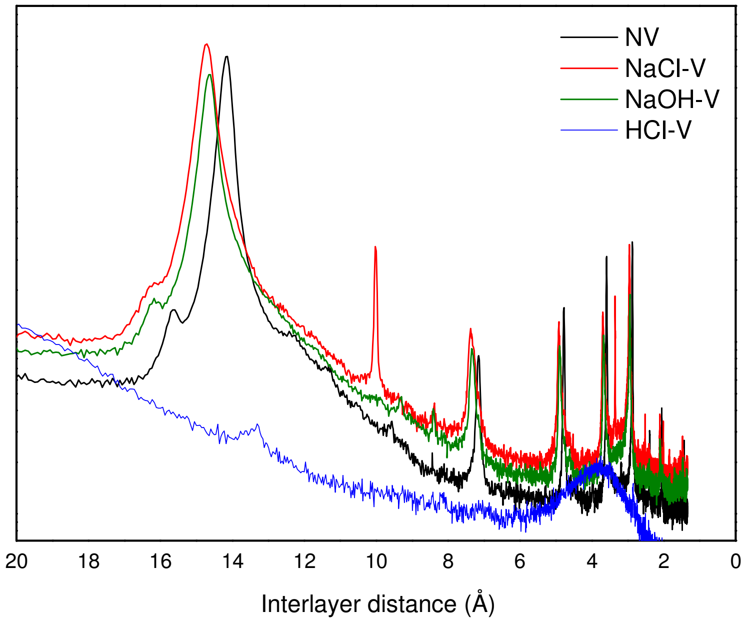

Fig. 2 – X-ray diffractograms of vermiculite samples, showing structural disorder of hydrochloric acid treated vermiculite (HCl-V).

For bentonite, the XRD analyses confirmed the nature of the clay, with a peak at around 4.5 Å, coinciding with those found in published works (Zhang, 2011). Treatments performed with hydrochloric acid and sulfuric acid showed similar and significant adsorption capacities, although provoking subtle changes on interlayer distance. The magnetic stirring tests confirmed the efficiency of the modifications compared to natural bentonite (Table 2).

The obtained results from performed treatments (magnetic stirring and column filtration, respectively) are shown in tables below.

Table 1 - Physicochemical properties measured after magnetic stirring testing.

Sample	Hardness (mgCaCO$_3$/L)	Salinity (% NaCl)	pH (25 °C)	Electrical Conductivity (μS.cm^{-1})	Total Dissolved Solids (ppm)
Standard Solution	999.95	4.6	10.2	2,357	1,179
Filtrate 1 (after contact with 1g natural bentonite)	905.57	4.2	8.59	2,275	1,137
Filtrate 2 (after contact with 1g hydrochloric acid treated bentonite)	806.90	4.4	9.28	2,251	1,123
Filtrate 3 (after contact with 1g sulfuric acid treated bentonite)	772.16	4.4	9.27	2,257	1,128
Filtrate 4 (after contact with 1g natural vermiculite)	914.00	4.1	8.79	2,191	1,096
Filtrate 5 (after contact with 1g sodium chloride treated vermiculite)	424.69	4.1	9.59	2,070	1,035
Filtrate 6 (after contact with sodium hydroxide treated vermiculite)	536.65	4.1	9.67	2,095	1,050
Filtrate 7 (after contact with 1g hydrochloric acid treated vermiculite)	564.17	5.3	8.90	2,681	1,341

Table 2 - Hardness percent reduction after magnetic stirring testing.

Analyzed Sample	Hardness Reduction
Filtrate 1 (after contact with 1g natural bentonite)	9.44%
Filtrate 2 (after contact with 1g hydrochloric acid treated bentonite)	19.30%
Filtrate 3 (after contact with 1g sulfuric acid treated bentonite)	22.78%
Filtrate 4 (after contact with 1g natural vermiculite)	9.15%
Filtrate 5 (after contact with 1g sodium chloride treated vermiculite)	57.53%
Filtrate 6 (after contact with 1g sodium hydroxide treated vermiculite)	46.33%
Filtrate 7 (after contact with 1g hydrochloric acid treated vermiculite)	43.58%

Table 3 - Physicochemical properties measured after column filtration testing.

Sample	Hardness ($mgCaCO_3/L$)	Salinity (% NaCl)	pH (25 °C)	Electrical Conductivity (µS.cm^{-1})	Total Dissolved Solids (ppm)
Standard solution	999.90	4.6	10.1	2,401	1,190
Filtration 1 (after contact with 1g natural vermiculite)	896.14	3.7	9.15	2.015	1,001
Filtration 2 (after contact with 1g sodium chloride treated vermiculite)	820.67	3.9	9.45	2,072	1,034
Filtration 3 (after contact with 1g hydrochloric acid treated vermiculite)	715.96	3.8	8.75	2,049	1,021
Filtration 4 (after contact with 1g sodium hydroxide treated vermiculite)	820.67	3.8	9.70	2.036	1,014

Table 4 - Hardness percent reduction after column filtration testing.

Analyzed Sample	Hardness Reduction
Filtration 1 (after contact with 1g natural vermiculite)	10.38%
Filtration 2 (after contact with 1g sodium chloride treated vermiculite)	17.92%
Filtration 3 (after contact with 1g hydrochloric acid treated vermiculite)	28.40%
Filtration 4 (after contact with 1g sodium hydroxide treated vermiculite)	17.92%

All materials tested have considerable efficiency on water softening, taking the used amount of each material (1g) and water destination purposes into account. The results show small pH changes on the standard solution. This is a fact of minor importance, since this parameter can be easily adjusted. Significant reductions were noted on the other analyzed parameters.

The test involving successive filtrations showed that for every 1g of hydrochloric acid treated vermiculite, about 60 mg of calcium ions are removed.

CONCLUSION

The obtained data shows that vermiculite has the best efficiency for water softening. Bentonites, however, also have a potential for that purpose, but need more intense treatments to enhance their adsorptive properties, which tend to be more costly.

The proved efficiency of the sodium chloride treated vermiculite for water softening generates optimistic expectations, given the simplicity and low cost of this technique, visioning future applications on treatment systems. Besides that, the cation-exchange mechanism allows regeneration of the adsorbent material.

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