

## INFLUENCE OF THE SYNTHESIS PARAMETERS ON SOME TEXTURAL PROPERTIES OF ROMANIAN ACID ACTIVATED BENTONITE

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**Abstract:** This paper presents the influence of synthesis parameters (concentration of acid solution and the solid: liquid ratio) on textural characteristics of bentonite activated clays: nitrogen adsorption/desorption isotherms, surface and pore size distribution. Acid activated clays present higher specific surface area than the natural bentonite used as feed stock and a better adsorption capacity.

**Keywords:** acid activated bentonite, specific surface area, pore size distribution.

### 1. INTRODUCTION

Clays are widespread natural mineral materials that are used in many fields. Between these, the bentonite (smectites) is a special group of materials that are used in many fields. Sodium and calcium bentonite are the most abundant type of bentonite and present some special properties that make it important in many industrial processes: abundant and low cost materials with high ionic exchange capacity, good adsorption properties, swelling capacity, relatively higher green compression strengths, good bounding properties, high plasticity [1-5]. They are used as agricultural carriers, as a bonding agent for foundry moulding sands, sealants, as filtrate materials in food industry, emulsion stabilizers, as matrix for insecticide distributors, palletizing iron ores, as feed stock in ceramic and refractory materials, as catalyst in photo oxidation reactions, in paper industry, dyes production, as sorbate and retention-insulation materials in the protection of environment, animal feed bonds, bleaching clay, pet litter, adhesives, pharmaceuticals, cosmetics, desiccants, and, recently, it has been used in nano composites [1,3,5-9].

As higher the montmorillonite content of bentonite as high is the specific surface area of the material. In order to increase the specific surface and the adsorption properties of bentonite are used some “activation” methods. The most important are: acid activation, alkaline activation, pillaring, ion exchange with cations/anions, intercalation

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of organic/polymeric compounds, thermal activation [5, 10-17]. For chemical activation are used natural clays and purified clays.

In this study was performed an acid activation of natural indigenous clays using a mineral acid. In order to decrease the activated material costs we propose as feedstock natural calcium bentonite (not purified) source Oraşu Nou (Romania). This material had a higher content of montmorillonite.

There weren't found studies regarding the influence of acid activation parameters on textural properties of Romanian bentonite from Oraşu Nou (Romania).

## 2. MATERIALS AND METHODS

Acid activation was performed using hydrochloric acid of analytical grade (Fluka Chemicals). Natural calcium bentonite (Oraşu Nou, Romania) was sieved and particles with diameter lower than 70µm were used as feedstock. Activation was carried out using acid solutions with strength varying between 0,1 and 10 moles/L, at 90°C temperature in a Pyrex vessel, under vigorous stirring (Fig. 1). The solid: liquid ratio was (g/mL): 1:5, 1:10 and 1:20. After activation, the obtained slurry was washed with distilled water until there was no found Cl<sup>-</sup> in the used waters, centrifuged and oven dried at 105°C overnight.

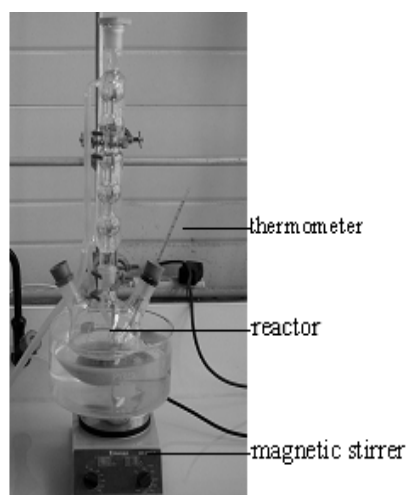


Fig.1. Device for acid activated clays obtaining.

Specific surface area (determined by Brunauer, Emmett and Teller – BET - technique), pore size distribution (Barrett, Joyner and Halenda - BJH - calculation) and nitrogen adsorption/desorption isotherms were performed using a Coulter SA 3100 Surface Area and Pore Size Analyzer.

## 3. RESULTS AND DISCUSSIONS

According to the mineral composition (Table 1), natural bentonite clay used as feed stock has a high content in montmorillonite (60% max.).

Table 1. Mineralogical composition of natural bentonitic clay.

Component	Montmorillonite	Cristobalite	Quartz
%	55-60	37-42	3

Clays pore are classified as micro pores (diameter lower than 2 nm), mezzo pores (diameter between 2 and 50 nm) and macro pores (diameter higher than 50 nm) [18]. Pore size distribution curves were realized *via* Barrett, Joyner and Halenda (BJH) method that use Kelvin equation.

In respect with acid activated clays, natural bentonitic clay exhibit macro-, mezzo- and micro pores (Fig. 2).

By acid activation, the initial micro pores are transformed in mezzo pores (Fig. 3-4). Pores size distribution curves are bimodal and present two maximum points, at 3.75 nm and 4.8 nm (Fig. 3) respectively 3.91 nm and 7.25 nm (Fig. 4). For the same solid: liquid ratio (1g/10 mL), the surface of the pore size distribution curves augment with the concentration of  $H^+$ , the maximum being reached at 10 moles/L (concentration of acid solution for clay activation).

The characteristic peaks of mezzo porous zone in acid activated clays case (Fig. 2 and 4) present an augmentation in high that demonstrate the augmentation of mezzo porous centres due to the adjacent condensation of the layer of micro porous silicium. Figures 4 and 5 show that the new mezzo pores formed during acid activation belong to 4...35 nm interval.

Figure 5 present the  $N_2$  adsorption-desorption isotherms of two activated clays in respect with natural bentonitic clay. All isotherms are similar as shape and, according to Brunauer these are of II type isotherms [19] and present a hysteresis that correspond to the constitution of some pore aggregates with various dimensions. The isotherm shape indicates that the activated clays contain mainly mezzo pores; this confirms the results plotted by pore size distribution curves. For lower  $p/p_0$  ratio (0,05-0,25) we have an nonlinear nitrogen adsorption that indicate a mezzo porous structure. Isotherms plotted in Figure 5 indicate that the volume of adsorbed gas augment with the concentration of activated solution for the same solid-liquid ratio.

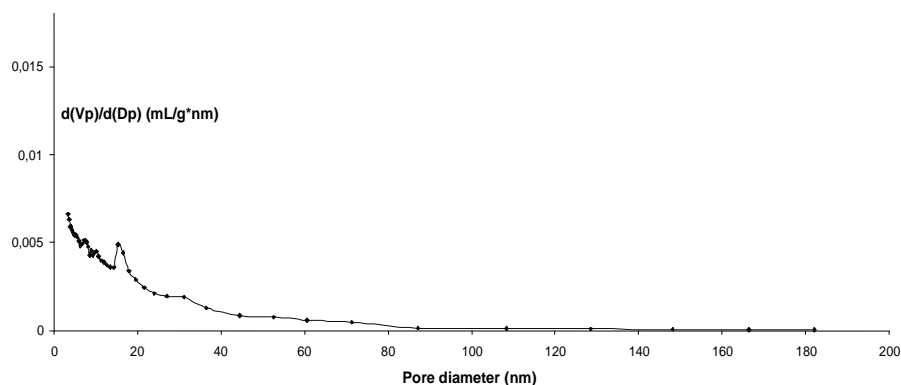


Fig. 2. Pores size distribution curve of natural bentonitic clay.

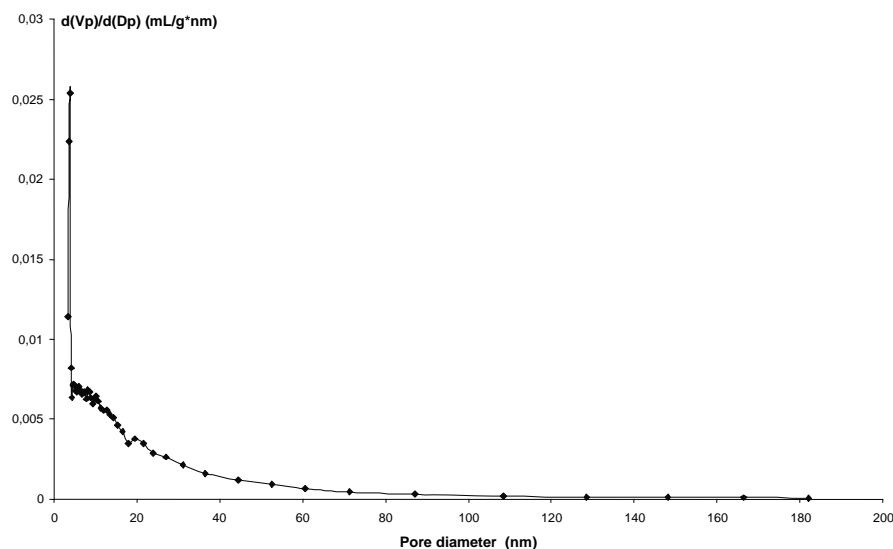


Fig. 3. Pores size distribution curve of an activated clay: concentration of activation solution = 5 moles/L, S:L = 1:10 (g/mL).

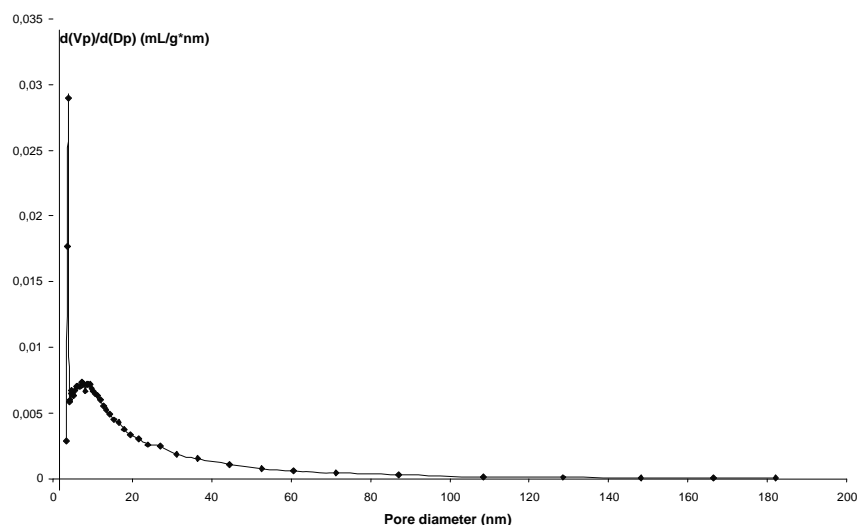


Fig. 4. Pores size distribution curve of an activated clay: concentration of activated solution= 10 moles/L, S:L = 1:10 (g/mL).

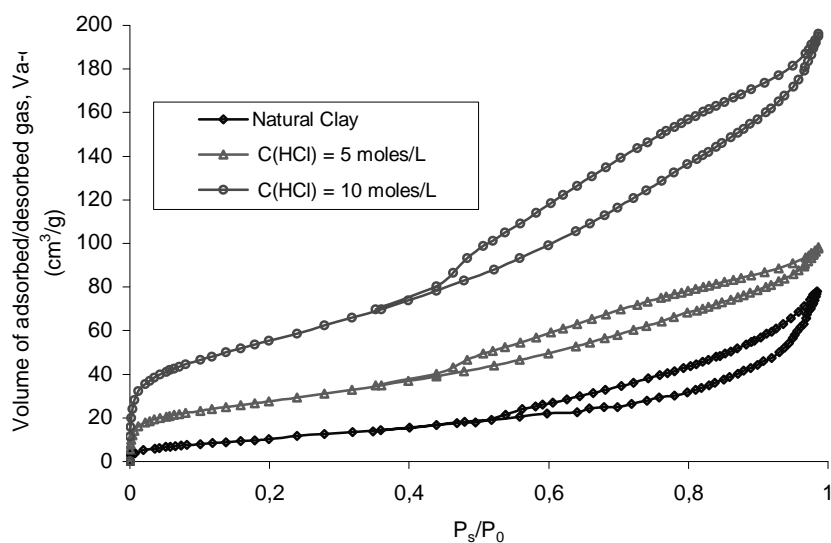


Fig. 5. Isotherm of  $N_2$  adsorption for activated and natural clay (S:L=1g/10 mL).

It is important to approach that, in the linear range of the isotherm, the monolayer and multilayer molecular adsorption are reversible. After the complete multilayer molecular adsorption ( $P_s/P_0 = 0.4 \dots 0.5$  for activated clay) begin the capillary condensation and all mezzo pores are occupied by nitrogen molecules.

Regarding the textural properties, the results plotted in Table 2 confirm that the concentration of activation solution influence the surface area (measured *via* BET method) of the activated clay.

Table 2. Specific surface area of natural and acid activated clays.

Sample	Activation parameters		Specific surface area (BET method) [m <sup>2</sup> /g]
	Concentration of acid solution [moles/L]	Solid:liquid ratio (g/mL)	
Natural bentonite clay	-	-	45.102
Activated bentonite clay	0.1	1:5	49.67
		1:10	51.06
		1:20	53.275
	0.5	1:5	49.89
		1:10	51.2
		1:20	54.03
	1.0	1:5	63.254
		1:10	66.378
		1:20	69.021
	2.0	1:5	66.250
		1:10	69.5
		1:20	74.37
	3.0	1:5	66.568
		1:10	72.975
		1:20	80.324
	4.0	1:5	69.998
		1:10	70.097
		1:20	82.325
	5.0	1:5	71.31
		1:10	77.65
		1:20	85.565
	6.0	1:5	72.345
		1:10	79.986
		1:20	90.35
	7.0	1:5	105.129
		1:10	111.016
		1:20	131.178
	8.0	1:5	145.758
		1:10	147.223
		1:20	150.075
	9.0	1:5	176.052
		1:10	179.054
		1:20	181.087
	10.0	1:5	193.67
		1:10	199.81
		1:20	202.025

By acid activation the specific surface of clays augment from 45.102 m<sup>2</sup>/g for natural bentonite to a maximum value of 202.025 m<sup>2</sup>/g if we use an acid solution with 10 moles/L concentration and 1:20 solid-liquid ratio (g/mL).

#### 4. CONCLUSIONS

Acid activation is a common method of clay structure modification in order to improve the natural clay characteristics. Acid activated clays are cheap materials that present better adsorption characteristics than the

natural bentonite. As higher is the concentration of acid activation solution higher is the specific surface area. In case of natural Romanian bentonite the specific surface area augments from 45.102 m<sup>2</sup>/g to higher than 200 m<sup>2</sup>/g. This is a result of mezzo pores developing during the acid activation. This is confirmed by pore size distribution curve and nitrogen adsorption/desorption isotherms. The resulted materials can be used as low cost adsorbent materials in environment depollution.

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