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# Investigation of the Surface Acidity of a Bentonite Modified by Acid Activation and Thermal Treatment

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The adsorption of n-butylamine from its solution in cyclohexane on acid-activated and thermally treated Kütahya/Turkey bentonite (KB) samples was followed using a UV-VIS spectrophotometric method. The experimental data were evaluated by the Langmuir adsorption equation and the total number of surface acid centers ( $n_m/\text{mol g}^{-1}$ ) was determined. The variation in  $n_m$  values as a function of the mass percent of  $\text{H}_2\text{SO}_4$  used in activation (10% -70% ) and its correlation with variations in surface area (A) and pore volume (V) as a function of the mass percent of  $\text{H}_2\text{SO}_4$  were investigated for acid- activated KB samples. The variation in  $n_m$  values as a function of thermal treatment temperature (200 °C-1300 °C) and its correlation with variations in A and V as a function of thermal treatment temperature were investigated for thermally treated KB samples and the results are discussed.

**Key Words:** Acid activation, bentonite, n-butylamine, pore volume, surface acidity, surface area, thermal treatment.

## Introduction

Bentonites are used as industrial raw materials in more than 25 application areas <sup>1,2</sup>, including the production of selective adsorbants <sup>3,4</sup>, bleaching earth <sup>5,6</sup>, catalyst beds <sup>7</sup>, carbonless copy paper <sup>8</sup> and medication <sup>9</sup>. They are also used as binders in foundries and in ceramic production since they produce muds of high plasticity with water <sup>10,11</sup>. The physicochemical properties of bentonites play a major role in all these applications. Bentonites may be subjected to high temperatures when used in these applications and their physicochemical properties may change as a result of thermal treatment. On the other hand, acid activation of clays has attracted considerable attention in recent years. Acid-activated smectites are used as catalysts, catalyst beds, adsorbents and bleaching earth in industry <sup>12</sup>. One reason for this interest is that acid-activated clays exhibit significantly different physicochemical characteristics compared to their non-activated counterparts. One of these physicochemical properties is surface acidity.

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All of the above-mentioned applications imply the interaction of bentonite surfaces with the environment. The interactions of clay surfaces with gases or liquids, which are relevant in the fields of adsorption and catalysis, are mainly governed by acid-base interactions<sup>13,14</sup>. These interactions are also involved in particle sintering<sup>15</sup>.

It is known that clay minerals possess attractive properties as solid acids<sup>16,17</sup>. Their acidities are due to active centers on the surface that exhibit Bronsted and Lewis acidities. Such an important property, which governs most of the clay's interactions in so many application areas, needs to be determined quantitatively in relation to structural changes during acid activation and thermal treatment. Therefore, the aim of this study was to investigate the relationship between the surface acidity, surface area and pore volume of bentonite samples that were either acid activated or thermally treated.

## Materials and Methods

A bentonite sample (KB) was taken from the Kütahya beds in Turkey. The characterization of the KB sample was described in our previous study<sup>18</sup>. We used K10-K70 coded samples<sup>19</sup> obtained by the acid activation of KB samples such that the mass percent of the acid in the bentonite-acid mixture during activation was respectively 10, 20, 30, 40, 50, 60 and 70, and K200-K1300 coded samples<sup>18</sup> obtained by the thermal treatment of KB samples at respectively 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200 and 1300 °C.

The surface acidities of K10-K70 and K200-K1300 samples were determined spectrophotometrically on the basis of irreversible adsorption of n-butylamine. A UV-VIS spectrophotometer (Varian Cary 50) was used. Cyclohexane (spectroscopic grade, Riedel-de Haen) and n-butylamine (analytical grade, Merck) were used in the determination of the surface acidity of the samples.

In each experiment, a series of 50 mL conical flasks were loaded with 0.1 g of sample. A sufficient amount of cyclohexane was added to each flask, which was then stoppered in order to saturate the bentonite samples. They were kept at 298 K for 75 h. Excess cyclohexane was then discarded and the flasks were shaken mechanically for 1 h for the evaporation of excess solvent. Then 10 mL each of freshly prepared n-butylamine ( $1.0 \times 10^{-4} - 4.0 \times 10^{-2}$  M) in cyclohexane was pipetted into each flask. For the system to reach equilibrium the flasks were again shaken mechanically at 298 K for 75 h. The concentration of n-butylamine in the solution that was in equilibrium with the adsorbed n-butylamine was determined spectrophotometrically. Each experiment was repeated twice. Sorption experiments were developed at the wavelength of maximum adsorption ( $\lambda_{max}$ ) and between the solution concentrations where the Lambert-Beer law fitted.

The adsorption produces adsorption isotherms of the first class type according to the Brunauer classification<sup>20</sup>. The chemical interaction between the adsorbate and surface is consistent with the Langmuir adsorption isotherm equation

$$c/n = (1/Kn_m) + c/n_m \quad (1)$$

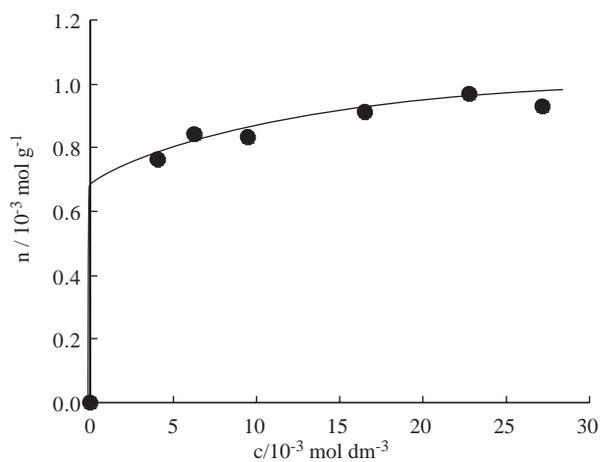
where  $c$  is the concentration of substrate in solution that is in equilibrium with the adsorbed substrate,  $K$  is the kinetic equilibrium constant of adsorption,  $n$  is the amount of adsorbed substrate per gram of solid, and  $n_m$  is the monolayer coverage, which corresponds to the theoretical amount of solute that covers all the sites in 1.0 g of sample.

## Results and Discussion

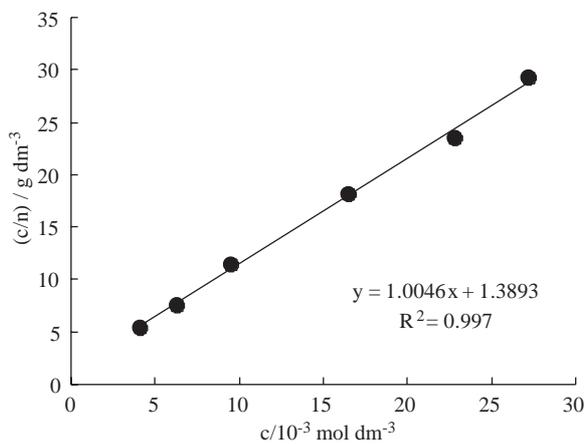
In surface acidity determination methods that are founded on the adsorption of a base from its solution, the amount of base that will cover the solid surface with a monolayer is defined as the surface acidity corresponding to the  $pK_a$  of the base used. According to this definition, Campelo et al.<sup>21</sup> claim that the total surface acidity of alkali promoted  $AlPO_4$  was determined in similar experiments in which cyclohexylamine ( $pK_a \approx 10.6$ ) was used as a base. Similarly, in this study in which n-butylamine ( $pK_a \approx 10.9$ ) was used as a base, the total surface acidities of the samples were determined. Moreover, n-butylamine reacts with the clay's surface either by binding the available protons of the surface of the clay or by sharing the unshared electron pair of its nitrogen with the electron accepting groups on the clay's surface. Therefore, the surface acidity determined by this method represents a combination of its Lewis and Bronsted acidity.

The Langmuir adsorption isotherms (n-c and c/n-c) of the acid activated bentonite sample K30 are respectively shown in Figures 1 and 2 as examples. The A and V values of the same samples were determined in our previous work<sup>19</sup>. The variations in  $n_m$ , A and V as a function of the mass percent of the acid used in activation are comparatively shown in Figure 3. It was observed that  $n_m$  gradually increased and reached its maximum when the mass percent of the acid was 40% and then decreased again. We can presume that the chemical changes that take place in the structure during acid activation lead to octet vacancies in the crystal lattice, thus leading to an increase in Lewis acidity. It is known that during acid activation, in order to provide charge equilibrium, the protons of sulfuric acid replace primarily the exchangeable cations such as  $Na^+$  and  $Ca^{++}$  that are between the layers. These protons do not contribute much to surface acidity. On the other hand, the protons of sulfuric acid cannot fill in the empty spaces left by ions such as  $Al^{3+}$  and  $Mg^{2+}$  that occupied the octahedron centers before being carried away by progressing activation, and hence, octet vacancies occur. It is also possible that the protons of the hydroxyl groups at the corners of the octahedrons may become more labile as a result of structural deformation due to acid activation and this may increase the Bronsted acidity, but the main reason for the increased acidity seems to be octet vacancies. In Figure 5, a good correlation was observed between  $n_m$ , A and V values as a function of mass percent of the acid, which indicated that, as the number of pores increased and surface area enlarged, surface acidity increased as a result of these structural changes. It was previously described that the empty spaces left from the above-mentioned ions carried away by progressing activation acted like micropores and mesopores. They increased the specific pore volume and their walls increased the specific surface area<sup>19</sup>. Therefore, the good correlation of the curves supports the presumption that  $n_m$  increases due to octet vacancies that occur as a result of cations being carried away by acid activation.

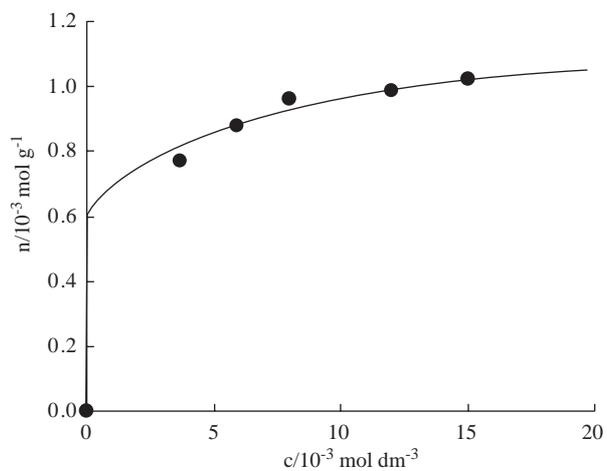
The Langmuir adsorption isotherms (n-c and c/n-c) of thermally treated bentonite sample K300 are respectively shown in Figures 3 and 4 as examples. The A and V values of the same samples were determined in our previous work<sup>18</sup>. The variations in surface acidities, specific surface areas and specific pore volumes as a function of thermal treatment temperature are comparatively shown in Figure 6. It was observed that the maximum  $n_m$  was reached at 500 °C where irreversible dehydration was completed, and another increase in  $n_m$  was observed at 700 °C, where dehydroxylation occurred. The good correlation between the curves implied that the octet vacancies resulting from structural changes due to dehydration and dehydroxylation increased the Lewis acidity. A general gradual decrease in  $n_m$ , A and V values was observed with increases in temperature and further decomposition of the structure.



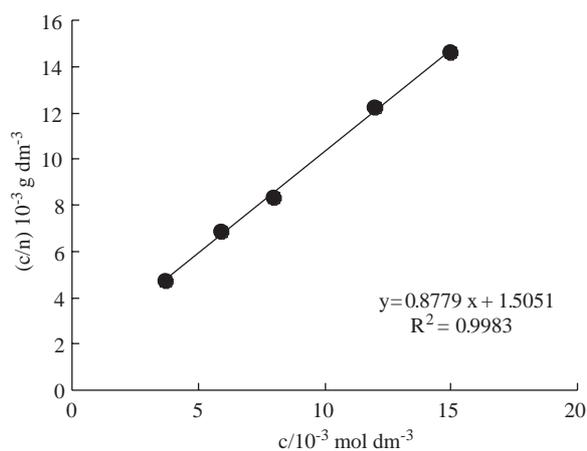
**Figure 1.** The (n-c) adsorption isotherm of the K30 sample.



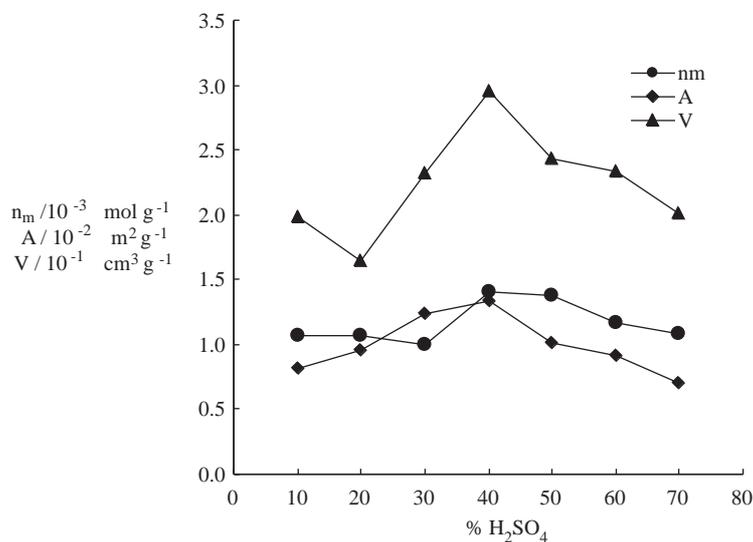
**Figure 2.** The (c/n-c) adsorption isotherms of the K30 sample.



**Figure 3.** The (n-c) adsorption isotherm of the K300 sample.



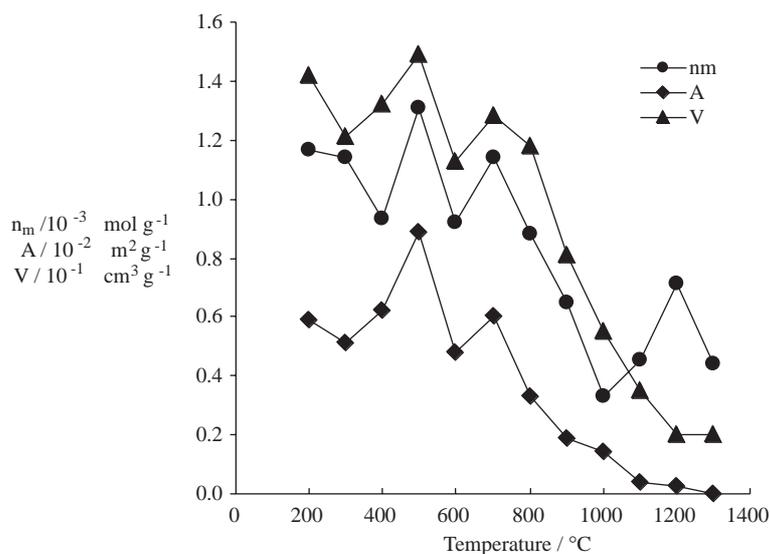
**Figure 4.** The (c/n-c) adsorption isotherms of the K300 sample.



**Figure 5.** The variations in surface acidity ( $n_m$ ), specific surface area (A) and specific pore volume (V) as a function of the mass percent of the acid used in the bentonite-acid mixture during activation.

## Conclusion

In this study, it was determined that variations in specific pore volume, specific surface area and surface acidity as a function of the mass percent of the acid used in activation were more or less parallel to each other for the case of acid-activated bentonite samples. The optimum interval where these 3 parameters were maximum corresponded to 40% of sulfuric acid. For the case of thermally treated bentonite samples, the good correlation between the  $n_m$ , A and V versus thermal treatment temperature curves indicated that increased acidity at certain temperature intervals was mostly due to increased octet vacancies resulting from structural transformations caused by dehydration and dehydroxylation. In this study, it was understood that the surface acidity, which plays a very important role in the application areas of bentonites especially when they are used as catalysts, may be adjusted to the required value by applying either controlled acid activation or controlled thermal treatment.



**Figure 6.** The variations of surface acidity ( $n_m$ ), specific surface area ( $A$ ) and specific pore volume ( $V$ ) as a function of thermal treatment temperature.

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