ASSESSMENT OF A SUITABLE METHOD TO DETERMINE THE SURFACE ACIDITY OF BENTONITE SAMPLES

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ABSTRACT

Bentonites are widely used in the industry. The evaluation of their physicochemical properties such as specific surface area, specific pore volume, pore size distribution, surface acidity e.t.c. is necessary for their best performance. Among others, the use of bentonites in catalyst bed and adsorbent production has attracted great attention in recent years, where surface acidity plays a major role in their functions. In this study, the assessment of a reliable and a practical method to determine the surface acidity of bentonite samples was realized. A method based on the adsorption of n-butylamine founded on the determination of the number of surface acid centers by using the Langmuir adsorption isotherms was chosen as a suitable, reliable and practical method to determine the surface acidity of bentonite samples.

1. INTRODUCTION

Bentonites are widely used as raw materials in the industry [1,2]. Namely, the production of bleaching earth [3,4], catalyst beds [5], selective adsorbents [6-8], carbonless copy paper [2] and medication [10] may be mentioned as some of the application areas of bentonites. Bentonites also produce muds of high plasticity with water, therefore they are used as binders in foundry and ceramic production [11,12]. The physicochemical properties of clays such as specific surface area, specific pore volume, pore size distribution, cation exchange capacity, surface acidity e.t.c. are extremely important in all these applications. On the other hand, acid-activated smectites that have attracted great attention in the production of catalysts, catalyst beds, adsorbents and bleaching earth in the industry [13] possess significantly different physicochemical properties compared to their non activated counterparts. The investigation of some of the physicochemical properties of some bentonites collected from different beds in Turkey was already undertaken in our previous studies [14-18].

In all of the above mentioned applications, bentonite surfaces interact 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 [19-20]. Clay minerals also possess attractive properties as solid acids [21-22]. The acidity of any sort of clay surface is due to active centers on the surface that

exhibit Bronsted and Lewis acidities. Therefore, being a very important property in governing most of the clay's interactions in so many application areas, the surface acidity of clays needs to be determined quantitatively.

Up to now, numerous methods have been applied to specify the surface acidity of solids [23]. Particularly, the adsorption of water and basic probe molecules followed gravimetrically [24], volumetrically and microcalorimetrically [25,26] and with IR [27,28], Raman and NMR [29] spectroscopies have been applied to investigate surface acidity. Contrarily, the desorption of such probe molecules followed by temperature-programmed techniques have also been applied [30]. Titration methods [31] and activity measurements in catalytic test reactions [32] have also been among the thoroughly applied methods. All of these studies have made considerable contribution to our knowledge about the surface acidity of solid surfaces, yet, depending upon the different objectives of each work, different aspects of surface acidity such as the type of acidity, acid strength or number of acid centers were preferentially expressed in each study. Therefore, the aim of this study was the assessment of a suitable, reliable and practical method to determine the surface acidities of either acid activated or non activated, thermally treated or non treated bentonite samples in the light of the above mentioned studies.

2. MATERIALS AND METHOD

A bentonite sample (CB) taken from the Çankırı region / Turkey supplied by Çankırı Bentonite Industries (ÇANBENSAN) was chosen as the material of this study. The characterisation of the CB sample was already given in a previous study[33]. In the experiments H_2SO_4, $CaCl_2$, NaOH, phenolphtalein, benzene, trichloroaceticacid, n-butylamine, 2,4 dinitrophenol (all supplied by Merck) and cyclohexane (Riedel-de Haen) were used as chemicals. A UV-VIS spectrophotometer (Varian Cary 50) was used for spectrophotometric measurements.

2.1. Acid activation method
40 mL of distilled water was added on 40 g of CB sample in a stoppered flask and was stored for one night for complete humidification. Sulphuric acid was added on the sample in such a way that the mass percent of sulphuric acid in the mixture would be 40 %. Distilled water was added on this mixture which was continuously shaken until the mixture became fluid. In order to transform the sodium smectite to calcium smectite dilute $CaCl_2$ solution was added dropwise on the fluid until complete precipitation occurred. The fluid sample was kept at 95-99°C and was thus activated. The activated sample was diluted by 1L of distilled water and filtered and was washed with distilled water until it was free of SO_4^{2-} and Cl^- ions.The prepared sample was dried at 105 ° C for 5 h and was labeled as C40.

2.2. Surface Acidity Determination Methods
2.2.1. Titration Method [34]
A certain amount of C40 sample was dried at 120 ° C for 6 hours. 0.5 g of this sample was put in a conical flask and 15 mL of 0.1N NaOH was added. The flask was shaken for 10 min and the mixture was titrated by 0.1N H_2SO_4 by using phenophtalein as an indicator. The surface acidity was determined as the number of miliequivalents (n') of NaOH adsorbed per 100 g of sample.

2.2.2. Amine adsorption method I [35]
4 flasks were loaded with 0.02g of air dried C40 samples and were heated at around 190 ° C for 30 min. 2, 3, 4 and 5 mL of 0.01M n-butylamine solution in benzene was added on each flask. The flasks were kept for 120 min in a desiccator containing $CaCl_2$. 1 mL portions of the equilibrated suspensions were transferred to other flasks and were titrated by trichloroaceticacid solution in benzene by using 2,4- dinitrophenol as an indicator.

2.2.3 Amine adsorption method II
The above method was repeated using this time cyclohexane as a solvent instead of benzene.

2.2.4. NaOH adsorption method
By considering the above amine adsorption methods, this method was developed for an aqueous medium determination.

12 flasks were loaded by 0.5 g of C40 samples.12 different NaOH solutions having various concentrations between 0.007N-0.052N were prepared. 15 mL of each NaOH solution was added to a different flask. The flasks were then stoppered and shaken and stored for 24 h in a desiccator containing $CaCl_2$. 5 mL of each equilibrated solution was transferred to a different flask and titrated by 0.052 N H_2SO_4 by using phenolphtalein as an indicator.

2.2.5. Spectrophotometric Amine Adsorption method [36,37]
A series of 50 mL conical flasks were loaded with 0.1 g of sample. Sufficient amount of cyclohexane was added on each flask and stoppered in order to saturate the bentonite samples. These were kept at 298K for 75 hours. 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 298K 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 (λ_{max}) and between the solution concentrations where the Lambert-Beer law was fitted.

3. RESULTS AND DISCUSSION

The pH value of the CB sample suspension was determined as 8.94.Therefore it was understood that the CB sample was an Arrhenius base. So, an acid activation was applied to the CB sample according to the method described in paragraph 2.1. The rest of the experiments were performed on hence produced C40 samples and each experiment was repeated twice. As a result of the applied titration method, it appeared that the surface acidity of C40 sample corresponded to 60 milliequivalents of NaOH adsorbed per 100 g of sample. Nevertheless, it did not seem appropriate to accept the result as a realistic representation of the surface acidity of the sample since this was a value found by only a single addition of a certain amount of base.Therefore, after a complete literature survey [23] of the studies on this subject mentioned in the introduction section and a preliminary elimination according to the objective and practicality,our studies were concentrated on base adsorption methods.

In the Amine Adsorption Method I in which benzene was used as a solvent, it has not been possible to reach at a conclusive result. The reason might be the competitive adsorptions of benzene and n-butylamine. This point is being considered to be investigated in our further studies. In the adsorption methods mentioned in paragraphs 2.2.3-2.2.5, the adsorption produces adsorption isotherms of the first class type according to Brunauer classification [16]. The chemical interaction between the adsorbate and surface is consistent with the Langmuir adsorption isotherm equation:

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

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 1.0g of sample. The total number of monolayer acid centers for 1.0 g of sample (N) can be calculated as follows:

$$N / g^{-1} = (n_m / mol\ g^{-1}) \times (6.02 \times 10^{23} / mol^{-1}) \qquad (2)$$

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.[37] claim that total surface acidity of alkali promoted $AlPO_4$ was determined in similar experiments in which cyclohexylamine (pK_a 10.6) was used as a base. Similarly, in this study in which n-butylamine (pK_a 10.9) was used as a base, we can state that 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 clay's surface. Therefore, the surface acidity determined by these 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 C40 according to the three methods are respectively shown in Figures 1-6. The n_m , N and K values deduced from the Langmuir adsorption isotherms for the acid activated CB sample according to the different methods applied are listed in Table 1. It was observed that the base adsorption methods realized in aqueous and non aqueous media produced very similar results as listed in Table 1. The apparent similarity of the results obtained by the NaOH Adsorption Method developed in this study and the Amine Adsorption Method II was quite satisfying since this will give us an oppurtunity to use either method depending upon the aqueous or non aqueous medium requirement. On the other hand, Spectrophotometric Amine Adsorption Method possesses more practicality in non aqueous medium from the instrumental point of view.

Table 1. The n_m, N and K values of C40 samples, obtained by Amine Adsorption Method II, NaOH Adsorption Method and Spectrophotometric Amine Adsorption Method

Method	n_m / mol g^{-1}	N / g^{-1}	K
Amine Adsorption Method II	$1{,}114 \times 10^{-3}$	$6{,}706 \times 10^{20}$	2900,38
NaOH Adsorption Method	$1{,}063 \times 10^{-3}$	$6{,}399 \times 10^{20}$	249,26
Spektrophotometric Amine Adsorption Method	$1{,}206 \times 10^{-3}$	$7{,}26 \times 10^{20}$	1315,54

Figure 1. The Langmuir Adsorption isotherm (n-c) of C40 sample obtained by
Amine Adsorption Method II.
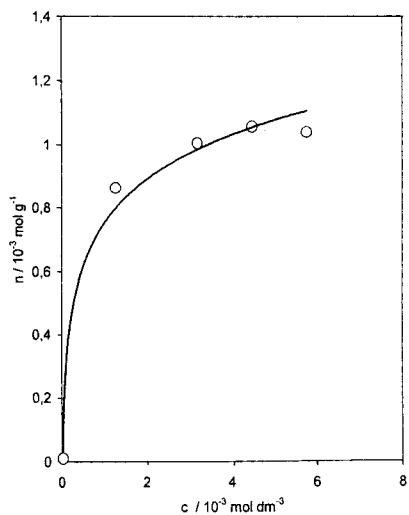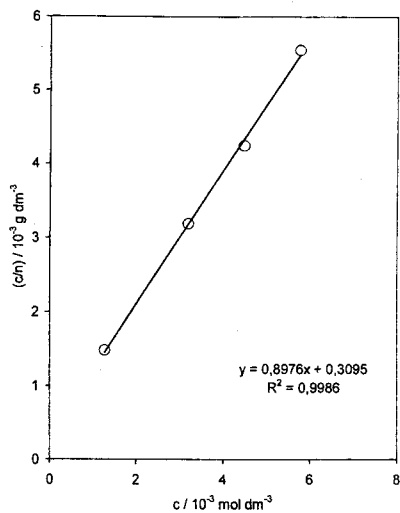

$$y = 0,8976x + 0,3095$$
$$R^2 = 0,9986$$

Figure 2. The Langmuir Adsorption isotherm (c/n-c) of C40 sample obtained by
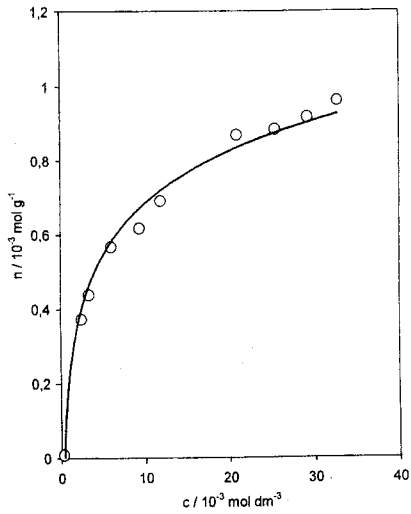Amine Adsorption Method II.

Figure 3. The Langmuir Adsorption isotherm (n-c) of C40 sample obtained by
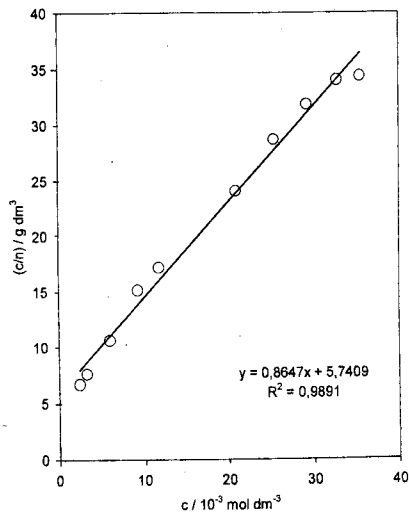NaOH Adsorption Method.

Figure 4. The Langmuir Adsorption isotherm (c/n-c) of C40 sample obtained by
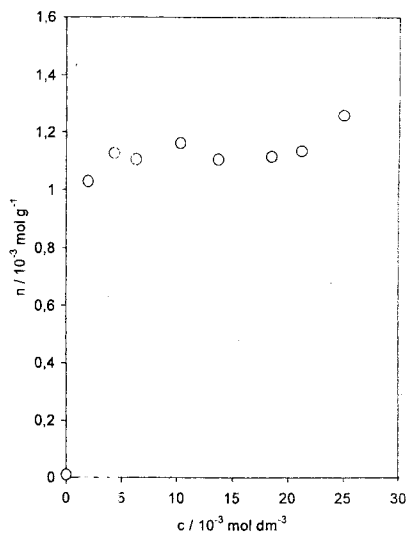NaOH Adsorption Method.

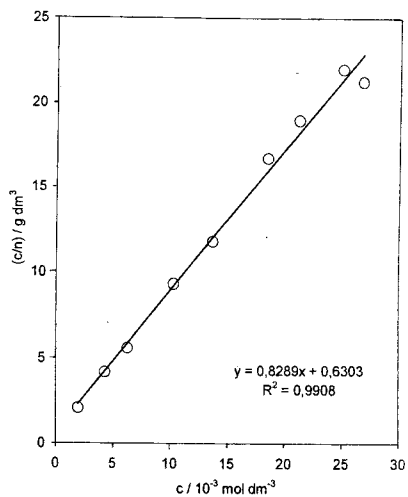Figure 5. The Langmuir Adsorption isotherm (n-c) of C40 sample obtained by Spectrophotometric Amine Adsorption Method.

Figure 6. The Langmuir Adsorption isotherm (c/n-c) of C40 sample obtained by Spectrophotometric Amine Adsorption Method.

4. CONCLUSION

The assessment of a method to determine the surface acidity of bentonites that are widely used in the industry mostly in the fields of adsorption and catalysis was necessary. In the light of a complete survey of literature, base adsorption methods were chosen appropriate for the objective of determining the total number of Lowry and Bronsted acid centers. According to the results obtained in this study the three methods based on the adsorption of a suitable base, either in aqueous or non-aqueous media, founded on the determination of the number of surface acid centers by using the Langmuir adsorption isotherms was proven to be a suitable, reliable and practical method to determine the surface acidity of bentonite samples.

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