USE OF MODIFIED CLAYS OBTAINED BY PILLARING IN GAS PURIFICATION

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The purpose of this paper is to characterize the modified clays obtained by pillaring and their application in gas purification by the adsorption process. The clays were characterized by the: nitrogen adsorption/desorption analysis for determination of the pore size and NH_3-TPD measurements to determine the total acidity. Following the analysis of the material characterization was selected the representative material for the ammonia adsorption process. The kinetics of adsorption was determined in the fixed bed.

Keywords: pillaring, pore size, total acidity, adsorption capacity, removal efficiency, gas purification

Symbols

C_0	initial concentration [mg·L^{-1}]
C	final concentration [mg·L^{-1}]
D	column diameter [m]
$\overline{d}_p$	average particle diameter [m]
L_0	adsorbed bed height [m]
m_{ads}	adsorbed mass of ammonia [mg]
m_p	mass of adsorbent particles [mg]
q_{ads}	adsorption capacity [mg/g]
Q_T	gas mixture flow [L·s^{-1}]
t	adsorption time [s]
η_{ads}	removal efficiency of the ammonia adsorption [%]

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1. Introduction

Air purification is a complex process regards the design and implementation of the efficient adsorption equipment and process control. In order to obtain higher performance must take into account the properties of the adsorbent and their dynamic and kinetic characteristics.

The main characteristics of the adsorption process are: small particle retention (colloids), the higher retention of the components which are in small concentration (impurities that induce undesirable odour, taste and coloration), the selectivity of the adsorbents towards some components of the mixture [1].

Depending on the impact of the air pollutants on the environment, they can be divided into: dust and aerosols (from natural environment), heavy metals (Hg, Cd, Pb, As, Cr, Cu), sulphur oxides (SO_2, SO_3), nitrogen oxides (NO, NO_2, N_2O), ammonia (NH_3), carbon oxides (CO, CO_2), volatile organic compounds (COV), and acid gases and aerosols (HCl, HF, H_2SO_4, HNO_3), ozone (O_3), odorant molecules, persistent organic products (POP), dioxins, furans, and others [2].

The adsorbents used at the industrial scale are the materials which can be partially or completely changed in their active anionic [3, 4, 5] or cationic groups [6-10] or both simultaneously for other ions in solution such as ion exchange and materials with double function like zeolites [11]. The adsorbent which provided a higher adsorption capacity is porous adsorbents [12, 13].

Thus, in function of the pores presence the adsorbents can be divided into: microporous (silica-alumina, synthetic zeolite dried, activated carbon, silica gels with very fine pore (porous glass), mesoporous (alumino-gels, active alumina and some catalysts based on the silica-alumina) and macroporous (porous adsorbents, chromatography and some catalysts used in organic synthesis) [14, 15].

In the gas/vapour adsorption process the most used adsorbent is activated carbon which presents the important characteristics [16], but has some disadvantages. Although, activated carbon possessing high specific surface area to obtain a good performance, the higher cost of production and the decreased of the adsorption capacity, porosity (becomes brittle) are the main disadvantages [17].

Ammonia is a colorless gas, toxic with a strong stifling smell, reactive and corrosive. The ammonia vapors can be felt by humans in an amount of up to 50 ppm, they cause irritation to respiratory and eyes in the case that the amounts ranging from 50 – 100 ppm [18], and when the human it is exposure to higher quantity the death is induced in few minutes. Ammonia air pollution is a major problem; this being identified in gas mixtures from industrial enterprises which produce chemical fertilizers and other industrial processes [19].

This gas is soluble in water becoming odorless and more difficult to detect. Therefore, it is necessary to develop strategies to capture the ammonia on different adsorbents by simple methods based on adsorption. Other methods

include the elimination of ammonia by thermal oxidation catalytic and catalytic decomposition, but these methods are generally very expensive and produce other secondary pollutants [20, 21].

The aims of this paper are to show the behavior of the adsorbents such aluminosilicates (clays) in gas purification by adsorption [22, 23, 24]. These adsorbents present major advantages, which are: cheaper than zeolites, non-toxic, easy to handle and easier to regenerate than activated carbon.

Pillaring is the process by which in the structure of the clay minerals are introduced various inorganic cations (Al, Zr, Cr, Fe, Ti) and organic compounds with maintaining lamellar structure which present a thermal stability [24, 25].

Pillared clays have been studied specifically for their catalytic properties, but these have an important capacity for gas adsorption. Since 1991 was published a few papers concerning the study of adsorption properties of pillared clays [26-28]. By pillaring of the clays are formed a free space [29, 30, 31] which is necessary to fixed the molecules of ammonia [32, 33]. Adsorption is limited only to certain active centers of adsorption and ammonia molecules adsorbed are able to migrate to the clay surface [34-36].

In the ammonia adsorption process it is necessary that the pillared clay to have two important characteristics: high pore size and surface acidity [37-40]. For a good control of the ammonia gaseous emissions is applied as preventive action at direct source, before discharge into the atmosphere using the classical method of contact – fixed bed [41], thus the pollution is reduced by the 90-98%.

The objective of this paper is to research the concepts and technologies in the case of fixed bed adsorption for the removal of ammonia from industrial gases utilized the natural and pillared clays.

The adsorption process of ammonia in the fixed bed is very important, because is a basis for analysis of fluidized bed adsorption modified by using magnetic field [42-45].

Ammonia adsorption capacity in fixed bed in the case of the saturation conditions of the clay (q_{ads}) represents the maximum amount of ammonia which the clay layer can adsorb in some experimental conditions [16, 21]. Depending by the mass balance can be determined the adsorbed mass of ammonia (m_{ads}), eq. (1):

$$m_{ads} = Q_T \cdot C_0 \int_0^t \left(1 - \frac{C}{C_0}\right) dt \tag{1}$$

The adsorption capacity of the bed (q_{ads}) is expressed in [mol of gas adsorbed / gram of adsorbent] (eq. 2):

$$q_{ads} = \frac{m_{ads}}{m_p} \tag{2}$$

The adsorption capacity is calculated in the saturation conditions as the ratio $C / C_0 = 0.95$. The removal efficiency of the ammonia adsorption [16] (η_{ads}), is calculated by the eq. (3):

$$\eta_{ads} = \frac{Q_T \cdot C_0 \cdot \int_0^t \left(1 - \frac{C}{C_0}\right) dt}{Q_T \cdot C_0 \cdot t} \cdot 100 \tag{3}$$

The removal efficiency of the adsorption process depends on many factors: the properties of the adsorbent, the gas-solid contacting conditions and processing parameters [16].

In this study there are used sodium clays and chemically modified clays by pillaring in the adsorption process of ammonia. The adsorption capacity of the ammonia on the clays is determined in various fixed bed conditions through the application of equations (1) and (2) and are identifying the optimal conditions by calculating the removal efficiency with equation (3).

2. Materials and methods

The materials used in this study are sodium clays (montmorillonite type):

- the raw material is commercial sodium clay, thermal untreated, which is supplied from Sigma Aldrich – named NaClay;
- the pillared clay prepared in the laboratory by the classical pillaring (ex-situ method) starting from raw material like NaClay [7, 30].

Preparation of the aluminium pillared clay

5 grams of NaClay are placed in distilled water (2% w/w). The clay suspension is stirring for two hours before the addition of the pillaring agent.

The pillaring agent is previously prepared from a solution of $AlCl_3 \cdot 6H_2O$ (0.2M) and NaOH (0.2M), with molar ratio OH/Al=2.2. The intercalation consist in adding drop by drop the pillaring agent in different amounts of aluminum cations (5; 12.5; 20 meq Al/g clay) in the clay suspension under stirring at room temperature. In this conditions are formed the intercalated clay with aluminum cations. Intercalated clay is separated from the mother liquid by decantation and is washed until the complete removal of chorine ions in the wash water and then is filtered under vacuum. After filtering the clay is recovered, dried at 120^0C for 4

hours and calcined for 2 hours at different calcinations temperature (300^0C, 400^0C, 500^0C). The pillared clay was named Al-PILC.

Characterization methods

1. NH_3-TPD (Ammonia - Temperature Programmed Desorption)

Total acidity was determined on sodium clay and pillared clay with aluminum cations by the method of temperature programmed desorption using molecules with basic character like ammonia. The main component of the experimental system is the furnace which is made by the ten ceramic bars arranged concentrically around a micro reactor. On these bars are found the spiral which is made from kantal and develops the necessary heat for the optimum thermal regime led by a computer. To reach the center of the reactor where is the thermocouple used for the measuring, the heat must to pass through three glass walls. At low temperature, the heat is transferred by conduction and at elevated temperatures over 300^0C by radiation. The thermocouple from the reactor and the column are from Cromel-Alumel with diameter of 0.7 mm, which can resist at higher temperature of 750^0C.

The plant operates under a nitrogen atmosphere. In the micro reactor are placed maximum 0.2 g clay in the fixed bed, and this is introduced into desorption column. Ammonia is introduced only during the experiment at 150^0C for 20 minutes. The desorbed ammonia by the temperature programmed desorption method was bubbled through the tubes which containing H_2SO_4 solution, followed by titration of excess with NaOH solution in the presence of Tashiro indicator. Total acidity is expressed in μmol NH_3 desorbed/ g clay.

2. Nitrogen adsorption/desorption

The structural characterization of the pillared clay selected in relation with NaClay was carried out by determining the pore size distribution by the adsorption/desorption of nitrogen. All this are measuring using Coulter SA 3100 Surface Area and Pore Size Analyzer.

The gas analyzed was nitrogen with 99.9% purity which is heated to boiling point of 77.3 K. Samples before to be analyzed was degassed at 120^0C for 240 minutes to remove any traces of impurities and water from internal structure.

Preparation of the materials for adsorption

The adsorbent materials used in the ammonia adsorption in fixed bed were: sodium clay untreated thermal and pillared clay selected after characterization. Sodium clay was supplied as a powder for to obtain clay particles, this was mixed with distilled water in a ratio of 1:3. The agglomeration of the particles was carried out by drying at a temperature of 110^0C for 42 hours and then grinding. NaClay and Al-PILC were separately sieved using a device Fischer Bioblock Scientific at the amplitude of 60 for 3 minutes [43].

Table 1 presents the experimental matrix for ammonia adsorption tests in fixed bed using the clay particles of NaClay and Al-PILC.

Table 1

Experimental matrix

Materials	C_0 [ppm]	$\overline{d}_p$ [$\cdot 10^{-3}$ m]	L_0 / D [-]
NaClay	3400	0.75	1
			2
		1.50	1
			2
Al-PILC		0.75	1
			2
		1.50	1
			2

The experimental plant (fig. 1) is a transparent adsorption column made by Pyrex, equipped with a porous plate (60-100 μm) used for a uniform distribution of the gas and to support the adsorbent particles layer. The gas mixture consists of anhydrous ammonia (purity 99.9%) and compressed air. Ammonia is provided from a bottle whose flow is controlled by a Brooks Shorate flowmeter (0-2.5 L·min^{-1}). The compressed air passes through a drying column with granular drierite particles, whose flow is regulated by a Brooks Shorate flowmeter (0-60 L·min^{-1}).

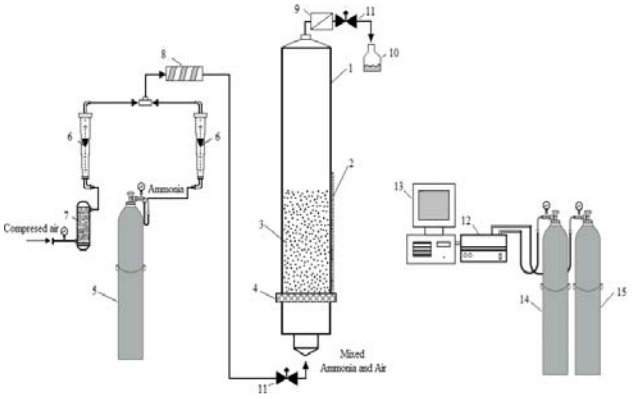


Fig.1. Experimental set-up
1 – adsorption column; 2 – scale; 3 – fixed bed of adsorbent particles; 4 – porous support; 5 – anhydrous ammonia bottle; 6 – flow meters; 7 – air desiccators column; 8 – gas mixing; 9 – air filter; 10 – acid solution; 11 – sampling points; 12 – micro-gas-chromatograph; 13 – computer; 14 – hydrogen bottle; 15 – argon bottle

The gaseous mixture upward through the adsorption column by a porous support, crossing the fixed bed of adsorbent particles according to the flow meters of the gases and are out on the top of the column.

The quantitative assessment of the adsorbent kinetics was carried out by calculating the ratio C / C_0 . The concentration is determined by the micro-gas-chromatograph Agilent 3000A MicroGC connected to a computer (France). This

device function based on the hydrogen and argon at a pressure which must be adjusted to 5 bars.

Computer screen automatically displays the concentration of ammonia, air, carbon dioxide and water expressed in ppm (parts per million). The test results were determined by reference to the calibration curve made in the six-point prior to the actual adsorption tests. The concentration of the components is proportional to the peak area of the experiment.

In order to avoid the transport of the fine particles in the top of the column is placed a filter. The adsorption is produced until the fixed bed of particles is saturated with the ammonia. Non-adsorbed ammonia is removed and neutralized by an acidic solution and the saturated particles will be regenerated.

3. Results and discussions

Before to be use in the adsorption tests NaClay and Al-PILC clays was characterized to determined the total acidity of the surface and the pore size distribution of adsorption/desorption of nitrogen.

Clays characterization

1. NH_3-TPD measurements

By the NH_3-TPD method clay come into contact with ammonia until saturation and the molecules are adsorbed by physical and/or chemical process, and by the application of the thermally program are desorbed from the clay surface. Ammonia molecules are fixed by hydrogen bonds or dipole interactions of the clays in the interlamellar spacing [30]. Total acidity represents the total amount of ammonia released by the programmed desorption by gram of clay. The number of desorbed molecules is equal with the number of the adsorption centers on the clay surface. Ammonia desorption temperature range is 150-500^{0}C. In the table 2 is presented the total acidity ($\mu mol \cdot g^{-1}$) at different temperatures for clays calcined.

Total acidity increases two times in the case of the pillared clays compared with the raw materials, NaClay. The increase of the total acidity at different temperatures is due to the structural change of the clay by the introduction of the aluminum cations. By increasing the temperature from 300^{0}C to 500^{0}C the metal oxides are formed which act as pillars which separating the layers of the silicate from the clay. Clays Al-PILC (2), Al-PILC (5) and Al-PILC (8) have many active centers remain stable after calcinations and the ammonium ion (NH_4^+) are fixed on the clay surface.

Table 2

Total acidity of the clays at different temperatures

Materials	Molar ratio [OH/Al]	Ratio [meq Al · g^{-1} clay]	Calcined temperatures [^{0}C]	Total acidity [µmol·g^{-1}]
NaClay	-	-	-	180
Al-PILC (1)	2.2	5	300	399
Al-PILC (2)			400	406
Al-PILC (3)			500	222
Al-PILC (4)		12.5	300	384
Al-PILC (5)			400	437
Al-PILC (6)			500	236
Al-PILC (7)		20	300	390
Al-PILC (8)			400	403
Al-PILC (9)			500	291

The clays Al-PILC (3), Al-PILC (6) and Al-PILC (9) present a lower total acidity because the calcination temperature is 500^{0}C and around of this value the metal pillars are gradually degraded and does not allow the fixation of the ammonia molecules. The best results for total acidity were registered by Al-PILC (5) of 437µmol·g^{-1}.

2. Nitrogen adsorption/desorption

By the analysis of the adsorption/desorption with nitrogen is determined the curves of the pore size distribution by the BJH method (Barret Joyner and Halenda) which is based on the Kelvin equation for the raw material NaClay (**fig. 2**) and Al-PILC (5) (**fig. 3**).

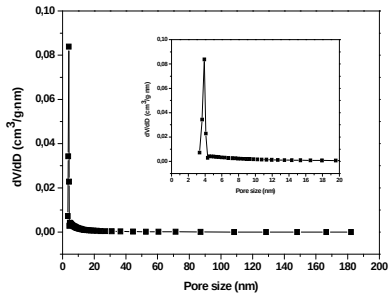


Fig. 2. The pore size distribution for NaClay

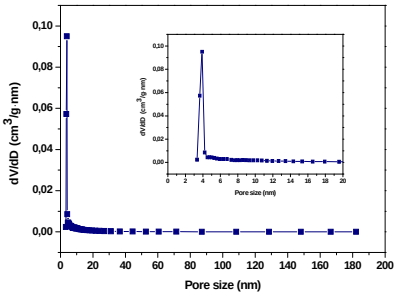


Fig. 3. The pore size distribution for Al-PILC (5)

From the experimental results obtained (fig. 2 and fig. 3) the clays containing mainly mesopores with a range size between 2 to 20 nm. NaClay presented two peaks for the pore size distribution, namely: one at 3.91 nm

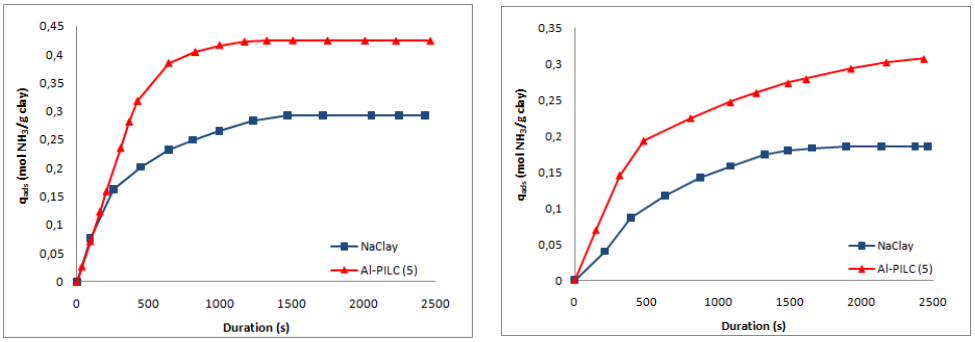
recording a pore volume (V_p) of 0.08364 $cm^3 \cdot g^{-1} \cdot nm^{-1}$ and other peak, less representative at 4.54 nm with V_p of 0.0042 $cm^3 \cdot g^{-1} \cdot nm^{-1}$. After the pillaring process the porosity of AI-PILC (5) increases. This increases is confirmed by the V_p value to the 0.0954 $cm^3 \cdot g^{-1} \cdot nm^{-1}$ at a maximum peak of 3.91 nm.

The increase in the height of the characteristics peak of the Al-PILC (5) compared to NaClay in particular in the mesopore region is due to the increased of the mesopores volume.

Kinetic of ammonia adsorption in the fixed bed

The adsorption of ammonia from a gas mixture (ammonia and air) was carried out in a fixed bed. Before to start the adsorption process the particles was dried at 120^0C for 8 hours to evaporated the water molecules.

In fixed bed adsorption tests were monitories the influence of thermal treatment applied in the pillaring process of the NaClay to obtain Al-PILC (5). Fig. 4 (a) and (b) shows the kinetics of adsorption for NaClay material (untreated) and Al-PILC (5) (treated at 400^0C).

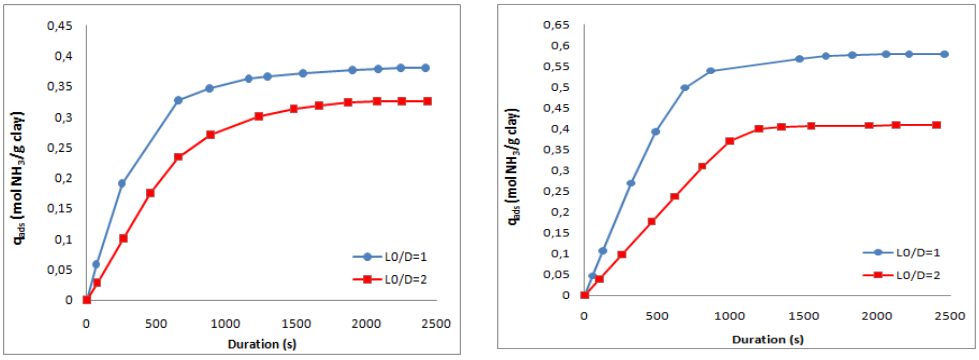


(a) (b)

Fig. 4. Influence of the thermal tratment applied of the clay on the adsorption capacity ($C_0 = 3400\,ppm$, $\overline{d}_p = 1.5mm$): (a) $L_0 / D = 1$; (b) $L_0 / D = 2$

By the thermal treatment on the clay surface are forms active centers able to fix the ammonia. Al-PILC (5) clay presented the ammonia adsorption capacity of 0.42 mol of NH_3 /g clay for the geometric simplex $L_0 / D = 1$ and respectively 0.3 mol of NH_3 /g clay for $L_0 / D = 2$. In both cases the adsorption capacity is higher than NaClay, untreated clay.

The ratio L_0 / D involves increasing the amount of clay particles in the fixed bed. The influence of the ammonia adsorption capacity is shown in the fig. 5.



(a) (b)

Fig. 5. Influence of the L_0 / D ration on the ammonia adsorption capacity

($C_0 = 3400\,ppm$, $\overline{d}_p = 0.75mm$): (a) NaClay; (b) Al-PILC (5)

In the case of fixed bed the NaClay at $L_0 / D = 1$ ratio shows the ammonia adsorption capacity of 0.37 mol of NH_3 adsorbed/ g clay which is higher than the geometric ratio $L_0 / D = 2$ where the adsorption capacity is 0.32 mol of NH_3 adsorbed / g clay. The same behavior is presented in the case of Al-PILC (5) with the adsorption capacity of 0.57 mol of NH_3 adsorbed / g clay in the case of ratio $L_0 / D = 1$ and 0.40 mol of NH_3 adsorbed / g clay for $L_0 / D = 2$. The removal efficiency for the case of operating in the fixed bed at different geometric ratio is presented in the fig. 6.

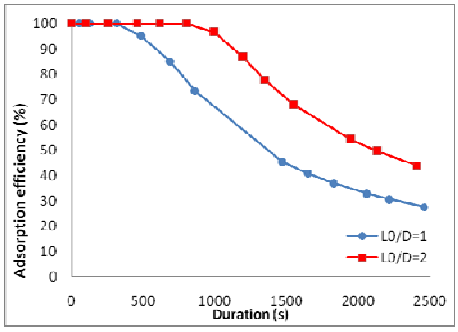


Fig. 6. The removal efficiency of the ammonia on Al-PILC (5)

($C_0 = 3400\,ppm$, $\overline{d}_p = 0.75mm$)

The results from fig. 5 are in accordance with the literature; as the fixed bed adsorption occurs in a limited area named the mass transfer zone which is moving from the inlet to the outlet of the column as the clay is saturated. The mass transfer inside it shows a gradient concentration of variable size. In the layer of Al-PILC (5) particles with geometric ratio $L_0 / D = 1$ are shows a higher

concentration gradient induces by the higher amount of adsorbed ammonia as compared to $L_0 / D = 2$. Due to the accumulation of ammonia in time the gradient concentration is reduced. But, the adsorption process is effectively in the case of the layer $L_0 / D = 2$ in which the saturation occurs after no more than 900 seconds, according to fig. 6.

4. Conclusions

Experimental studies have focused on obtaining the materials with acidic properties and porous morphology to be a good adsorbent for gaseous pollutants such ammonia. By pillaring the clays present a higher total acidity compared to the raw material providing a more accessible surface retention of ammonia. The material selected, Al-PILC (5) for the ammonia adsorption was characterized to verified the porosity and was found a great mesoporous number (2-20 nm). Thermal treatment has a positively influences on the adsorption capacity due to the porous structure that allows the retention of high concentrations of ammonia.

Therefore, in the future is recommended to be used in the fixed bed adsorption process the particles with a higher granulometric class $\overline{d}_p = 1.5mm$ and in the intensive adsorption processes such as the fluidization bed the particles with $\overline{d}_p = 0.75mm$. The removal process efficiency of ammonia is obtained at optimum ratio, $L_0 / D = 2$, because the particles which form the layer are saturated after 900 seconds when the efficiency starts to drop by 96%. According to the experimental results, the Al-PILC (5) investigated may be used as an adsorbent effective in purifying air as basic compounds such as ammonia.

In the future, the Al-PILC (5) with $\overline{d}_p = 0.75mm$ it will be used as an adsorbent with geometric ratio higher than $L_0 / D = 2$ for the intensive adsorption processes in fluidized bed. In addition, these particles will enter in the constitution of layers like mixed type or mixed multi-layer with other types of magnetic particles used in magnetic field.

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