Silver Adsorption on the Low Temperature Activated Alumina Grades. I. Adsorption Capacity and Kinetics

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Abstract: Aluminum hydroxide is a key product for the industrial production of alumina and aluminium, ceramics insulator and refractories, desiccants, absorbents, flame retardants, fillers for plastics and rubbers, catalysts, and various construction materials. The production of these arrays of useful material products is grounded on the multiple thermal decomposition pathways of Al(OH)₃, which involve major crystallographic dislocations and many microstructure reconfigurations on variable lines of phase transitions, from the raw material up to large varieties of precursors and commercial grade products. A wide range of literature on this subject is available, and recent reviews cover suitable information about preparation and characterization of different activated alumina products with specific properties and applications. In our previous papers, there was studied the mechanisms of aluminum hydroxide phase transitions, during low temperature calcination, namely, at 260ºC, 300ºC, 400ºC and 600 ºC, under chosen particularly conditions, for promoting the nucleation of the amorphous phases. Collected data suggest that raw aluminum hydroxide; dried, milled and classified is a precursor for the new low temperature activated alumina transition phases, carrying distinctive characteristics and properties, due to products enrichment in amorphous phases. Accordingly, as effects of the main driving factors (temperature and rate of heating, and initial particle size dimension) on the aluminum hydroxide as new precursor, notable changes were observed in products mineral composition, morphology and specific surface area, pore size, pore distribution, and the particle size distribution. Beside, some other secondary effects have to be apprehended. For example, the main phase transition process dynamic factors control over some physical and technical properties of the new products, like: absolute density, brightness, oil absorption capacity and water absorption capacity. The purpose of this work was to continue the characterization of low temperature activation alumina products, and also, to measure the adsorption capacity and to reveal adsorption kinetics mechanisms. Thus, the first step of survey was silver adsorption maximum capacity measurements for all sample prepared by heating the precursor alumina hydroxide, milled and classified as 5 different dimension size fractions to 260, 300, 400 and 600ºC. Hereinafter, four samples, carefully selected as representative for the entire lot of samples, were used for the study of kinetics mechanism and data fitting to the adequate kinetic equations. Confident data validate the pseudo second order kinetic model for the entire activation process, independently of samples heating temperature and particles dimension.

Keywords: aluminium hydroxide, activated alumina, silver, waste water, adsorption, kinetics

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1. Introduction

Metallic silver has many industrial uses in the production of mirrors, photographic films, batteries, electrical and electronic components, catalysts and antimicrobial materials, as well as anticorrosive materials and galvanic coatings. Due to the excellent properties of silver, such as malleability, high thermal and electrical conductivity, high resistance to corrosion and oxidation, its widespread use in various fields of industrial use has led to a significant impact of silver on the environment and especially on waste waters. Silver, as toxic threat for health and environment is acting by full toxicity to all living cells, by depositing around nerves and in deeper skin layers, which may cause permanent skin damage and by associating with environmental contamination of other toxic heavy metals such as mercury and lead. Also, silver contributes to antibiotic resistance, disturbs bacterial activity when cleaning sewage and prevents the use of sludge as fertilizer, needed for nutrient recycling [1-6]. The main pollution sources with silver are: wastes from batteries production and recovery (Ni, Cd, Ag), electric and electronic technology wastes (Cu, Sn, Ag, Ni, Al, Zn), wastes from X-ray films production and from their processing (Ag), as well as the wastes from the industrial metal finishing processes (Cr, Ni, Cu, Zn, Au, Ag, Cd) [7-11]. These materials are usually processed by the thermal technologies, including refining and smelting [11-14] and hydrometallurgical and bio-metalurgical technologies, including leaching, cementing, reducing agents, peeling, electro-coagulants, adsorbents, electro-dialysis, solvents extraction, ion exchange resins and bio-sorbents [15-18].

There are three important features of the silver recycling processes. First is flexibility of the applied recycling technologies for wastes with variable origin, sources and compositions. Second is the economy of recycling technologies in the terms of costs and marketability. Third is the silver toxicity and requirements to prevent secondary pollution by technology itself or by reactants used in silver separation. For these three reasons, new relevant studies are continuously carried out for improving silver recovery processes and finding new friendly environmentally technologies. Beside classical hydrometallurgical processes, like dissolution and precipitation [19-21] and solvent extraction of silver [22-24], new other technologies were studied for improving performances in the silver recovery and lessening the production costs. As examples, below are presented the recent studies concerning the silver adsorption from waste industrial waters on different type of low cost materials (for decreasing costs) and modified materials (for improving performances) [25]. Old adsorbent materials, like activated carbon [26-28] and natural ion-exchanging compounds (like perlite, clinoptilolite, vermiculite) modified or non-modified [29-32], were re-evaluated. Also, some new adsorbents based on silicate compounds have been tested recently [33-36]. Other research topics on silver recovery and recycling include the testing of various mixed adsorbents formulations based on chitosan [37, 38], the testing of bioadsorbents [39, 40] and synthetic polymer adsorbents [41,42], and the study of coagulation, as a method of recovering silver from residuals waters [43-45]. However, adsorption-desorption processes remain a large field of investigation, due to their selectivity for different metal ions and the variety of available materials at reasonable prices. At the same time, the increased interest in obtaining materials with adsorbent properties has grown in the last decade, due to the availability of materials with large specific surfaces, adequate pore distributions and with significantly increased reactivity, generated by the large number of active centres on the particle surface. An important class of adsorbents with multiple applications, coming from common sources of alumina, is manufactured under the name of low calcination temperature alumina products. Also, there are available numerous reviews about manufacture, characterization and application of this category of alumina products [46-60]. The low calcination temperature alumina products are the molecular species emerging during aluminium hydroxide dehydroxilation at temperatures lower than the last phase transitions to α-Al₂O₃. During dehydroxilation, the precursor phase, which is gibbsite, may undergo various phase transitions, arranged in one of two lines of successive transitions and recrystallizations:

Line 1: Gibbsite χ-Chi ϴ-Kappa α-Alfa Line 2: Gibbsite Boehmite γ-Gamma δ-Delta Θ-Teta α-Alfa
The precursor purity and its mineral properties control the row of transitions which has priority. In fact, four dynamic factors control the entire process: a) the certain processing of the gibbsite or boehmite, as precursors targeting a particular phase transition; b) the final temperature and rate of heating; c) the particles size dimension of precursor phase before the heating treatments; d) advanced grinding and intensive mechanical activation before or during the precursor thermal activation. All these driving factors and their influence on gibbsite phase transitions have been presented in our previous papers [61-64]. Additionally, some more information about the the gibbsite phase as precursor, manufactured by Alum SA Tulcea Romania from Sierra Leone bauxite by Bayer modified process (under European Regional Development Fund through the Competitiveness Operational Program of 2014–2020), can be find in the papers [61-63, 65-68]. This paper purpose concerns the study of silver adsorption from pure silver solutions on the low calcination temperature alumina products, which have been fully described in the papers [61,62]. Thus, the measurement of the maximum adsorption capacity of low calcination temperature distinct classes of products will furnish a good data basis for selection the best silver charged adsorbents to be used as antimicrobial materials in particularly treatments of the waste waters Part 2 of this paper.

2. Materials and methods

2.1. Samples materials

The samples of aluminum hydroxide were collected from the last test of the new production line at Alum SA Tulcea, Romania, which was built up by implementation of the project “Endow the Research and Development Department of SC ALUM SA Tulcea with independent and efficient research facilities to support the economic competitiveness and business development”, project co-funded by the European Regional Development Fund through the Competitiveness Operational Program 2014-2020. This new production unit can deliver new grades of aluminum hydroxide dried, milled and classified. Some representative specimens, for each defined dimension particle class, were carefully selected as precursors for studying their thermal behaviour and possibility to find new outcome products with required properties as adsorbents. The samples composition and particle size distributions are presented in the Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>GDAH-01</th>
<th>GDAH-02</th>
<th>GDAH-03</th>
<th>GDAH-04</th>
<th>GDAH-05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles dimensions</td>
<td>&lt;45µm=5.7% &gt;150 µm=6.4%</td>
<td>&lt;45µm 98.29%</td>
<td>&lt;20µm 92.13%</td>
<td>&lt;10µm 76.28%</td>
<td>&lt;45µm=5.0% &gt;150=3.42%</td>
</tr>
<tr>
<td>Al (OH)₃</td>
<td>99.65</td>
<td>99.66</td>
<td>99.69</td>
<td>99.64</td>
<td>99.73</td>
</tr>
<tr>
<td>Al₂O₃, %</td>
<td>65.15</td>
<td>65.16</td>
<td>60.18</td>
<td>65.15</td>
<td>65.21</td>
</tr>
<tr>
<td>Na₂O, %</td>
<td>0.21</td>
<td>0.200</td>
<td>0.190</td>
<td>0.210</td>
<td>0.200</td>
</tr>
<tr>
<td>SiO₂, %</td>
<td>0.009</td>
<td>0.007</td>
<td>0.009</td>
<td>0.009</td>
<td>0.008</td>
</tr>
<tr>
<td>CaO %</td>
<td>0.035</td>
<td>0.041</td>
<td>0.038</td>
<td>0.039</td>
<td>0.0546</td>
</tr>
<tr>
<td>Fe₂O₃, %</td>
<td>0.007</td>
<td>0.013</td>
<td>0.010</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>LOI</td>
<td>34.62</td>
<td>34.62</td>
<td>34.61</td>
<td>34.62</td>
<td>34.58</td>
</tr>
<tr>
<td>Umiditate</td>
<td>0.082</td>
<td>0.158</td>
<td>0.134</td>
<td>0.180</td>
<td>0.081</td>
</tr>
</tbody>
</table>

In order to study the thermal transformations, the samples were first dried at 60°C for 24 h, then heated in an electric furnace (in air atmosphere) at 260°C, 300°C, 400°C and 600°C, with a heating rate of 5°C/min and then held for thermal stabilization 2h at the above mentioned temperature values. The samples were afterwards slowly cooled in the oven until room temperature. After heating and stabilization, the number of samples ready for any type of tests became 25, meaning 5 sample lots, each for the temperature values 25, 260, 300,400 and 600°C and each for all the initial five samples GDAH-01, GDAH-02, GDAH-03, GDAH-04 and GDAH-05, with its own particle size distribution. In all
experiments, there were used only common chemical analysis standard reactives, along with samples of low calcination temperature alumina products, manufactured in an industrial pilot plant. All analyses were repeated for three times and the results were mediated. At the end of adsorption experiments, the recovered adsorbents main properties were measured again for monitoring the eventual damages in each sample quality.

2.2. Silver adsorption capacity of on low calcination temperature alumina products

Adsorptive performances of low calcination temperature alumina products were demonstrated in many studies by determining the influence of specific adsorption parameters (pH, sorbent dose, contact time, silver initial concentration etc.) on maximum adsorption capacity.

Adsorption capacity has been determined using the equation (1):

\[ q = \frac{(C_0 - C_f)}{m} = \frac{V}{m} \]  

where: \( C_0 \) - initial concentration of Ag (I) in solution, (mg/L); \( C_f \) - residual concentration of Ag (I) from solution, (mg/L); \( V \) - solution volume, (L); \( m \) – adsorbent mass, (g). Efficiency of adsorption process has been determined using equation 2:

\[ \eta = 100 \left( \frac{(C_0 - C_f)}{C_0} \right) \]  

where: \( C_0 \) - initial concentration of Ag (I) from solution, (mg/L); \( C_f \) – residual concentration of Ag (I) from solution, (mg/L).

To measure materials from Table 2 solutions with different concentrations of Ag (I) were prepared: 10, 20, 40, 60, 80, 90, 100 and 120 mg/L). The adsorption capacities were determined at \( pH = 5 \), for a contact time of 60 min (considered optimal for achieving the ives objectf the initiated study) at the temperature values of 298 K, 308K and 318K. Thus, the samples of 0.1 g of each material from table 1 and Table 2 were dispersed in volumes of 25 mL solution containing Ag(I) and mixed for 60 min. At equilibrium, the samples were filtrated and analysed for finding the residual Ag(I) concentration, and subsequently computing the quantities of adsorbed Ag(I) per g of each sample of low temperature activated alumina product. Preliminary analyses have shown that 60 min mixing time is enough for reaching the equilibrium, because the tested alumina products are very reactive adsorbents.

2.3. Silver adsorption kinetics on low calcination temperature alumina products

The effect of contact time and temperature are important factors in assessing the affinity of the adsorbent materials for Ag (I). To determine the influence of contact time and temperature on the adsorption capacity of the materials presented above, samples 0.1 g of each tested material were weighed over which 25 mL of Ag (I) solution of 10 mg/L concentration was added. The samples were stirred at different time intervals (15, 30, 60, 90, and 120 min) in a water bath provided with stirring and thermosetting at some values of the temperature (298K, 308K, and 318K). The working \( pH \) was 5. The value \( pH \) 5 was chosen because the selected samples are very sensitive to the \( pH \) variation, and samples should be compared under the same conditions. Actually, the alumina products have been introduced in silver nitrate solutions at \( pH \) 5, and further the \( pH \) was controlled by adding some solution drops. All the residual concentrations of Ag (I) in the collected solutions were determined by atomic adsorption spectrometry. Knowing the concentrations of solutions in contact with the adsorbent material and the concentrations of the solutions after adsorption, one can calculate the evolution of the concentrations of Ag (I) adsorbed at each moment of the adsorption process.

2.4. Analysis equipments

All samples composition was carried out using the X-ray sequential fluorescence spectrometer (XRF); Thermo Fisher Scientific ARL PERFORM’X, Waltham, MA, USA, equipped with an X-ray
tube with a Rh anode and a Be window of 30 µm, was used for qualitative and quantitative analyses of the elements. The entire surface of the sample was analyzed under a dry He flow. Particle size distributions in the analysed samples were determined using a Malvern Panalytical Mastersizer 2000 diffraction analyzer (Almelo, The Netherlands) in the dynamic range of 0.1 to 3000 µm. Samples were dispersed in water using ultrasound and mechanical stirring. The Mie scattering theory specific to the instrument’s software was used for the particle size distribution assessment. The morphology and elemental composition of the particulate material samples was characterized by scanning electron microscopy (SEM: Quanta FEG 250, FEI, The Netherlands) using back scattered electron detector (BSD) coupled with energy dispersive X ray spectroscopy (EDS: using Apollo SSD detector, EDAX Inc. US). The microstructure and EDS analyses were performed at about 10 nm working distance (WD) in low vacuum mode in order to avoid surface charging and damage of the analysed material. For some samples was used a Quanta Inspect F50 FEG scanning electron microscope (Thermo Fisher, Eindhoven, Netherlands), with a resolution of 1.2 nm and an Everhart–Thorlony secondary electron detector (BSD) coupled with energy dispersive X ray spectroscopy (EDS: using Apollo SSD detector, EDAX Inc. US), were used to analyse the morphologies and the chemical compositions of the samples. Other details about these equipments and their use in the study of low calcination temperature alumina products can be found in the papers [61, 62]. Silver concentration in all filtrated solutions has been determined by atomic adsorption spectrometry using a Varian SpectrAA 280 FS instrument. Solutions pH has been determined using a Seven Compact S 210 Mettler Toledo pH-mete. For kinetics studies at some different temperature values were used a SW23 shaking water bath, JULABO, Germany.

3. Results and discussions
3.1. Maximum adsorption capacity
Maximum adsorption capacity of the adsorbents is a very important parameter, because it helps a quick evaluation of the adsorption performance for any material under various common or uncommon circumstances. Some more papers, recently published, recommend to use Langmuir, Freundlich, Dubinin-Radushkevich [69,70] or Sips isotherms [71] to compute the maximum adsorption capacity from experimental isothermal adsorption data. However, these methods are requiring additional data, which can be very laborious, to overcome discrepancy between the predictions and experimental data. Both linear and nonlinear isotherm model have to enable, more or less, simplifications to fit experimental results to the model data. Since this paper purpose is to characterize a new family of adsorbents coming out from low temperature activated alumina products, and to find their industrial applications, the maximum adsorption capacity of each individual product was evaluated from experimental saturation curve at constant temperature 298 and 318 K.

In the Figure 1, the saturation curves for one family of low temperature activated alumina products encompassing the samples GDAH-01 25, GDAH-03 25 and GDAH-04 25. Maximum adsorption capacity value is find by extrapolation of the two segments of each curve. The choice of samples was intended to illustrate the common forms of curves, specific for all the type of low temperature activated alumina products, manufactured at small pilot scale and characterized in our previous papers [61-64].

In the Table 2 are given the values of maximum capacity of silver adsorption at equilibrium at 25°C for all samples of low temperature activated alumina products under survey in this paper. There are five groups of samples which differ by the temperature of calcination and in each group five samples which differ by particle size dimension. The values of maximum capacity of adsorption have to be evaluated with regard to all changes induced by the four dynamic factors which control all the low temperature activated alumina products properties, mainly, the mineral phases conversion extent, as well a71s the physical and technical properties associated with these materials [61-63]. These dynamic factors are: a) initial gibbsite (as raw material and phase transitions precursor) preliminary processing; b) calcination temperature and rate of heating; c) particles size dimension of gibbsite, before the heating treatments, advanced grinding and intensive mechanical activation of gibbsite;
Figure 1. Saturation curves of the low temperature activated alumina products at 25°C. Products family GDAH-01 25, GDAH-03 25 and GDAH-04 25

Table 2. Maximum silver adsorption capacity on low temperature activated alumina products at 25°C, experimental values

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle sizes</th>
<th>Maximum silver adsorption capacity, mg/g</th>
<th>Samples</th>
<th>Particle sizes</th>
<th>Maximum silver adsorption capacity, mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDAH-01 25</td>
<td>0-150 µm</td>
<td>4.90</td>
<td>GDAH-04 25</td>
<td>0-150 µm</td>
<td>10.18</td>
</tr>
<tr>
<td>GDAH-02 25</td>
<td>0-45 µm</td>
<td>5.90</td>
<td>GDAH-05 300</td>
<td>45-130 µm</td>
<td>7.69</td>
</tr>
<tr>
<td>GDAH-03 25</td>
<td>0-20 µm</td>
<td>6.70</td>
<td>GDAH-01 400</td>
<td>0-150 µm</td>
<td>5.09</td>
</tr>
<tr>
<td>GDAH-04 25</td>
<td>0-10 µm</td>
<td>6.20</td>
<td>GDAH-02 400</td>
<td>0-45 µm</td>
<td>6.43</td>
</tr>
<tr>
<td>GDAH-05 25</td>
<td>45-150 µm</td>
<td>5.20</td>
<td>GDAH-03 400</td>
<td>0-20 µm</td>
<td>8.12</td>
</tr>
<tr>
<td>GDAH-01 260</td>
<td>0-150 µm</td>
<td>5.02</td>
<td>GDAH-04 400</td>
<td>0-10 µm</td>
<td>9.67</td>
</tr>
<tr>
<td>GDAH-02 260</td>
<td>0-45 µm</td>
<td>6.73</td>
<td>GDAH-05 400</td>
<td>45-150 µm</td>
<td>7.02</td>
</tr>
<tr>
<td>GDAH-03 260</td>
<td>0-20 µm</td>
<td>8.78</td>
<td>GDAH-01 600</td>
<td>0-150 µm</td>
<td>4.76</td>
</tr>
<tr>
<td>GDAH-04 260</td>
<td>0-10 µm</td>
<td>9.98</td>
<td>GDAH-02 600</td>
<td>0-45 µm</td>
<td>6.01</td>
</tr>
<tr>
<td>GDAH-05 260</td>
<td>45-150 µm</td>
<td>7.32</td>
<td>GDAH-03 600</td>
<td>0-20 µm</td>
<td>7.98</td>
</tr>
<tr>
<td>GDAH-01 300</td>
<td>0-150 µm</td>
<td>5.29</td>
<td>GDAH-04 600</td>
<td>0-10 µm</td>
<td>9.21</td>
</tr>
<tr>
<td>GDAH-02 300</td>
<td>0-45 µm</td>
<td>6.92</td>
<td>GDAH-05 600</td>
<td>45-150 µm</td>
<td>6.89</td>
</tr>
<tr>
<td>GDAH-03 300</td>
<td>0-20 µm</td>
<td>9.02</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Also, these dynamic factors contribution explain the diversity and variation in the values of maximum silver adsorption capacity from Table 2. The first group of samples GDAH-01 25 - GDAH-05 25 represents the raw material parted in five fractions, on the basis of particle size dimension. It was mentioned in the paper [66] that the gibbsite is produced at Vimetco Alum SA Tulcea, Romania under special conditions required by the chemical and mineral composition of processed bauxite. Consequently, the gibbsite product bears the imprints of raw bauxite, and might be considered in this paper as a preliminary processed raw material, mainly when is compared with other gibbsite grades coming out from alumina Bayer processing with other bauxite source [66]. All samples are containing gibbsite with large content of amorphous phase. The second group GDAH-01 260 - GDAH-05 260 is coming from samples calcined under special conditions at 260°C, which have lost around 3-4% water. The main phase remains the gibbsite 33-62%, accompanied by 2-10% Boehmite and 45-60% amorphous phase. The third group of samples GDAH-01 300 - GDAH-05 300 have lost around 20% water and undergoes great changes in samples mineral composition: gibbsite 23-58% and 10-14% boehmite, associated with 0-6% gama-alumina and 54-60% amorphous phase. The fourth group of samples GDAH-01 400 - GDAH-05 400 did lost around 28% of water and the gibbsite content dopped to 0.1-3.1%. At the same time the content of boehmite raises to 5-13%. Also, significant increase were noticed in gama alumina content, 10-16%, as well as in amorphous phase, 73-81%. In the last fifth group, the GDAH-01 600 - GDAH-05 600, all samples exhibit a total change in mineral composition, with 10-29 % gama alumina and amorphous...
phase. The above significant changes in the mineral phases composition and in amorphisation degree of the recrystallized phases are the straight effect and contribution of the second dynamic factor, the calcination temperature and rate of heating. These data sustain the large variation in maximum silver absorption capacities from Table 2. The third dynamic factor, the particle size dimentions before heating treatments, acts with the same intensity as calcination temperature and rate of heating on values of the maximum absorption capacity parameter (Table 2). But, for illustrating the intensity of this factor, the significant data have been selected from Table 2 and presented in a more adequate graphical configuration in the Figure 2. According to this new arrangement there are five groups of bars, each one standing for stanging for each temperature the aluminum hydroxide was activated. Each group of bars holds in une bar for each particle size dimension fraction. Thus, the Figure 2 displays very clearly a global image of maximum silver adsorption capacities for all the representative samples of low temperature activated alumina products.

![Figure 2. Maximum Ag(I) adsorption capacity on the low temperature activated alumina at 25ºC](image)

This image highlights the distinct impact of particle size dimension on the values of the parameter maximum silver adsorption capacity on low temperature activated alumina products. Also, this image points up the higher values of silver capacity adsorption for the smaller particle size fractions, as effect of the above presented dynamic factor impact.

### 3.2. Kinetics of silver adsorption on low temperature activated alumina products

Kinetic studies usually help to understand the mechanism of adsorption process and its chemical side and possible reactions, as well as the reaction rate and the mass transfer coefficient. Moreover, the kinetic data knowledge opens the paths to find out the optimal conditions necessary for improving the adsorption process rate and yield. In order to ascribe a general expression for describing the sorption kinetics of a ionic or non-ionic compound on different solid adsorbents, it is necessary to perform some preliminary tests for fitting the experimental data [72].

In this paper the selected samples of low temperature activated alumina products were GDAH-01 25, GDAH-04 25, GDAH-04 300, and GDAH-04 400. The reason of this selection stands in the samples processing ways to be converted from the raw precursor GDAH-01 25 (aluminum hydroxide, fraction 0-150 µm) into the other adsorbents.
Sample GDAH-04 25 (aluminum hydroxide fraction 0-20 µm) differs from sample GDAH-01 25 by its particles size dimensions. Also, the samples GDAH-04 300 and GDAH-04 400 differ from the other two samples by their thermal treatments, which bring about large changes in specific surface and pores size distribution. Therefore, each sample is a distinct product from a family of low temperature activated alumina products.

Additionally, all thermal and mechanical (milling and classifying) treatments applied on all individual sample sums up all types of dynamic impact during low temperature alumina activation process.

After preliminary tests, the linear equations appear to provide the best fit of experimental data. Most often used linear equations, which describe the adsorption process kinetics are:

- Pseudo-first order model (Lagergren model) [73]:
  \[
  \ln(qe - qt) = \ln qe - k1t
  \]  
  where: \( qe \) - equilibrium adsorption capacity, (mg/g); \( qt \) - adsorption capacity at time \( t \), (mg/g); \( k1 \) - rate constant for pseudo-first order (1/min); \( t \) - contact time, (min).

- Pseudo-second order model (Ho și McKay model) [74]:
  \[
  1/qt = 1/(qe)^2 + 1/qe
  \]  
  where: \( qe \) - equilibrium adsorption capacity, (mg/g); \( qt \) - adsorption capacity at time \( t \), (mg/g); \( k2 \) - rate constant for pseudo-second order, (g/mg∙min); \( t \) - contact time, (min).

When the experimental data are modelled using pseudo-first-order model, kinetic parameters (\( k1 \)– rate constant and calculated adsorption capacity - \( qe \), calc) were evaluated from linear dependence between \( \ln(qe - qt) \) and \( t \). By modelling the acquired experimental data with pseudo-second-order model, the associated kinetic parameters (rate constant \( k2 \), and calculated adsorption capacity - \( qe \), calc.) were determined from linear dependence between \( t/qt \) and \( t \). The adsorption kinetic of Ag(I) has been studied for all four selected adsorbent samples at three different temperature values (298, 308, and 318 K).

Kinetic isotherms (pseudo-first-order and pseudo-second-order) are visualized in Figures 3 to 6.

Based on experimental data, presented in Figures 3 to 6, the pseudo second order kinetic model was ascertain as valid model and the values of adsorption capacity \( q_{exp} \), as well as the value of rate constant \( K2 \) were computed and presented in the Table 3 at 298K and 318K.

Based on experimental data, presented in Figures 3 to 6, the pseudo second order kinetic model was ascertain as valid model and the values of adsorption capacity \( q_{exp} \), as well as the value of rate constant \( K2 \) were computed and presented in the Table 3 at 298K and 318K. Also, in Figure 7 are presented comparatively the kinetic parameters obtained by modeling experimental data with pseudo-second-order model at two different temperature values. From both data presented in Figures 3 to 6 and in Table 3, it can be observed that the experimental data are better described by pseudo-second order model. Such observation is in concordance with the regression coefficient obtained value (which is near a unity).

Also, the calculated values for maximum adsorption capacity are similar with those coming from experimental data. Moreover, the data from Figure 7 are reflecting the impact of the dynamic factors, which control all the physical and technical properties of chosen adsorbents, including also the adsorption rate of (Ag 1) on the same materials.
Table 3. Kinetic parameters of the adsorption process, according the pseudo-second-order kinetic model at 298 and 318 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>$q_{e,exp}$ (mg g$^{-1}$) 298K</th>
<th>$q_{e,exp}$ (mg g$^{-1}$) 318K</th>
<th>$K_2$ (min$^{-1}$) 298K</th>
<th>$K_2$ (min$^{-1}$) 318K</th>
</tr>
</thead>
<tbody>
<tr>
<td>GHAH-01 25</td>
<td>2.06</td>
<td>2.14</td>
<td>1.61</td>
<td>1.74</td>
</tr>
<tr>
<td>GDAH-04 25</td>
<td>2.29</td>
<td>2.35</td>
<td>4.15</td>
<td>5.89</td>
</tr>
<tr>
<td>GDAH-04 300</td>
<td>2.30</td>
<td>2.42</td>
<td>2.26</td>
<td>6.88</td>
</tr>
<tr>
<td>GDAH-04 400</td>
<td>2.03</td>
<td>2.19</td>
<td>2.63</td>
<td>4.42</td>
</tr>
</tbody>
</table>

Thus, the rate of (Ag 1) adsorption is dependent on both temperature and particles size dimension of the adsorbents, as results from Figure 7A. At the same time, the rate of (Ag 1) adsorption is dependent on temperature variation, according to the results from Figure 7 B, which predict significant increase with temperature in the rate constant $K_2$. 
4. Conclusions

This paper is the fifth from row of published research works, regarding the low temperature activated alumina products coming out from the same precursor, the aluminum hydroxide dried, milled and classified manufactured at Vimetco Alum SA Tulcea, Romania after implementation of the project “Endow the Research and Development Department of SC ALUM SA Tulcea with independent and
efficient research facilities to support the economic competitiveness and business development”, project co-funded by the European Regional Development Fund through the Competitiveness Operational Program 2014–2020. The previous papers described the principles of low temperature alumina activation and the samples preparation, as well as the products chemical structure and mineralogy, and also their industrial properties. This paper discloses the results of researches about silver adsorption capacity of all the low temperature activated alumina samples from Table 2 and also, the results of investigation the silver adsorption kinetics on some mindfully selected samples. Thus, only four samples, reasonably accepted as representative for the entire lot of samples, were used for the study of kinetics mechanism and data fitting to the adequate kinetic equations. Confident data validate the pseudo second order kinetic model for the entire activation process, independently of samples heating temperature and particle size dimension.

Acknowledgments: This study was made possible by the implementation of the “Endow the Research and Development Department of SC ALUM SA Tulcea with independent and efficient research facilities to support the economic competitiveness and business development” project, which was co-funded by the European Regional Development Fund through the Competitiveness Operational Program of 2014–2020. Under this project, the following were purchased and commissioned: “Independent equipment/installation for research and development of the technology for wet aluminum hydroxide classification”, “Independent equipment/installation for research and development of technology for obtaining the dried aluminum hydroxide”, and “Independent equipment/installation for research and development of the technology for grinding and screening the dried aluminum hydroxide”.

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