Mechanical properties and functional durability of Fly Ash pellets, adsorbents in wastewater treatment

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ABSTRACT

Using fly ash (FA) as heavy metals adsorbent in advanced wastewater treatment represents an issue well addressed in literature. Most reports contain results obtained at laboratory level by using dispersed fly ash in the wastewater, in batch processes. However, this is not a fully up-scalable solution, as large amounts of wastewaters need a continuous flow treatment. An alternative of this process is pelletizing FA, without modifying the adsorption efficiency, which is not solved yet.

The paper analyses various pelletization paths, involving pressing at room temperature modified FA (with high adsorption efficiency and fast kinetics) and using common additives (alcohol polyvinilic), bentonite or diatomite.

The most important mechanical properties (compression and impact resistance) represent the output properties used for selecting the best pelletization recipes. Further on, the selected pellet types are tested for their durability in the working environment, by long term immersion (24h) in static regimes. The mechanical properties after the stability/durability tests are measured and compared to the initial values.

The design of the testing experiments allows also the development of correlation considering the initial content of the pellets, the additives (type and amount) and the stability limits, as prerequisites in selecting the scaled up applications.

1. INTRODUCTION

The products of coal combustion (CCP) are materials that remain after the coal is burned: the boiler slag, bottom ash (in the bottom of the combustion chamber) and fine particles (fly ash) which are removed from the flue gas by electrostatic precipitators and flue gas desulphurization materials.

Fly ash is a waste powder generated from the central heat power plants, every year over 500 million tons of ash is generated and from these, 75-80% is fine fly ash [1]. Its
composition (silica 60-65%; alumina 25-30%; magnetite 6-15%) make it suitable for adsorbent materials even zeolites synthesis [2]. Zeolites are crystalline microporous aluminosilicates with numerous excellent properties, non-toxicity, high porosity, good thermal stability, well defined structures [3].

Ash, resulting from coal or biomass burning, is a mixture of oxides with less unburned carbon and other minority inorganic compounds, thus has a predominant negative surface charge and represents promising adsorbent materials. Many applications in wastewater treatment are already reported, most of them at pilot scale [4].

Many researchers from different countries (Spain, Italy, Greece, China, India) were tested the fly ash in adsorption [5] of heavy metals, dyes, and surfactants, because the priority compounds from fly ash favour the heavy metals adsorption and are active sites in dyes’ immobilization.

For avoiding flora, fauna and health problems, the discharge limits are strict and require advanced wastewater treatment processes. Depending on the initial composition, many alternatives are proposed: adsorption [6], chemical precipitation, coagulation and flocculation, ion-exchange, reverse osmosis, membrane nanofiltration, photo-degradation using wide band gap semiconductor [7,8]: choosing one or a complex of solutions is subject of efficiency and cost analysis.

Among these, technologies based on or involving adsorption have several advantages: are effective, easy operation, well known technology, inexpensive equipments, adsorbents’ reuse after desorption, but in the most of the cases they produce a large amount of toxic sludge, which is difficult to be managed. The utilization of fly ash in form of pellets an adsorption agent ensures plenty of advantages: easy stabilization in column, easy separation after saturation, minimum risk for column clogging up. After adsorption the pellets loaded with pollutants can be stabilized in concrete blocks [9] where over 70% of cement has been replaced by raw fly ash [10].

Pelletizing FA, in low energy consuming processes, without modifying the adsorption efficiency and preserving good mechanical properties, represents a problem not solved yet.

The paper analyses various pelletization paths, involving pressing at room temperature modified FA with binding materials and materials which to ensure the pore structure. Based on mechanical property of compression the best pelletisation recipes are selected.

Further on, the selected pellet types are tested for their durability in the working environment, by long term immersion (24h) in water at different pH values (5.5 ... 7.5), in static regimes. The mechanical properties after the stability/durability tests are measured and compared to the initial values. One application of the pellets is adsorption of methylene blue and cadmium cations from pollutant system.

2. EXPERIMENTS
2.1. SYNTHESIS THE SUBSTRATE – ZEOLITE PELLET

Fly ash used in the present study was collected from power plant CET Brasov, Romania. According to the ASTM standards [11], the FA collected from the electro-filters of the plant is of F type. The sum of the major compounds, oxides SiO₂ (53.32%), Al₂O₃ (22.05%) and Fe₂O₃ (8.97) is over 70%, CaO < 8% and it doesn’t aggregate in water. The fly ash collected with oxides composition SiO₂/Al₂O₃ over 2.4 were used for obtaining a zeolite materials in the form of pellets with good adsorption capacity for heavy metals and dyes from wastewater.

The pH value of the raw fly ash was evaluated by mixing FA: ultra pure water (1:10), then stirring, at room temperature 24h. The initial TDS value of the batch is 600 mg/L and after 24 h increases to 820 mg/L. The conductivity value and the pH are 1.71 µS and 10.2, respectively.

The modified fly ash was obtained by mixing FA with NaOH solution 2N at room temperature for 48h when the outer part of fly ash particle, the glass phase, were dissolved into alkaline solution in the amount that higher than the crystal phase due to its higher solubility into the alkaline solution

The pore forming agent and binder added to this suspension was poly(vinyl alcohol) (PVA with degree of hydrolysis =88% and degree of polymerization =50, diatomite and bentonite respectively. To improve the adsorption/photodegradation activity of the pellets were synthesized a new type of pellets adding Degussa P25( 80% Anatase and 20% Rutile). These pellets were denoted: FA-ZD, FA-ZB and FAZB-TiO₂.

In order to remove the water and to obtain slightly wet solid materials it is introduced into a thermostatic oven to a 80°C for 2h. The material obtained was ground in the mill in order to obtain a very homogeneous powder mixture. The next step is to obtain the pellets size: A=314mm², D=20mm and h=2.5mm. Figure 1 shows the form of pellets produced using a hydraulic press.

![Figure 1. The pellets obtained](image)

To remove the traces of carbon the pellets were introduced in a furnace at different temperatures (200°C, 400°C, 600°C, 800°C and 900°C) with a constant rate 10°C/min. After 3h the pellets were cooled rapidly down to room temperature in desiccator and used to measure the hardness.

2.2. MECHANICAL PROPERTIES – COMPRESSION TESTING
The compression strength (Ϭ) of the FA-ZD, FA-ZB and FAZB-TiO₂ pellets type were evaluated with the Z020 Zwick/Roell equipment, according to SR EN ISO 527-4:2000. The mechanical test results are presented in Figure 2.

![Figure 2](image-url)

Figure 2. The compression resistance (Ϭ) of the FA-ZB (a) and FA-ZD (b) pellets at temperature range of 200...900°C.

The parameters at compression (F_{max}, A, \varepsilon F_{max}) for FA-ZB, FA-ZD and FAZB-TiO₂ are shown in Table 1.

It was noticed that the FA-ZD pellets type exhibit higher compressive strength (70.21-70.64 N/mm²) than FA-ZB type (69.07 N/mm²). This is due to the diatomite (in the FA-ZD), which has higher hardness than bentonite (FA-ZB). Silica the main diatomite compound led to a higher compatibility to fly ash matrix than did bentonite, Fig. 2 (a) and (b). Fig.2b shows the higher annealing temperature, the higher FA-ZD ductility. The graph shape (allure) of FA-ZB, Fig.2 (a) confirms its more brittle behavior. The results presented indicate an optimal behavior of the pellets with diatomite and bentonite treated at 400°C and 800°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A  [mm²]</th>
<th>F_{max} [N/mm²]</th>
<th>\varepsilon F_{max} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA-ZB 200°C</td>
<td>314.2</td>
<td>62.46</td>
<td>79.91</td>
</tr>
<tr>
<td>FA-ZB 400°C</td>
<td>314.2</td>
<td>69.07</td>
<td>79.93</td>
</tr>
<tr>
<td>FA-ZB 600°C</td>
<td>314.2</td>
<td>65.05</td>
<td>79.93</td>
</tr>
<tr>
<td>FA-ZB 800°C</td>
<td>314.2</td>
<td>62.06</td>
<td>68.93</td>
</tr>
<tr>
<td>FA-ZB 900°C</td>
<td>314.2</td>
<td>62.06</td>
<td>79.84</td>
</tr>
<tr>
<td>FA-ZD 200°C</td>
<td>314.2</td>
<td>61.23</td>
<td>34.42</td>
</tr>
<tr>
<td>FA-ZD 400°C</td>
<td>314.2</td>
<td>70.64</td>
<td>45.71</td>
</tr>
<tr>
<td>FA-ZD 600°C</td>
<td>314.2</td>
<td>70.38</td>
<td>50.71</td>
</tr>
<tr>
<td>FA-ZD 800°C</td>
<td>314.2</td>
<td>70.21</td>
<td>47-.78</td>
</tr>
</tbody>
</table>
Compression behavior of the pellets corresponds to a force over 65 N/mm² except the pellets with 10% TiO₂. The composite FAZB-TiO₂ with Degussa P25 was obtained with bentonite, because the adsorption properties of bentonite are better. In the case of the FAZB-TiO₂ pellets the optimal behavior is at 400°C and at 500°C heat treated.

### 2.3. DURABILITY TESTING

Further on, the pellet types are tested for their durability in the working environment, by long term immersion 24h in distillate water at different pH values (5.5 ... 7.5), in static regime. The Figure 3 presents the images of pellets in distilled water for 24h at room temperature, after that the pellets were taken out, dry at 105-115°C temperature and again compression test Figure 4.

<table>
<thead>
<tr>
<th></th>
<th>σ [N/mm²]</th>
<th>Crush [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA-ZD 900°C</td>
<td>314.2</td>
<td>69.54</td>
</tr>
<tr>
<td>FAZB-TiO₂</td>
<td>314.2</td>
<td>45.28</td>
</tr>
<tr>
<td>FAZB-TiO₂ 200°C</td>
<td>314.2</td>
<td>50.53</td>
</tr>
<tr>
<td>FAZB-TiO₂ 400°C</td>
<td>314.2</td>
<td>47.62</td>
</tr>
<tr>
<td>FAZB-TiO₂ 500°C</td>
<td>314.2</td>
<td>63.86</td>
</tr>
<tr>
<td>FAZB-TiO₂ 600°C</td>
<td>314.2</td>
<td>70.73</td>
</tr>
</tbody>
</table>

The stability of the pellets indicates the –OH polar in the each structure group which forms a large number of hydrogen interchange bonds. The water colored of the pellets treated at 200°C indicates a diffusion of compounds resulting in the degradation of polyvinyl alcohol. This pellet is less resistant at break (34.433 N/mm²) and is unstable to water (pollution increases). Most pellets stable in water are the pellets heat treated at 900°C >800°C >600°C. The mechanical properties after the stability/durability tests are measured and compared to the initial values. Compression strength decreases with 15%.
Other testes. The pellets were immersed in real synthetic solution with copper and cadmium 0.05N at pH 5.6, Figure 5.

![Figure 5. Behavior immersion of FA - ZB pellets in: (a) mixed solution of Cd$^{2+}$ and Cu$^{2+}$; (b) Cd$^{2+}$ solution 0.005N](image)

Behavior immersion in water and in solution of the pellets show that it's not to damage the pellets. A negative aspect is the behavior of the pellets embedded in solutions copper or copper and cadmium. In these situations it forms a blue precipitate of copper hydroxide or a copper complex.

### 2.4. CHARACTERIZATION OF THE SUBSTRATES

The atomic force microscope (AFM/ Ntegra Spectra, NT-MDT model BLRNTE) was used to obtain the information about the surface topography and roughness of the raw fly ash or adsorbent materials before and after treated Figure 6 and Figure 7.

The results show a strong increase in the specific surface from 6.14m$^2$/g in FA to 42.56m$^2$/g in FA-ZB after substrates conditioning, and a decrease in the average pores diameter; corroborated with the surface, this indicates a new type of organization in the new materials.

The XRD patterns (Bruker D8 Discover Diffractometer), confirm these crystalline structures, and show the main components of modified fly ash: (1) anatase syn, (2) rutile, (3) Na$_6$Al$_6$Si$_{10}$O$_{32}$12H$_2$O(NaP1zeolite), different types of aluminosilicates (4) hematite (Fe$_2$O$_3$), clinoptilolite (Na,K,Ca)$_5$(Al$_6$Si$_{30}$O$_{72}$18H$_2$O)[12], Figure 8.

![Figure 6. AFM images of the: (a) FA-ZB pellet untreated; (b) distribution of phases, (c) 3D image. Average roughness: 242,752 nm](image)
The crystallites size ($\tau$) was calculated using Scherrer Eq. (1) [13].

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

Where: $K$– shape factor with a value 0.94, $\lambda$- is the X-ray wavelength (1.541Å), $\beta$-the line broadening at half the maximum intensity (of a peak), $\theta$-the diffraction angle. With the heat treatment increases the degree of crystallinity increases from 27.44% in bentonite up to 46.72% in composite FAZB-TiO$_2$ and there is a move of the peaks due to the formation of new aluminosilicate structures. We can also see the crystallites size of anatase and of aluminosilicate which are declined with increasing the temperature to 500°C Table 2.

<table>
<thead>
<tr>
<th>Compound /Temperature</th>
<th>200°C</th>
<th>400°C</th>
<th>500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatas syn- crystalite size - [Å]</td>
<td>282.61</td>
<td>262.0</td>
<td>184.8</td>
</tr>
<tr>
<td>Aluminosilicate- crystalite size - [Å]</td>
<td>262.8</td>
<td>203.8</td>
<td>113.7</td>
</tr>
<tr>
<td>Quartz syn- crystalite size - [Å]</td>
<td>320,2</td>
<td>180,5</td>
<td>317,9</td>
</tr>
</tbody>
</table>
2.5. APPLICATION-ADSORPTION OF THE METHYLENE BLUE AND THE Cd\(^{2+}\)

Synthesized pellets FA-ZB were tested in adsorption processes for to remove the methylene blue (MB) and Cd\(^{2+}\) cations from a system with two pollutants. The MB, cationic dye, was chosen in this study because of its known strong adsorption onto solids. The dye stock- solutions were prepared by dissolving an appropriate quantity of Methylene Blue (MB), \((\text{C}_{16}\text{H}_{18}\text{N}_{3}\text{SCl})\) (Fluka AG, reagent grade) with \((319.85\text{g/mol})\) molecular weight and \(\text{CdCl}_2\cdot2.5\text{H}_2\text{O}\) (Scharlau Chemie S.A., c<98%), in ultrapure water (Direct-Q3 Water Purification System). The initial concentration of MB solution is 0.003125mMol/L and Cd\(^{2+}\) in the concentration range of \(c_{\text{Cd}}= 400-410\text{mg/L}\).

The concentration of (MB) in the supernatant solution before and after adsorption was analysed by UV-VIS spectrometry (Perkin Elmer Lambda 25), on the calibration curve registered at the maximum absorption peaks of MB (\(\lambda=665\text{ nm}\)), in order to evaluate the momentary concentration of dye. The supernatant was further analysed by AAS (Analytic Jena, ZEEnit 700), at: \(\lambda_{\text{Cd}} = 228.8\text{nm}\). Preliminary experiments proved that, dye and Cd\(^{2+}\) loses due to the adsorption to the walls of the flasks were negligible.

The amount of pollutants uptake by adsorbents (adsorption capacity), \(q_t\), the removal efficiency, \(\eta\), percentage were calculated based on the initial \(c_{\text{MB/Cd}}^i\) and equilibrium momentary \(c_{\text{MB/Cd}}^t\) concentrations of the pollutants by the following equation (2).

\[
\eta = \frac{(c_{\text{MB/Cd}}^i - c_{\text{MB/Cd}}^t)}{c_{\text{MB/Cd}}^i} \cdot 100
\]  

(2)

The adsorption efficiency correlated with crystalline structure, the surface morphology (AFM) of the pellets were evaluated based on the initial and momentary concentration of the cations and of the dyes, Figure 9.

The results of adsorption experiments in system with these pollutants MB and Cd\(^{2+}\) show that the adsorption of Cd\(^{2+}\) cations onto the pellets was inhibited in the present of MB dye and vice-versa. After equilibration between 2- 4h the MB is adsorbed up to saturation of the pellet with 65.75% efficiency.
The adsorption experiments have to continue evaluating the kinetic parameters and thermodynamic mechanisms.

CONCLUSIONS

Palletised FA is a feasible path which contains the following steps: synthesis the substrate, mechanical properties testing, durability testing, mechanical properties testing after durability testing, substrates characterisation, pellets testing in adsorption processes.

Three types of pellets were tested: FAZB-TiO₂ (FA+PVA+bentonite+Degussa P25); FA-ZB (FA+PVA+bentonite) and FA-ZD(FA+PVA+diatomite);

FA-ZD pallets have higher compressive strength than FA-ZB type. The optimal behaviour of FA-ZD pallets is at 400°C and 800°C; for FAZB-TiO₂ at 400°C and 500°C.

The higher stability in water have the pallets heat treated at 600-900°C. The pellets are no damaged in solution with Cu²⁺ and Cd²⁺, but they form a blue precipitate of Cu(OH)₂.

Compression test after durability testing indicates a strength decreasing with 15 %.

The results of substrates characterisation show a strong increase in the specific surface after substrates conditioning and a decrease in the average pores diameter, as result of a new type of organisation in these structures, but the degree of crystallinity increases from 27.44 % in FA-ZB up to 46.72 % in FAZB-TiO₂.

Testing the pallets in adsorption processes of two pollutants (MB and Cd²⁺ ) shows that the MB is adsorbed up to saturation of the pallets.

Based on new experiments and different pallets structure, optimised pallets could be obtained.

REFERENCES


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