# Removal of Fluoride from Aqueous Solutions Using Biomass Ash

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Various techniques of defluoridation like coagulation and precipitation, reverse osmosis, nanofiltration, electrodialysis and electrolysis, membrane processes, ion-exchange, Donnan dialysis, and adsorption have been used to reduce the excess of fluoride (Xiaotian, 2011). Adsorption method seems to be as one of the most suitable techniques for the defluoridation because it is economical, environmental friendly and efficient. Many kinds of adsorbents have been reported to be effective for fluoride adsorption, like: activated carbon, activated alumina, calcite, tricalcium phosphate and activated soil sorbents (Meenakshi, 2006). There are also studied described concerning the use of ash as fluoride adsorbent material (Ranjeeta, 2015). Coal fly ash is one of the major industrial solid wastes and its amount is increasing year by year all over the world. Recycling of coal fly ash is, therefore, attracts the broad concern of the researcher. Fly ash has been successfully used by several investigators for the removal of metal ions from water and wastewaters (Polowczyk *et al.,* 2010). Generally, using of coal fly ash as fluoride sorbents is connected with the preliminary thermal or chemical modification of ash. Studies described (Urkude *et al,* 2015) present test of fly ash using for fluoride removal from water and wastewaters instead of costly adsorbents such as activated carbon, activated alumina, activated bauxite, etc. In view of the increase in the amount of energy obtained from renewable energy sources obligation, including biomass, there also need of utilization of ash, obtained after biomass combustion or co-combustion with carbon. Due to content of components in biomass ash that can fluoride bind, studies of fluoride sorption by this kind of ash have been done.

Fly ash samples were collected from several Polish power plants as well from heat power plants. Ash was obtained by biomass combustion only or by co-combustion with coal. In the first step, preliminary research of each ash sample fluoride sorption properties were carried out. Based on these test results, one sample of ash with the best sorption properties has been chosen for further steps of study. Selected ash sample, derived from combustion of biomass only (forestry biomass: conifer and leafy tree) has been examined for main ingredients concentration (XRF analysis), presence of main crystallographic phases (XRD analysis), particle size distribution (by laser particle size analyzer) and bulk density, pH and moisture content. For further research, dried ash were used without sieving and grinding of them.

All the adsorption tests were carried out in batch mode, in a 100 ml plastic containers with a cap, with 50 ml of ammonium fluoride test solution, using multi-station magnetic stirrer, with the same agitation speed. At the end of the experiment, the samples were filtered using paper filter and subsequently the filtrate was analyzed for residual concentration of fluorides. The removal percentage of fluoride was calculated as the difference in the concentration of the test solution before and after the experiment.

The fluoride concentration in the test solutions was measured by the direct potentiometric method. A fluoride selective electrode (MONOKRYSTALY, 09-37 type) made of lanthanum fluoride single crystal ($LaF_3$) was used as the indicating electrode, combined with the AgCl electrode used as the reference electrode. The citrate buffer to maintain the pH of the samples at a fixed value of 6 was used. The calibration curve was designated for illustrating the relationship between the measured signal and $\log_{10}$ of molar concentration of fluorides, using NaF solutions as the standard.

In the present study the influence of various parameters like adsorbent dose, initial fluoride concentration, contact time, pH and temperature has been investigated. To optimize certain parameter, one parameter was changed and all other variables were kept constant.

The effect of adsorbent dose was studied by varying the dose in the range 1-20 g per liter of test solution with the variable fluoride concentration in the 0.05-1g$F^-$/l range. The influence of the initial fluoride concentration on the adsorption degree was evaluated by varying the fluoride concentration in the range from 0.05 to 1 g$F^-$/l and the constant amount of ash. Both experiments have been done with the same, maximally extended time of sorption, 15 hours approximately, to ensure conditions of maximum adsorption. To investigate the effect of contact time on the degree of sorption, experiments were carried out with a dose of ash of 0.5g/l and with a fluoride solution of 0.5g$F^-$/l and with variable contact time from 30 to 240, and with 900 minutes when the equilibration state was achieved. The effect of pH was studied in the range of approximately 2-10 and pH of test solution was adjusted by adding sulfuric acid or ammonia solution without dilution of them, to prevent of reduction in fluoride concentration. Each pH value test solutions of the around 0.5gF/l were added to the same dose of ash and were agitated for the same time.

Each experiment with the same measurement parameters were repeated twice and then the average value has been set.

In the tables 1- 4 the results of carried out tests has been shown. As can be seen from table 1, much better adsorption efficiency at the same dose of adsorbent was obtained for 0.1-0.5 $gF^-/l$ than for very low and high fluoride concentration, i.e. 0.05 and 1.0 $gF^-/l$ of test solutions. In the case of each of the test solution concentrations, the fluoride removal efficiency increased with the increase in the adsorbent dose.

The effect of contact time on the removal of fluoride is shown in table 2. In the case of 0.5 $gF^-/l$ test solution, there was no significant adsorbent efficiency change with contact time increasing. Different effect was observed for 1.0 $gF^-/l$ test solution. Extending the contact time from 30 to 120 minutes brought fluoride removal increasing by about 7% but further increasing of contact time didn't cause significant growth of adsorption efficiency. Even after 240 minutes the amount of fluoride removed didn't reach a value corresponding to the maximum test time of 900 minutes.

Table 1. Effect of initial fluoride concentration and of adsorbent dose on adsorption of fluoride

| Adsorbent dose [g/l] | Fluoride removal [%] depending on the initial concentration of test solution | | | | |
|---|---|---|---|---|---|
| | **0.05 [$gF^-/l$]** | **0.1 [$gF^-/l$]** | **0.2 [$gF^-/l$]** | **0.5 [$gF^-/l$]** | **1.0 [$gF^-/l$]** |
| 1 | 11.3 | 32.1 | 21.0 | 7.5 | 2.0 |
| 2 | 23.3 | 51.6 | 61.8 | 29.8 | 18.3 |
| 6 | 67.7 | 85.9 | 91.2 | 79.8 | 55.3 |
| 10 | 81.3 | 90.1 | 93.5 | 94.8 | 81.5 |
| 14 | 86.0 | 93.0 | 94.9 | 97.4 | 95.1 |
| 20 | 90.0 | 94.8 | 96.4 | 98.0 | 98.3 |

Table 2. Effect of contact time on adsorption of fluoride

| Contac time [min] | Fluoride removal [%] depending on the initial concentration of test solution | |
|---|---|---|
| | **0.5 [$gF^-/l$]** | **1.0 [$gF^-/l$]** |
| 30 | 95.5 | 63.4 |
| 60 | 96.5 | 65.6 |
| 120 | 96.7 | 70.4 |
| 180 | 96.9 | 70.7 |
| 240 | 97.0 | 71.1 |
| 900 | 97.8 | 81.5 |

Significant improvement of sorption capacity has been achieved at temeperature higher by about 50 degrees than ambient temperature, as it can be seen in the table 3. Generally, it couldn't be seen a significant temperature influence on fluoride sorption process on the fly ash examinated.

The adsorptiom of fluoride increased at lower pH and decreased as the pH is increased (Table 4). The highest effeciveness of adsorption of fluoride on biomass fly ash was obtained at pH 3-4.

Table 3. Effect of temperature on adsorption of fluoride

| **Effect of temperature [K]** | **Fluoride removal [%]** |
|---|---|
| 298 | 74.3 |
| 303 | 72.7 |
| 313 | 74.2 |
| 323 | 76.8 |
| 333 | 78.1 |
| 343 | 75.9 |
| 353 | 80.7 |

Table 4. Effect of pH on adsorption of fluoride

| **pH of test solution** | **Fluoride removal [%]** |
|---|---|
| **2.19** | 77.8 |
| **3.63** | 89.4 |
| **5.25** | 63.4 |
| **8.56** | 61.9 |
| **9.63** | 64.1 |

The presented research was undertaken to test the biomass fly ash ability, without any pretreatment, for the fluoride removal from aqueous solution. The highest adsorption efficiency has been achieved for initial values of fluoride concentrations of the test solutions in the range of 0.1-0.5 $gF^-/l$. The optimum dosage for these concentrations was found to be 10 g of ash per liter of test solution. Very high adsorbent efficiency has been already achieved after a contact time of 30 minutes. No significant temperature influence on the fluoride removal has been noticed. The removal efficiency decreased with an increase of pH.

The results suggest, that low-cost material like biomass fly ash is effective in removing fluoride from water to acceptable levels, even without previous pretreatments of it.


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