Removal of Fluoride from Aqueous Solutions Using Sewage Sludge Ash

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Fluoride is an ionic form of the element fluorine that occurs naturally in water or appears in industrial wastewaters. Presence of fluoride beyond the permissible limit in drinking water is harmful and not suitable. There are a lot of methods of fluoride removal described, especially from aqueous media (Tomar *et al.*, 2013). Many of these methods aren't used on a large scale because of unwanted factors like high operational and maintenance costs, generation of toxic byproducts and due to complex treatment. To reduce the operational costs, it is found more frequently that are used "low cost" type sorbents (Urkude *et al.*, 2015; Poudyal *et al*., 2015). Research show the ability of waste products do decontaminate wastewaters containing various toxic pollutants including fluoride (Chaturvedi *et al.*, 1990). Taking into account that sewage sludge ash contain some components that can catch a fluoride, studies of fluoride sorption by this kind of ash have been done.

Sewage sludge ash samples were collected from several Polish incineration plants of sewage sludge from municipal wastewaters treatment plants. In the first step, preliminary studies 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 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 0.05-1gF^-/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 gF^-/l and the constant amount of ash (0.5g). 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 0.5gF^-/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.

On the figures 1- 4 the results of carried out our tests have been shown. The removal percentage increased with the the increase in initial concentration of the fluoride ions (Fig.1). 88% removal was observed for 0.05 g/l of fluoride concentration when 1 g/l of ash was added. It can be seen that for the solutions 0.05-0.2 gF^-/l, use of 2 g of adsorbent ash caused fluoride concentration decreasing of around 90% an increasaing of adsorbent dose to the 20g didn't bring significant effects. In the case of 0.5-1.0 gF^-/l test solutions, there is need to use 5g of ash per liter of fluoride solution at least to achieve a high adosrption efficiency.

The effect of contact time studies (Fig.2) show that very high efficiency of 88% has already been achieved after 30 minutes. Mixing time lengthing to 4 hours has given effectiveness increasing for about 7%, while after 15 hours contact time, sorption capacity is around 95%. After 5 hours of contact time, the maximal adsorption efficiency has been achieved, coresponding with 15 hours of contact time, around 98%.

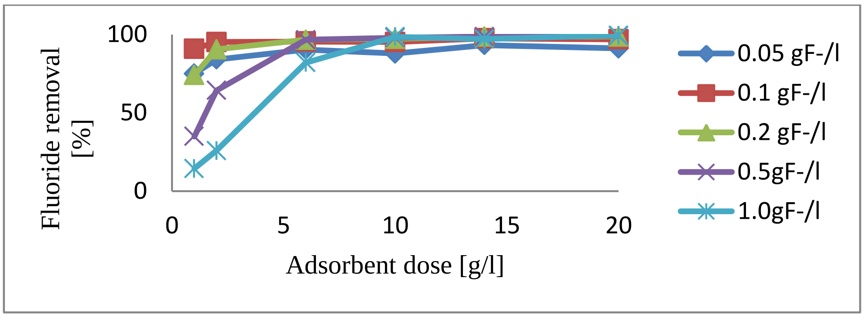

Fig. 1: Effect of adsorbent dose on adsorption of fluoride for various ininital fluoride concentration of test solutions

It has been noticed that with temperature increase the adsorption efficiency increased gradually (Fig.3), but the most significant increasing of fluoride removal achieved for the highest test value of temperature.

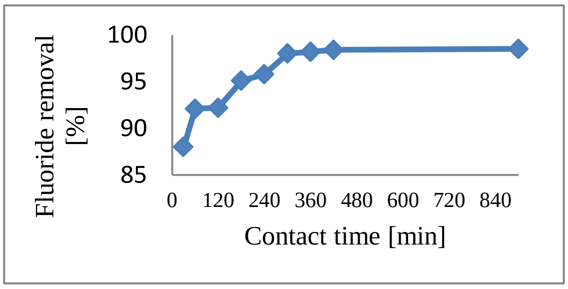

Fig. 2: Effect of initial fluoride concentration on adsorption of fluoride by sewage sludge ash.

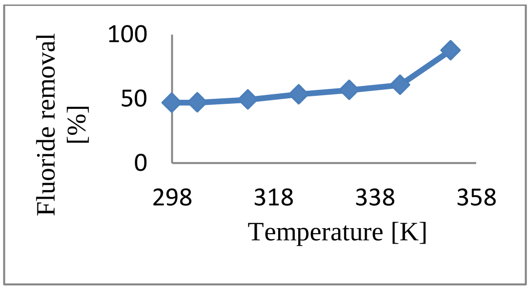

Fig. 3: Effect of contact time on adsorption of fluoride by sewage sludge ash.

The removal of fluoride by adsorption on sewage sludge ash was found to decrease significantly at very low pH, below 2, but with the increase of pH above 3, caused the crucial efficiency of adsorption increase and further pH increasing didn't bring important changes (Fig.4).

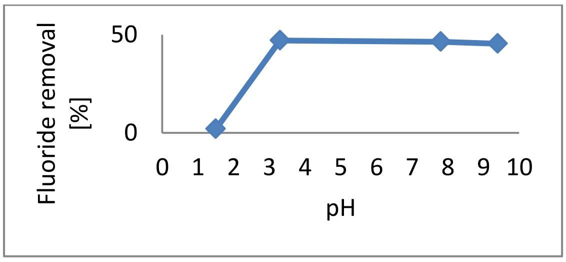

Fig. 4: Effect of pH on adsorption of fluoride by sewage sludge ash.

From the results achieved it can be found that the sewage sludge ash can be used as adsorbent of fluoride from water solutions. The highest fluoride adsorption efficiency has been achieved for low initial fluoride concentration of test solutions, e.g. below 0.2 gF^-/l, even at the very low amounts of ash dosed. In the case of more concentrated test solutions, the significant adsorbent efficiency has been achieved at the higher than 5 g/l of ash dose. Further dosage didn't bring important increase of fluoride removal efficiency. It can therefore be concluded that the sewage sludge ash can be a very effective fluoride adsorbent, from low as well from high fluoride concentration solutions.
This researches can show one of the reuse method of sewage sludge ash.

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