Removal of Fluoride from Ammonium Sulphate Solutions Using Bentonite

A. Zdunek[1], K. Borowik, D. Kołodyńska[2]

[1]Łukasiewicz Research Network - New Chemical Syntheses Institute , Pulawy, 24-110, Poland
[2]Maria Curie-Sklodowska University, Lublin, 20-031, Poland
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Presenting author email: krzysztof.borowik@ins.pulawy.pl

Fluoride removal issue is generally concerned with drinking water. The fluoride concentration in it is about 30 mg L^{-1} and the goal of fluoride removal process is to achieve the value of 1.5 mg L^{-1}, as is recommended by WHO [1,2]. In studies on fluoride removal from drinking water, there is also considered an influence of other than fluoride anions presence, such as: sulphates, nitrates and chlorides. Another type of systems contained fluoride ions are streams of industrial process water and wastewater. From the one hand, fluoride removal process from drinking water is easier than in the case of industrial streams because of low concentration of competing ions as well as neutral pH and not raised temperature. From the other hand, relatively low fluoride concentration in water causes that some of the fluoride removal methods are ineffective. Some kind of industrial process streams containing fluoride are process waters generated in the flue gases desulphurization process by wet ammonia method. The main ingredient of these streams is an ammonium sulphate $NH_4(SO_4)_2$, as the product of the ammonium ions reaction with sulphur oxides removed from flue gases. After the ammonium sulphate (*AS*) crystallization, the saturated solution of AS is generated. In this kind of streams, there are very specific conditions because of much higher than in water fluoride concentration and the presence of ammonium and sulphate ions in significant amounts. High value of ionic strength of AS solutions can reduce the solubility of precipitant in precipitate fluoride removal methods as well as affect on access to the active sites of the adsorbent in sorption methods. Another factors influencing on fluoride removal efficiency from desulphurization processes water streams are the pH and the temperature conditions. High AS concentration in these solutions contributes to specific value of pH factor equals around 5, without any possibility of its change. For this reason, some of the fluoride removal methods can turned out to be ineffective. After sulhpur oxides from hot flue gases absorption in ammonia water, there are process waters generated at temperature of 353 K, that similarly to pH factor, cannot be changed for the fluoride removal process. Presence of fluoride in that solutions causes a corrosive action of them, contributing to significant damages of individual elements of the desulphurization plant. Considering that AS is a known nitrogen-sulphur fertiliser and the component of other solid and liquid fertilizers, in addition to ammonium nitrate, urea and ammonium nitrate and urea simultaneously as well, the presence of some amounts of fluoride in ammonium sulphate can also affect the properties of these fertilizers.

One of the fluoride removal methods, apart from the precipitation, coagulation and ion exchange methods is the adsorption process [3]. In this kind of process, the fluoride removal can be caused by the physical adsorption as well as by the chemically bounding of them by cations that reveal the affinity to fluoride, and by the anion exchange process. There are many various types of adsorptive materials to fluoride removal, described in the literature [4]. One of them are bentonites, as natural materials that reveals the ability of fluoride binding [5].

The results of fluoride ions removal research, in the form of NH_4F, from aqueous and from ammonium sulfate solutions at concentration of 10-40% by mass, using two bentonites samples, has been described. The chemical composition obtained by XRF method, the characterization of crystal phases revealed by XRD method and the FTIR spectra obtained for bentonites used have been presented. The XRD and FTIR analyzes have been done both for the bentonites and for the solid rest obtained after contact of these materials with fluoride solutions as well. The characteristic of porosity and the specific surface area (BET) of materials used as well as their grain size distribution have been presented. For the characterization of ammonium sulphate influence on the fluoride removal by bentonites and to know a mechanism of this process, the pH of the point of zero charge (pH_{PZC}) was determined.

The research on impact of $(NH_4)_2SO_4$ presence on fluoride removal efficiency depending on the: bentonite dose, initial fluoride concentration, contact time and temperature was done. 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 effect of adsorbent dose was studied by varying the dose in the range 10-40 g per liter of test solution with the variable fluoride concentration in the 0.05-1 gL^{-1} 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 gL^{-1} and the constant amount of bentonite. These experiments have been done with the same sorption time of 60 minutes. To investigate the

effect of contact time on the degree of sorption, experiments were carried out with a dose of bentonites of 40 gL^{-1} and with a fluoride solution of 0.5 gL^{-1} and with variable contact time from 30 to 420, and with 900 minutes when the equilibration state was achieved. Each experiment with the same measurement parameters were repeated three times and then the average value has been set. Every test with special conditions was carried out as well for aqueous and for ammonium sulphate solution, contained fluoride ions.

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 tables 1 and 2 the results of fluoride concentration impact research on removal efficiency obtained, from aqueous and ammonium sulphate solutions as well, have been shown. In these tests, the dose of 40 gL^{-1} of bentonites and the 60 minutes of contact time have been used.

Table 1. Effect of initial fluoride concentration on removal efficiency by use of bentonite I (dose of 40 gL^{-1}, 60 minutes of contact time.

Initial fluoride concentration [gL^{-1}]	Fluoride removal efficiency from aqueous solution of NH_4F [%]	Fluoride removal efficiency from ammonium sulphate solution of NH_4F [%]			
		10% by mass	20% by mass	30% by mass	40% by mass
0.05	31.33	3.38	3.75	10.89	5.57
0.1	20.05	13.52	6.65	15.86	16.12
0.2	16.45	41.66	32.80	19.27	17.71
0.5	13.93	53.26	48.96	51.99	57.84
0.7	15.68	48.18	44.91	50.50	43.85
1	18.47	40.53	43.63	44.27	38.92

Table 2. Effect of initial fluoride concentration on removal efficiency by use of bentonite II (dose of 40 gL^{-1}, 60 minutes of contact time.

Initial fluoride concentration [gL^{-1}]	Fluoride removal efficiency from aqueous solution of NH_4F [%]	Fluoride removal efficiency from ammonium sulphate solution of NH_4F [%]			
		10% by mass	20% by mass	30% by mass	40% by mass
0.05	51.53	3.75	7.71	8.11	4.12
0.1	53.38	12.85	7.36	18.78	22.29
0.2	20.38	48.37	36.78	20.79	19.88
0.5	6.53	55.52	51.44	55.86	57.52
0.7	14.27	67.49	47.78	54.14	45.54
1	19.97	42.54	43.42	46.97	40.76

As it can be seen in tables 1 and 2, efficiency of fluoride removal using bentonites is different for aqueous and ammonium sulphate solutions. Presence of AS causes significant decrease of it for lower concentration of fluoride ions, but with the increase of initial amount of fluorides, there is a considerable increase of fluoride removal effectiveness observed. Therefore, it can be concluded that the use of bentonites to purify of AS solutions from fluoride can be beneficial under special conditions.

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