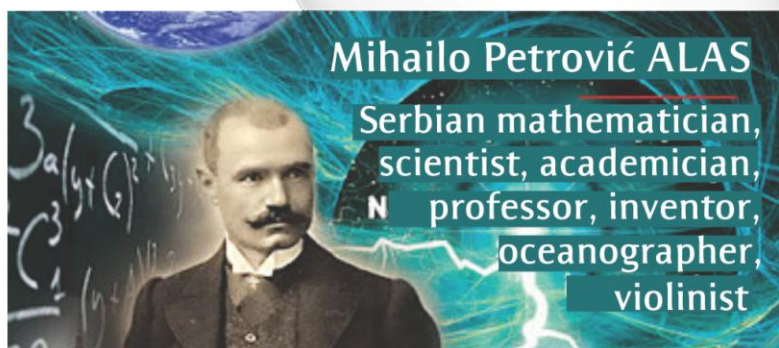




ОТЕН 2020



9th INTERNATIONAL SCIENTIFIC CONFERENCE
ON DEFENSIVE TECHNOLOGIES
Belgrade, 15-16, October 2020



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QUALITY, STANDARDIZATION, METROLOGY, MAINTENANCE AND EXPLOITATION



Belgrade, 15-16 October 2020
MILITARY TECHNICAL INSTITUTE
Belgrade, Serbia

Publisher

The Military Technical Institute
Ratka Resanovića 1, 11030 Belgrade

Publisher's Representative

Col **Bojan Pavković**, PhD (Eng)

Editors

Miodrag Lisov
Ljubica Radović

Technical Editing

Dragan Knežević

Printed by

The Military Technical Institute
Ratka Resanovića 1, 11030 Belgrade

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

NAUČNO-stručni skup iz oblasti odbrambenih
tehnologija (9 ; 2020 ; Beograd)
Proceedings [Elektronski izvor] / 9th
International Scientific Conference on
Defensive Technologies, OTEH 2020, Belgrade,
15-16 October 2020 ; [organized by] Military
Technical Institute, Belgrade ; [editors Miodrag
Lisov, Ljubica Radović]. - Belgrade : Military
Technical Institute, 2020 (Beograd : Military
Technical Institute).

Sistemska zahtevi: Nisu navedeni. - Nasl. sa
naslovne strane dokumenta. -
Bibliografija uz svaki rad.

ISBN 978-86-81123-83-6

1. Vojnotehnički institut (Beograd)

- a) Војна техника - Зборници
- b) Технички материјали – Зборници
- c) Телекомуникациони системи - Зборници

9th INTERNATIONAL SCIENTIFIC CONFERENCE

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PREFACE

Military Technical Institute, the first and the largest military scientific-research institution in the Republic of Serbia with over 70 years long tradition, has been traditionally organizing the OTEH scientific conference, devoted to defense technologies. The Conference is supported by the Ministry of Defense and it takes place every second year.

Its aim is to gather scientists and engineers, researchers and designers, manufactures and university professors in order to exchange ideas and to develop new relationships.

The ninth International Scientific Conference OTEH 2020 is scheduled as follows: lecture on the occasion of “Mihailo Petrovic Alas”, given by Prof. Žarko Mijajlović, PhD, and plenary lecture on “Electromagnetic Pulsed Weapon Treat Hmp and Hemp“, given by Prof. Momčilo Milinović, PhD Eng, and working sessions according to the Conference topics.

The papers which will be presented at the Conference have been classified into the following topics:

- Aerodynamics and Flight Dynamics
- Aircraft
- Weapon Systems and Combat Vehicles
- Ammunition and Energetic Materials
- Integrated Sensor Systems and Robotic Systems
- Telecommunication and Information Systems
- Materials and Technologies
- Quality, Standardization, Metrology, Maintenance and Exploitation.

The Proceedings contain 97 reviewed papers which have been submitted by the authors from 13 different countries. I would also like to emphasize that 23 papers are from abroad. The quality of papers accepted for publication achieved very high standard. I expect stimulated discussion on many topics that will be presented online, during two days of the Conference.

On behalf of the organizer I would like to thank all the authors and participants from abroad, as well as from Serbia, for their contribution and efforts which made this Conference possible and successful.

I would also like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for its financial support.

Finally, dear guests and participants of the Conference, I would like to wish you a pleasant and successful work during the Conference. I am looking forward to see you again at the tenth Conference in Belgrade. All the best and stay healthy.

Belgrade, October, 2020

Col. Miodrag Lisov PhD Eng
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REMOVAL OF FLUORIDE IONS FROM WATER SOLUTIONS BY HYDROXYAPATITE LOADED ALUMINIUM GELLED ALGINATE PARTICLES

MILAN MILIVOJEVIC

Faculty of Technology and Metallurgy, Belgrade University, Belgrade, mmilan@tmf.bg.ac.rs

MARIJA JOCIC

Faculty of Technology and Metallurgy, Belgrade University, Belgrade, marija.ofelija@gmail.com

MLADEN BUGARCIC

Institute for Technology of Nuclear and other Mineral Raw Materials, Belgrade, m.bugarcic@itnms.ac.rs

ANJA ANTANASKOVIC

Institute for Technology of Nuclear and other Mineral Raw Materials, Belgrade, a.antanaskovic@itnms.ac.rs

RADA PJANOVIC

Faculty of Technology and Metallurgy, Belgrade University, Belgrade, rada@tmf.bg.ac.rs

ZORICA LOPICIC

Institute for Technology of Nuclear and other Mineral Raw Materials, Belgrade, z.lopicic@itnms.ac.rs

Abstract: Fluoride ions (F^-) might be found in drinking or wastewaters in too high concentrations either due to the anthropogenic activity or some natural sources. Due to their negative effects on human health, allowed concentrations for F^- content in drinking water have been decreased. Therefore, in the last decade, investigations into researches in new materials/techniques for fluoride removal from water streams have been intensified. This paper examines the potential of hydroxyapatite loaded aluminum gelled alginate particles as an efficient and cheap sorbent for F^- removal. The adsorbent characterization before and after F^- adsorption was performed using FT-IR technique. Adsorption experiments were conducted in a stirring batch mode, varying concentration of adsorbate. Obtained results indicate good adsorption capacity and removal efficiency, while FTIR spectra analysis point to the increased stability of investigated adsorbent compared to Al-alginate without HAP.

Keywords: adsorption, fluoride ion, aluminum alginate, hydroxyapatite.

1. INTRODUCTION

Fluorides are naturally present in water from the dissolution of fluoride bearing minerals and dominant form of fluoride present in waters is fluoride-ion (F^-), although other forms of dissolved fluorine can be present due to fluoride strong tendency to form ligands [1]. Consequently, fluoride ion could form many different stable complexes. With Be^{2+} , Al^{3+} and Fe^{3+} ions fluorine in water forms stable complexes, with boron it forms mixed fluoride-hydroxyl complexes, with silicon, in acid solutions it make complex ions, while the most stable complexes it forms with aluminum [2]. Those geological sources are the main ways of drinking water contamination with fluoride, while drinking water is the major source of daily fluoride intake. Another fluoride entry into the ground and surface waters are aluminum, copper, nickel and zinc production facilities and smelters, uranium enrichment and beryllium extraction facilities, ceramic, glass, steel, cement, glues and adhesives manufacturing processes, coal fired power stations, oil

refineries, treatment of phosphate minerals, production and usage of phosphate fertilizers or fluorine-based pesticides, semiconductor, display panel and photovoltaic solar cells industries, municipal waste incineration plants and others [1,2,3].

Optimal fluoride intake dose depends mainly on person's age, health and weight. However, fluoride in small concentration can bind to the functional amino acid groups located around the active center of some enzymes (contains metal ion which creates metal-fluoride complex) causing decreasing of their activity [2,4]. In addition, surplus of fluorides in organism due to the excessive intake of fluoride (i.e. by the continuous consumption of drinking water with excess amount of fluoride (>1.5 mg/L) can provoke mild (dental and skeletal fluorosis [1]) to serious (masculine infertility and cancer, induction of birth, reproduction and immunological defects, lesions of the thyroid, endocrine glands, and brain [1,3,5]) health problems as the concentration and time period of exposure to elevated fluoride concentrations increase.

Thus WHO recommended a fluoride level in drinking water from 0.5 to 1.5 mg/L as the permissible limit due to its possible detrimental effects, although doses of 0.073 mg/kg body weight may be considered as tolerable, while those over 0.150 mg/kg are chronically toxic [6].

Increased demands for healthy drinking water as well as awareness of fluoride toxicity induced, raised the need for development of new techniques for fluoride removal from drinking water. In order to prevent contamination of the groundwater by the fluoride or to decrease its concentrations in drinking water to acceptable levels researchers have developed various techniques for fluoride removal like [1,7]:

- Coagulation and chemical precipitations (very efficient but expensive, pH and pI dependent, produce toxic waste);
- Membrane filtrations (very efficient and may remove other pollutants at the same time, but have high capital, maintenance and operational costs);
- Electrochemical treatments (high efficiency and selectivity but high operational and maintenance costs);
- Ion exchange methods (very efficient but no selectivity for other interfering anions, strongly dependent on pH, and generate toxic waste);
- Adsorption by different natural and synthetic materials (most used methods for fluoride removal due to its advantages although it is pH dependent and with some interfering of other anions).

In recent decade's adsorption have become the most used method for fluoride ion removal since it is economic, environmental friendly and effective method. Its advantages over other methods are numerous such as low cost, efficient removal even at low concentrations and high capacities, simplicity, no sludge generation and wide range of potential adsorbents [1,7,8].

Among adsorbents of fluoride ion the mostly applied are carbonaceous materials and activated or modified carbon and activated alumina, hydroxyapatite or bone char, zeolite, zirconium and/or cerium modified materials, bauxite, hematite, clays, modified ferric oxide/hydroxide, and many others [1,3,5]. In recent years, biosorbents become increasingly popular, most notably chitin, chitosan, alginate, cellulose, and various agricultural and biological waste biomass from leaves, algae, yeast, bacteria and others. [4,6,9]. However, the main problem is that most adsorbents can't adsorb fluoride ion at low concentrations (< 2 ppm), or work only at extreme pH values [9]. Therefore, finding efficient, cheap, and environmentally friendly adsorbent is still an open problem.

Alginates are mainly obtained from seaweed and belong to natural, water-soluble, anionic polymers, consisted of differently distributed blocks of manuronic and guluronic acid. Their most important property, which made them one of the most widely used polymers in various branches of science, is the formation of gels in contact with multivalent cations [10]. Alginates are a good substitute for more expensive adsorbents as they are cheap and very effective [11]. If alginate gel is formed by positively

charged multivalent cations (i.e. Fe^{3+} , Al^{3+} , Ce^{3+} , La^{4+} , Zr^{4+}), the adsorption capacity of the alginate can be increased [12]. Alginate gels gelled by aluminum ions are physically most stable and have a high affinity for fluoride ion adsorption [3,6].

Hydroxyapatites (HAP), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, naturally occurs in the form of calcium apatite. The OH^- ion can be replaced by fluoride, chloride or carbonate, forming fluoroapatite or chlorapatite. The HAP has shown an excellent capability for the uptake of F^- ion from water [13]. The HAP is commonly used for adsorption in the powder form in order to enhance adsorption kinetics. However, powder form prevents their wider application on industrial scale due to the problem of their removal from the water solution after adsorption.

In order to solve this problem the HAP powder was immobilized in microparticles of natural gelling polymer - alginate. This polymer was gelled by Al^{3+} ion in order not only to immobilize hydroxyapatite but also to eventually help additional adsorption of fluoride ions. Due to all the above, in this paper, the possibility of removing F^- ions on composite particles made of HAP immobilized in Al^{3+} gelled alginate was investigated.

2. MATERIALS AND METHODS

Preparing of fluoride ion solutions

A standard fluoride ion solution (1 g/L) was prepared by dissolving appropriate amount of NaF (PA, Sigma, Sigma-Aldrich CO., St. Louis, MO) in deionized water. In order to test the adsorption properties of the adsorbent at different initial concentrations (c_0), the standard solution was diluted to 5, 10 and 22 mg/L. The pH of the solution was adjusted by adding small amounts of 0.1 M HNO_3 or 0.1 M NaOH with a micropipette, and the pH was maintained using TISAB (Total Ionic Strength Adjustment Buffer).

Preparation of adsorbent

A solution of Na-alginate (2% w/v), was obtained by adding 2 g of alginate to 98 ml of distilled water which was then stirred vigorously on a mechanical stirrer at 200 rpm and room temperature for 1-3 h. When Na-alginate was completely dissolved 2 g of HAP was added to solution and stirred for 1 h in order to suspend HAP powder into alginate solution. A gelling solution (4% w/v), AlCl_3 , was obtained by adding 4 g of AlCl_3 in 96 ml of deionized water. The alginate solution with suspended HAP powder was then dripped from a 20 ml plastic syringe into the AlCl_3 solution using an infusion pump (Razel, Scientific Instruments, Stanford, CT) to form HAP loaded aluminum alginate particles. The particles stay in AlCl_3 solution for 24 h to gel completely, and then were separated from the solution and washed four times with distilled water to remove residual AlCl_3 . The particles were then left in deionized water for 24 h to complete the rinsing, and subsequently filtered and dried in an oven at 60 °C for 24 h.

Measurements

The pH of the solution was monitored by pH meter (SensION MM340), and the fluoride concentration was measured with a combined fluoride electrode (9609 BNWP). After the adsorption process was completed, the residual concentration of residual adsorbate, C_f , was measured, and the degree of removal q (mg/g) was calculated by equation (1):

$$q = [(C_i - C_f)V] / M \quad (1)$$

The percentage of removal, R (%), as a quantity that describes the sorption efficiency, was calculated according to equation (2):

$$R(\%) = [(C_i - C_f) / C_i] * 100 \quad (2)$$

In equations (1) and (2) V is the volume of the adsorbate solution (L), M is mass of the adsorbent (g), and C_i and C_f concentrations of the sorbate at the beginning and end of the adsorption process (mg/L).

Experiments described in this paper were performed in duplicate, and given values represent the mean value of the obtained results.

Analysis of the FTIR spectra of the tested samples was performed on an FTIR spectrometer (Bomem-Hartmann & Braun, Canada). The prepared samples were analyzed at a resolution of 4 cm^{-1} in the range of $4000\text{-}600 \text{ cm}^{-1}$.

3. RESULTS AND DISCUSSION

The influence of the initial fluoride concentration is an important factor because with the increase of the fluoride ion concentration, the adsorption capacity of the adsorbent increases, while the percentage of the total removed fluoride ions decreases [14]. Fluoride adsorption was examined at initial fluoride concentrations of 5, 10, and 22 mg/L. The influence of initial fluoride concentrations on adsorption efficiency was investigated in a batch system with stirring, for constant ratio of solid and liquid phase $M/V = 2 \text{ g/L}$, at a temperature of $25 \text{ }^\circ\text{C}$, $\text{pH} = 6$ and 200 rpm. The experimentally obtained results for adsorption capacities and removal efficiencies are shown in Figures 1 and 2.

Figure 1 shows that the adsorption capacity increases with increasing fluoride concentration, which is expected because the utilization of the adsorbent is higher at a higher initial concentration of adsorbate. From Figure 1, we can also see that the adsorption process is fast, especially at lower concentrations, so the use of this adsorbent can very efficiently and in a relatively short time (70 min) achieve equilibrium. For the comparison, when fluoride was adsorbed on zeolite and titanium dioxide, the equilibrium states were reached after 120 and 180 min respectively [14,15]. However, as in can be seen from Figure 2 with increasing concentration, the removal efficiency decreases (after 60 minutes at a fluoride concentration of 5 mg/L the removal efficiency is 79.5%, at 10 mg/L it is 66%, while at 22 mg/L it is only 39%), so it is necessary to find a balance in choosing the optimal

operating parameters in order to get fast process with appropriate removal efficiency. It should be also emphasized that obtained results are worse compared to the results obtained for Al-alginate particles without HAP [6].

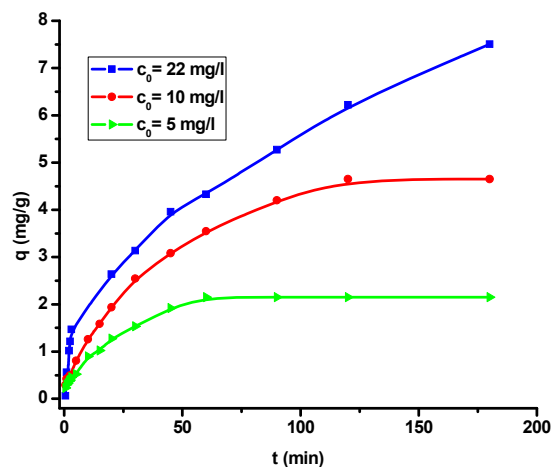


Figure 1. Adsorption capacity (q) as function of time and fluoride ion concentration ($C_0 = 5\text{-}22 \text{ mg/L}$, $\text{pH} = 6$, $M/V = 2 \text{ g/L}$, $T = 25 \text{ }^\circ\text{C}$, stirring speed 200 rpm)

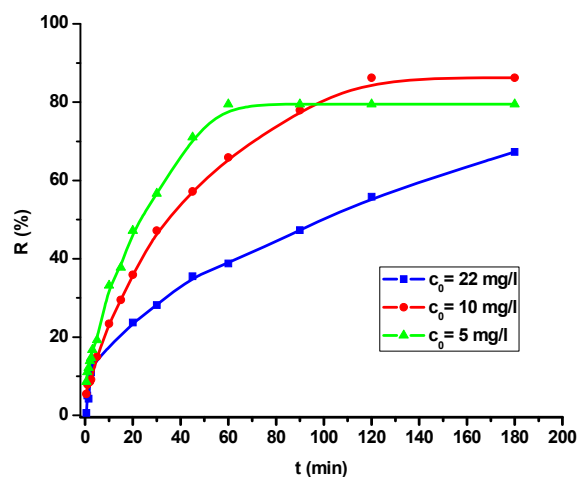


Figure 2. Fluoride ion removal efficiency (R) as function of time and fluoride ion concentration ($C_0 = 5\text{-}22 \text{ mg/L}$, $\text{pH} = 6$, $M/V = 2 \text{ g/L}$, $T = 25 \text{ }^\circ\text{C}$, stirring speed 200 rpm)

Adsorbent characterization by the FTIR analysis

HAP loaded Al-alginate particles were characterized before and after adsorption using the FTIR method. This was done in order to get a clearer picture of the strength of interactions between system components, as well as, about the groups involved in the binding of components to HAP and/or Al-alginate, based on the difference of these spectra.

Figures 3 and 4 shows the FTIR spectra of the HAP loaded Al-alginate particles before and after fluoride adsorption.

In Figure 3 the result of FTIR analysis for the HAP loaded Al-alginate particles before fluoride ion adsorption

is presented. The FTIR spectra contain characteristic bands for HAP presence. Bands characteristic of phosphate groups are observed at 595, 958 and 1024-1115 cm^{-1} . The bands characteristic for hydroxyl group occur at 3584 and 1636 cm^{-1} , and the band characteristic for the HPO_4^{2-} ion is noticeable at 873 cm^{-1} . Wide bands at 1650 and 3440 cm^{-1} indicate the presence of adsorbed water in the material.

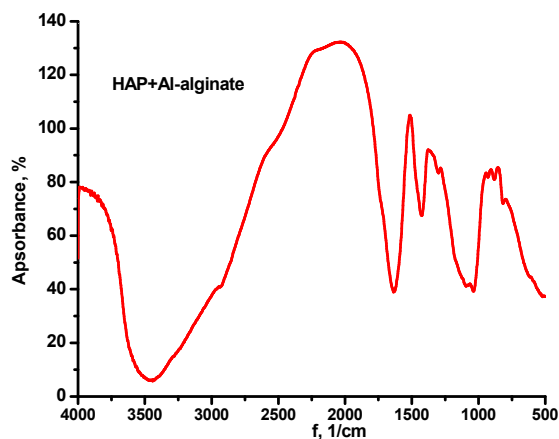


Figure 3. FTIR spectra of HAP loaded Al-alginate sample before fluoride adsorption

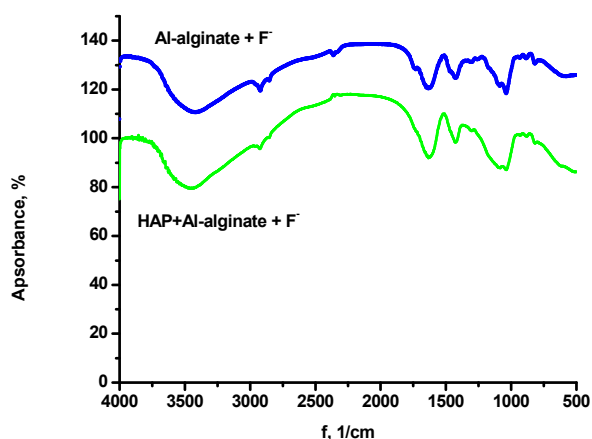


Figure 4. FTIR spectra of HAP loaded Al-alginate sample after fluoride adsorption

Figure 4 present FTIR spectra comparison of the HAP loaded Al-alginate particles and Al-alginate particles without HAP after fluoride ion adsorption. Analyzing the FTIR spectra of samples of alginate gelled with Al^{3+} ions (Al-alginate) and HAP loaded Al-alginate material after adsorption of fluoride ions (F^-), it may be observed that there are significant differences in the structure of the spectrum after adsorption to Al-alginate compared to HAP loaded Al-alginate. The band at 1724 cm^{-1} indicates the presence of adsorbed fluoride ion on the Al-alginate adsorbent while that peak is not present on Al-alginate with added HAP. The presence of HAP in the hybrid structure of HAP loaded Al-alginate contributes to significant competition of HAP- F^- bounds with regard to the construction of Al- F^- structures in Al-alginate. The mechanism of F^- binding to the surface of HAP is simple

physical adsorption, which indicates that this process is more energy efficient. Adsorbing F^- ions on HAP, is competitive to less pronounced Al- F^- bond forming by breaking the Al-carboxylate bonds. This makes HAP loaded Al-alginate particles more stable in the presence of higher concentrations of F^- ions preventing their degradation in this case. In addition, Al-alginates with added HAP increase the vibration intensity at 1088 cm^{-1} , and also have wider bands at 1221-1283 cm^{-1} indicating a significant adsorption capacity of HAP towards fluoride ions. Thus although the HAP loaded Al-alginate particles have somewhat slower kinetic compared to the Al-alginate [6], they are more stable and still have good adsorption capacities.

4. CONCLUSION

Based on the obtained results it can be concluded that HAP loaded Al-alginate particles are a good adsorbent that can be used to reduce the concentration of fluoride ions in drinking or wastewater in a cheap and efficient way. The FTIR spectra analysis point to the increased stability of investigated adsorbent compared to Al-alginate without HAP.

ACKNOWLEDGMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No. 451-03-68/2020-14/200135 and 451-03-68/2020-14/200023).

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