Available online at www.ejournals.uofk.edu

UofKEJ Vol. 9 Issue 1 pp. 5- 10 (February 2020)

UNIVERSITY OF KHARTOUM ENGINEERING JOURNAL (UofKEJ)

Fluoride Removal from Drinking Water Using Aluminium Oxide Coated Charcoal – effectiveness of repetitive regenerations

Motwkel M. E. Alhaj [1], **Bashir M. Elhassan** [2]

Ministry of Irrigation and Water Resources[2] *University of Khartoum,*
Chemical Engineering Department
(E-mail: motwkel-dwsu@wre.gov.sdand, bashirelhassan.14@gmail.com)

Abstract: There are many techniques to remove fluoride from drinking water. However, adsorption was found to be very effective and easy to apply. Along with this line, many studies were done to find an effective and affordable fluoride adsorbent. Activated Alumina (AA), Aluminum oxide coated sand (AOCS), pumice (AOCP), bauxite (AOCB) and charcoal (AOCC) were recently investigated. Nevertheless, AOCC found to be more promising for two reasons: it is cheap and can be regenerated. This paper aims to further contribute to feasibility of AOCC for fluoride removal in order to reduce the operation cost. Batch and continuous flow filter runs were conducted AOCC regenerated batch-wise, and used for the next filter run. AOCC was consequently regenerated three times. The results showed a considerable increase in AOCC fluoride adsorption capacity after each regeneration cycle. Characterization of virgin charcoal, virgin AOCC and regenerated AOCC after the first, the second and the third regeneration cycle, showed that virgin charcoal has highest specific surface area and micro porosity. For virgin AOCC and regenerated AOCC after the first, the second regeneration cycle a reduction in the specific surface area occurred, coupled with a reduction of micro porosity. AOCC after third regeneration cycle showed an increase in specific surface area likely due to aluminum hydroxide deposits on re-coated AOCC surface. Most of the pores after the third regeneration cycle were found to be meso pores. This means that, specific surface area alone cannot explain the increase in the AOCC adsorption capacity after regeneration. The paper recommends investigating the fluoride removal mechanism onto AOCC in order to produce affordable fluoride removal material from drinking water.

Keywords: fluoride removal, adsorption, regeneration, removal mechanism, characterization, aluminum oxide coated charcoal.

1. INTRODUCTION

Fluorine is very active element; it is the first element of the halogens group with a molar mass of 37.99g/mole. Fluoride forms about 0.1% of the earth crust. (Farwell et al, 2006).

Fluoride is a useful element for human health when its concentration in drinking water is below WHO guidelines of less than 1.5 mg/l. If fluoride is found in high concentration in drinking water then it could cause serious problems for the human health. Many areas around the world have high fluoride concentrations in ground water. The source of fluoride in groundwater comes from fluorspar, cryolite and fluropatite which are abundant in the earth crust. Groundwater in the areas rich with these minerals probably contains high levels of fluoride (WHO 2011).

Bhatnagar et al (2011) stated that when fluoride dissolves in water it is colorless and odorless, so the only way to detect fluoride is through chemical analysis. The dissociation process of fluoride from its minerals depends on many factors such as the concentrations of other aqueous ionic elements, the contact time between water and Minerals, electrical conductivity, temperature and pH (Saxena and Ahmed 2003). Exposure to high concentrations of fluoride for long periods of time can cause many serious health problems for the human. Fluoride concentration of 3 to 6 mg/l in drinking water, coupled with high water consumption may lead to changes in bone structures. When the concentration exceeds 10 mg/l, probably crippling skeletal fluorosis will develop (WHO, 2011). Many areas around the world suffer from high fluoride concentrations in groundwater. The most affected areas are Eastern Africa, the Eastern Mediterranean and southern Asia, China, America and Japan (WHO, 2011). There are three main methods to remove fluoride from drinking water; precipitation, membrane filtration and adsorption. Calcium and Sulfate compounds could be used to precipitate fluoride (Fawell et all, 2006). Although membrane technology is very efficient even with very high fluoride concentration; the problem is that for economic and technical considerations this technique is not suitable for remote areas in developing countries.

Different adsorbents could be used for fluoride removal. For example, aluminium compounds, clay, soils, calcium compounds, bone charcoal, etc. Aluminium hydroxide is widely used for fluoride adsorption due to its high efficiency. However, aluminium oxide coated charcoal (AOCC) found to be the best adsorbent to remove fluoride from groundwater.

Dava, 2015 found that (AOCC) has high capacity for fluoride removal. Single regeneration of fluoride saturated AOCC also showed not only full recovery of adsorption capacity, but an increase of the capacity of this adsorbent. However, no one tried to conduct multiple regenerations of fluoride saturated (AOCC) to see to what extent will the adsorption capacity be recovered or even further increased.

On the other hand, characterization of the material saturated with fluoride is limited. So additional characterization with Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) before and after adsorption process, including after multiple regenerations will be very useful to better understand the adsorption process of fluoride on (AOCC).

Furthermore, Brunauer- Emmett–Teller (BET) method will be very important to understand the effect of multiple regeneration of AOCC on its physical properties and to link them with adsorption capacity.

This study aims to investigate fluoride removal performance of repetitively regenerated Aluminium Oxide Coated Charcoal AOCC, in continues flow adsorption experiments. Furthermore, it aims to characterize fluoride-saturated (AOCC) to better understanding the effect of multiple regenerations on physical properties of AOCC.

2. Literature Review

2.1. Fluoride occurrences in groundwater

Fluoride found in nature as a component of many minerals such as fluorspar, rock phosphate, apatite, cryolite, mica and fluorite (Petrusveski, 2016). There are similarities between fluoride and hydroxide ions. Both of them has the same charge and diameter and can exchange in the mineral structures.

In addition to natural minerals there are anthropogenic sources of fluoride in groundwater. Some industrial waste such as toothpaste, steel, glass and fertilisers contain high fluoride concentrations. When fluoride rich water is mixed with receiving water bodies, fluoride concentration can exceed the standards allowed for drinking water (Kumara and Sillanpaa, 2011).

2.2. Health impact of fluoride

Fluoride is a very important element for human health especially for the teeth. If the fluoride concentration in drinking water is less than 0.5 mg/l, the teeth may suffer from dental carries. On the other hand, if the concentration is more than 1.5 mg/l this will cause mild dental fluorosis. The fluoride concentrations exceeding 5 mg/l will strongly increase the probability of skeletal fluorosis. (Farwell, et al, 2006).

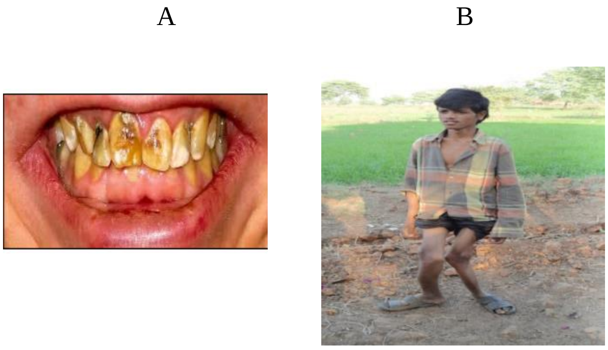

Fig .1. (a) Dental and (b) skeletal fluorosis

[Source: Sunil Kumar and Sanjay K Sharma, 2017]

2.3. Adsorption Technique

Thompson 1995 stated that Adsorption is a process of collection of a specific substance at the surface of other substance. The substance accumulates at the interface between two phases. The substance which accumulates at the interface is called adsorb ate, while the material which is used in adsorption is called adsorbent. Most of the chemical processes which occurs at the surfaces are affected by adsorption.

There are three different types of adsorption: Chemical adsorption, physical adsorption and ion-exchange. In the chemical adsorption, chemical bond links between the substances and the adsorbent, while physical adsorption occurs due to weak attraction force between molecules. Ion-exchange adsorption results from electrostatic attractions between different ionic charges (Uwamariya, 2013).

2.4. Adsorption Isotherms

There are many models to describe adsorption process. Freundlich, Langmuir and BET isotherms are the most famous adsorption models.

(a) The Freundlich adsorption isotherm

Freundlich isotherm gives a quantitative description to the movement of the solute between the solutions and the adsorbent. (Skopp, 2009).

The Freundlich isotherm equation is:

$$q = K\, C_e^{1/n} \tag{1}$$

Where:

q = amount of solute adsorbed per unit weight of adsorbent (g/g)

C_e = equilibrium concentration of the solute (g/m^3)

K = adsorption capacity (constant)

1/n = adsorption intensity (constant)

By taking logarithm for both sides, the equation will be linear.

$$\text{Log } q = \log K + 1/n \log C_e \tag{2}$$

From equation 2 it is clear that, as equilibrium concentration C_e increase, the adsorptive capacity q also increases.

(b) The Langmuir adsorption isotherm

The Langmuir adsorption isotherm assumes that most of the adsorption occurs at the adsorbent surface. Each site of the adsorbent can adsorb one molecule, so it is a monolayer adsorption (Chen, 2016)

$$q = \frac{b q_m C_e}{1 + b C_e} \tag{3}$$

Where:

q = amount of solute adsorbed per unit mass of adsorbent (g/g)

q_m = maximum adsorption capacity (g/g)

C_e = equilibrium concentration of the solute (g/m^3)

b = Langmuir isotherm constant, related to the energy of adsorption (m^3 of adsorbent/ g of adsorb ate)

The linear form of Langmuir isotherm equation is

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{b q_m}\frac{1}{C_e} \tag{4}$$

The separation factor (r) which predicts if an adsorption system is favourable or unfavourable can be calculated as follows:

$$r = 1/\,(1 + bC_o) \tag{5}$$

Where:

b = adsorption constant C_o= initial concentration

(c) Brunauer–Emmett–Teller (BET) Isotherm

BET is the best isotherm which can describe multilayer adsorption process (Andrade, 2010).

$$\frac{q}{q_m} = \frac{BC_e}{(C_s - C_e)[1 + (B-1)(C_e/C_s)]} \tag{6}$$

Where:

q = amount of solute adsorbed per unit weight of adsorbent (g/g)

q_m = maximum adsorption capacity (g/g)

C_s = saturation concentration (g/m^3).

Ce = equilibrium concentration of the solute (g/m_3)

B = constant (dimension less).

C_s = saturation concentration.

2.5. Factors affecting fluoride adsorption onto aluminium oxide coated charcoal

2.5.1. Effect of particle size

Dava (2015) conducted fluoride adsorption experiment with AOCC. He found that, when fine AOCC particles (0.425 to 0.8 mm) are used, the adsorption capacity increased by about 32% from that obtained when coarse AOCC particles (0.8 – 1.12 mm) were used. Furthermore, the adsorption intensity was found to be inversely proportional to particle size, the smaller the particle size, the higher the adsorption intensity.

2.5.2. Effect of pH

Similarities between fluoride ions and hydroxyl ions in terms of charge make the replacement of hydroxyl ions with fluoride ions very easy. Hence, fluoride removal using aluminium hydroxide is very effective (Faust and Aly 1998). Bhatnagar (2011) found that, fluoride removal efficiency using aluminium oxide is very sensitive to pH value, and the fluoride concentration to aluminium concentration ratio. When pH is less than 6, and the ration of fluoride to aluminium ions is more than 2.5, then, formation of aluminium fluoride will happen, which, resultsin the dissolution of amorphous aluminium hydroxide. While at lower fluoride to aluminium ratios, the dissolution rate is less. So, amorphous aluminium hydroxide is present, even in the pH range between 4 and 7. The amorphous aluminium hydroxide adsorbs fluoride ions effectively from the solution. The highest fluoride adsorption capacity of about 9 mole/kg is at pH values between 5.5 and 6.5. When pH is less than 5.5, soluble aluminium fluoride compound will be produced. So, fluoride removal efficiency decreases. On the other hand, when pH is more than 6.5; hydroxyl ions replace fluoride ions in the solid compound, which lead to a decline in fluoride removal rate.

2.5.3. Effect of temperature

López et al. ((2006) reported that, the point of zero charge of aluminium oxide has an inverse linear relationship with temperature. When the temperature and pH increase, accordingly aluminium oxide surface will increase, and hydroxyl group surface stability will increase too. So, when water temperature increases from 25 to 40 °C, the fluoride adsorption rate decreases.

Fig 2 shows adsorption efficiency of fluoride on aluminium oxide in different temperatures.

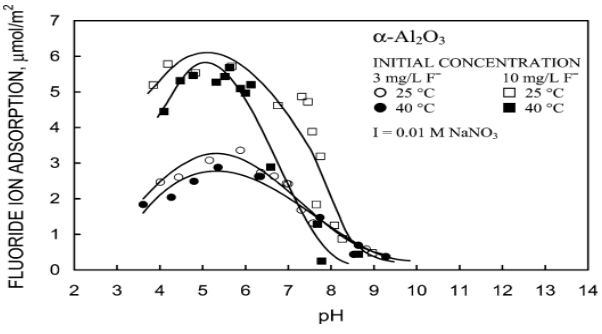

Fig .2. (Adsorption of fluoride on α-Al2O3 as a function of pH at 25 and 40°C. Initial fluoride concentration is 10 mg/L.

[Source Valdivieso, et al 2006]

3. Materials and methods

3.1. Model water preparation

Model water was prepared by adding fluoride and bicarbonate stock solutions to tap water, in order to targeted model water composition, namely bicarbonate concentration of 350 mg/l, fluoride concentration of 5 mg/l and pH 7.

3.2. adsorbent preparation

Virgin charcoal with particle size varied between 0.425 and 0.8 mm was prepared. Raw charcoal was crushed and sieved using the sieving machine. Then washed to remove fine particles and dried in order to be ready for the coating process.

3.3. coating and regeneration processes

According to procedures suggested by Salifu, et al., 2013 and Msilama, 2014; Virgin charcoal which has a particle size between 0.425 and 0.8 mm was immersed in enough amount of 0.5 M of aluminium sulfate solution, then it was mixed for 30 minutes, and then left for 30 minutes. The coated charcoal was then separated from the solution and left to dry.

Subsequently, Aluminium oxide coated charcoal was mixed with 3M aluminium hydroxide and stirred gently for 30 minutes in order to convert aluminium oxide to aluminium hydroxide. Then coated and neutralized charcoal was separated from the solution and dried with air for one day. After using of adsorbent; the regeneration process will be same as coating process mentioned above.

$$2\,NH_4OH + Al_2O_3 + H_2O \text{ ---------> } 2\,Al(OH)_3 + N_2 + 3\,H_2 \qquad (7)$$

3.4. Experimental set-ups and procedures

Two experments setup were used in order to achieve the study objectives.

3.4.1. Batch experiments to establish adsorption isotherm

The aim of this batch experiment was to establish the adsorption capacity of virgin AOCC. In order to conduct this experiment, different weights of AOCC namely: 0.5, 1.0, 2.0, 3.0, 3.5, 4.0, and 5 grams were taken and placed in 500 ml poly ethylene bottles. This step was duplicated. Then all bottles were filled with model water (5.0 mg F^-/l and 330 mg HCO^-_3/l). Following steps were applied for all bottles:

a) Model water pH was adjusted to 7.0±0.1 by using concentrated hydrochloric acid and/or 6.0N sodium hydroxide solution.
b) AOCC was added to the bottles.
c) PH was readjusted again to 7.0±0.1.
d) The bottles were closed properly to avoid any change in pH during the shaking process.
e) Samples were taken through syringe after 96, 120, 168, 176 and 200 hours to ensure that the equilibrium reached. Then the samples were filtered immediately through Whatman filter paper (25 mm diameter and 0.45µm pore size). 25 ml of filtrate water was collected.

Fig .3. Batch isotherm experiment set-up

3.4.2. Continuous flow column experiments

In this study; PVC tube (0.06 m diameter and 3.5 m length) was used. The aim of filter runs allowed assessment of the fluoride adsorption capacity after repetitive regenerations of AOCC saturated with fluoride.

The characteristics of the filter as follows:

a) 4.2 liter of AOCC was packed in the column. The total filter bed depth was 1.5 m.

b) Tap water was used to prepare model water as explained in paragraph 3.2. Then a flow of 235 ml/min was fed to the column.

c) Three sampling points S_1, S_2 and S_3were placed, at filter bed depth of 0.5, 1.0 and 1.5 m respectively.. In addition to that, the quality of the inflow was tested as well.

d) The experiment was continued until fluoride breakthrough (1.5 mg/l in the effluent).

e) After fluoride breakthrough, fluoride saturated AOCC was taken outside the column for regeneration.

Four successive filter runs were conducted in this study; in order to investigate the recovery of fluoride adsorption capacity after multiple regenerations. The first filter run with fresh virgin AOCC was conducted till the fluoride breakthrough of 1.5 mg/L in filtrate was achieved. Then; the AOCC regenerated and used for the second filter run. Also after the fluoride breakthrough of 1.5 mg/L in filtrate was achieved. Then the AOCC regenerated again and used for the third filter run. At the same way, after fluoride breakthrough in the third filter run; the AOCC regenerated again to be used for the fourth filter run.

3.4.3. Characterization of the adsorbent

Quanta chrome Autos orb 6B adsorption analyser was used to measure the specific surface area, pore volume and pore size distribution. During preparation stage, the samples were degassed in vacuum at 50°C for 16 hours. Nitrogen gas cooled to liquid nitrogen at temperature 77 K. and introduced to the samples cell, part of liquid nitrogen adsorbed on the sample surface. Finally equilibrium between gas phase and liquid phase will occur. At equilibrium point adsorption and desorption points can be recorded at different pressure values. Then, adsorption and desorption isotherm can be constructed. (Gregg, 1982).

4. Results and Discussion

4.1. Batch adsorption experiments

4.1.1. Langmuir isotherm

Langmuir isotherm was used in order to determine the maximum fluoride adsorption.

Fig 4.1 shows the Langmuir isotherm for fluoride adsorption on the AOCC produced in this study.

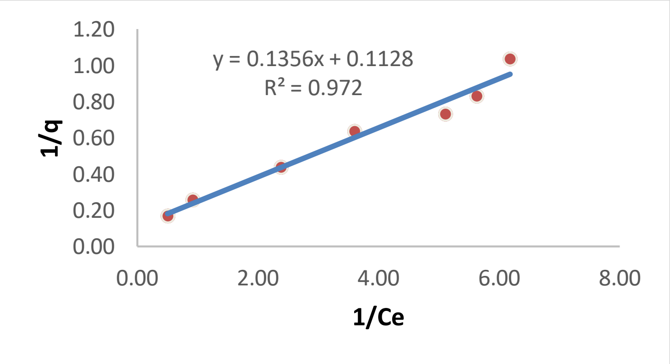

Fig .4.1. Langmuir isotherm model for adsorption of fluoride using virgin AOCC

$$\text{Separation factor}(r) = \frac{1}{1+bCo} = \frac{1}{1+0.11*5} = 0.64 \qquad (8)$$

The data from experiment fitted reasonably well in Langmuir model, with R^2 of 0.97. The separation factor -r is less than 1.0. So, the adsorption process is favourable.

4.1.2. Freundlich isotherm

Data from batch adsorption experiments fitted well also in the Freundlich isotherm model. From the adsorption isotherm coefficients: (K) and intensity (1/n) for fluoride adsorption on AOCC were determined.

Fig 4.2 shows Freundlich isotherm model for virgin AOCC.

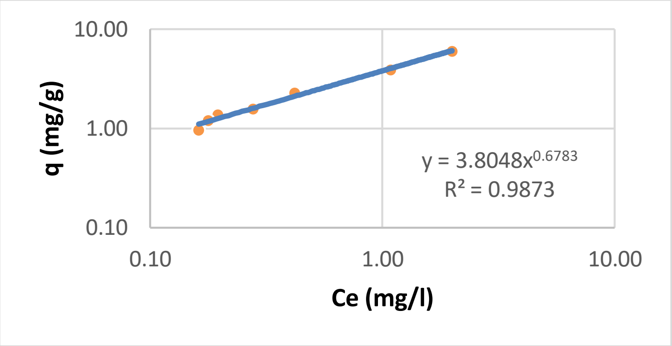

Fig .4.2. Freundlich isotherm model for adsorption of fluoride using virgin AOCC

Adsorption capacity of AOCC at an equilibrium concentration of Ce=1 mg F/L was found to be 3.8 mg /g, while the adsorption intensity was found to be 0.6783.

By considering R2 values, Freundlich isotherm was found to be the better model to describe adsorption process in this study. On the other hand, Langmuir isotherm describes the adsorption as a monolayer adsorption on a homogeneous adsorbent surface; it is also fit the data obtained in this study as well.

4.2. Continuous flow column experiments

Fig 5 shows fluoride concentration in filtrate as a function of filter run time for virgin AOCC, and regenerated AOCC after the first, the second and the third regeneration cycle.

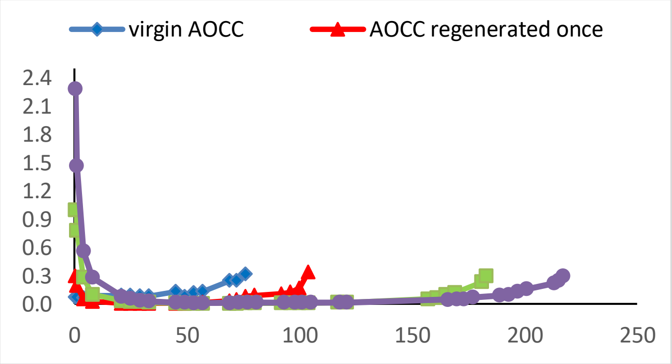

Fig .5. Fluoride removal efficiency for virgin and regenerated AOCC after the first, the second and the third regeneration cycle.

From Fig 5 it is clear that there is a consistent improvement of fluoride removal capacity after every regeneration cycle conducted.

After the first regeneration cycle of AOCC, more effective fluoride removal was observed during longer filter run time. It is clear that AOCC regeneration resulted in higher fluoride removal capacity. 27% longer filter run before fluoride breakthrough was recorded. Moreover, after the second regeneration of AOCC saturated with fluoride; fluoride removal capacity was increased by 90% longer filter run before breakthrough compared to previous run that was conducted after the first regeneration cycle. Furthermore, after the third regeneration cycle of AOCC saturated with fluoride, fluoride removal capacity further increased, resulted in 20% longer filter run before the breakthrough compared to the previous filter run. Also, after the fourth regeneration cycle, the fluoride removal capacity increased by about 30% compared with the removal capacity after the third regeneration cycle.

4.3. Characterization of the adsorbent

4.3.1. Effect of regeneration on the pore size

Total surface area is a very important factor in adsorption process, and is related to particle size, particle morphology, surface texturing and porosity. The texture of AOCC which includes; pore size and shape was changed after each regeneration cycle. Repetitive regenerations may lead to blocking of adsorbent pores.

Fig 6: shows scanning electron micrograph (SEM) of virgin AOCC and after each AOCC regeneration cycle.

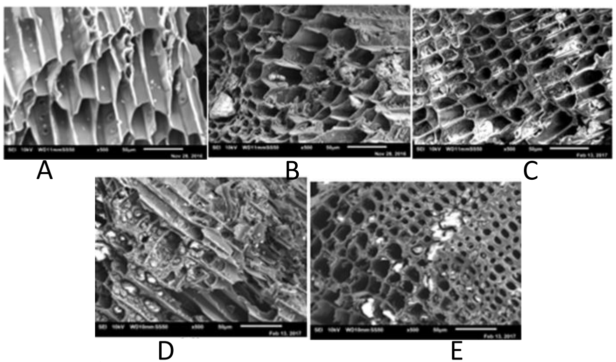

Fig .6. SEM for the charcoal (A) virgin charcoal (B) virgin AOCC (C) regenerated AOCC (D) twice regenerated AOCC (E) thrice regenerated AOCC.

Initial regeneration cycles possibly resulted in more aluminium attached to fluoride saturated AOCC due to Al-F links. However, with repeated regeneration cycles AOCC pores are possibly getting partially closed. This could lead to less easily accessible surface for fluoride adsorption. From Fig 6 it is clear that the pores become smaller after each successive regeneration cycle.

4.3.2. Pore size distribution

Fig 7 shows the pore size distribution of the virgin charcoal, virgin AOCC and regenerated AOCC after the first, the second and the third regeneration cycle.

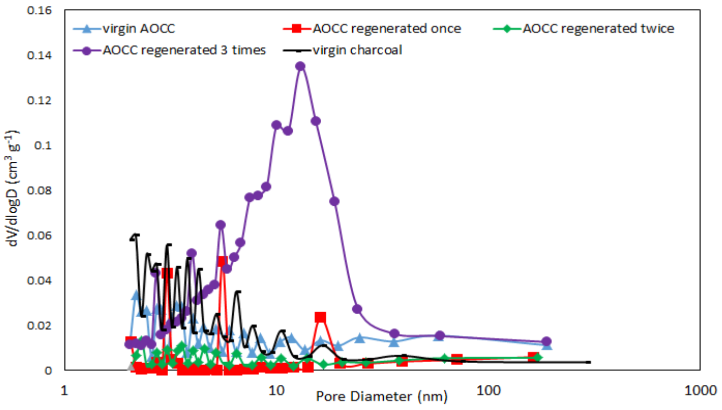

Fig .7. Pore size distributions of the virgin charcoal,virgin AOCC and regenerated AOCC after the first, the second and the third regeneration cycle.

From Fig 7 it is clear that, for the virgin charcoal, a maximum contribution to total pore volume was from pores around 2 nm, which confirming the micro-porosity of virgin charcoal. The intensity of the distribution then drops towards a baseline level at larger pore sizes. AOCC regenerated once and twice, hardly contain any pores over the entire pore size region, supporting the low specific surface area values for both of them. The distribution of virgin AOCC shows a similar trend, but with a higher intensity, indicating that virgin AOCC is more porous compared to AOCC regenerated once and twice. The pore distribution of AOCC regenerated 3 times indeed shows that it is meso porous, showing a large contribution of pores in the range from 2 – 50 nm with a mode around 13 nm. To sum up, repetitive regeneration of fluoride saturated AOCC, likely leads to clogging (closure) of microspores.

5. Conclusion

Fluoride adsorption on AOCC matched both Langmuir and Freundlich isotherm. The maximum adsorption capacity (q max) of virgin AOCC from Langmuir was 8.86 mg/g and the Adsorption capacity of virgin AOCC at Ce=1 mg F/L was found to be 3.8 mg /g.

Successive regeneration cycles of fluoride saturated AOCC by re-coating with aluminum sulfate and ammonium hydroxide solutions; were very effective and resulted in increased fluoride adsorption capacity of AOCC. After each regeneration cycle; filter run time before the fluoride breakthrough become longer. For virgin, one, twice and three times regenerated AOCC, the filter run time before the breakthrough was 74, 94, 183 and 217 hours, respectively.

REFERNCESS

[1] Bhatnagar, Amit, Kumar, Eva, Sillanpää, Mika (2011). "Fluoride removal from water by adsorption—A review." Chemical Engineering Journal 171(3): 811-840.

[2] Dava, A. A. (2015). Fluoride removal for groundwater using aluminium oxide coated charcoal (AOCC): effect of co-ions and adsorbent particle size. Delft, UNESCO-IHE.

[3] Faust, Samuel D., Aly, Osman M. (1998). Chemistry of water treatment. Chelsea, MI, Ann Arbor Press.

[4] Fawell, J. K. and O. World Health (2006). Fluoride in drinking-water. London; Seattle, IWA Pub.

[5] Gregg S.J., Sing K.S.W. (1982). Adsorption, Surface Area and Porosity, 2nded. Academic Press, London.

[6] Jones, O. A., Lester, J. N., Voulvoulis, N. (2005). "Pharmaceuticals: a threat to drinking water?" Trends in biotechnology 23(4): 163-167.

[7] Lopachin, Richard M., Gavin, Terrence, DeCaprio, Anthony, Barber, David S. (2012). "Application of the Hard and Soft, Acids and Bases (HSAB) Theory to Toxicant–Target Interactions." Chemical Research in Toxicology 25(2): 239-251.

[8] López Valdivieso, A., Reyes Bahena, J. L., Song, S., Herrera Urbina, R. (2006). "Temperature effect on the zeta potential and fluoride adsorption at the α-Al2O3/aqueous solution interface." Journal of Colloid and Interface Science 298(1): 1-5.

[9] Mandal, S., Mayadevi, S. (2009). "Review of fluoride removal from drinking water." Journal of Environmental Management 91(1): 67-77.

[10] R. Buamaha, C.A. Oduro, M.H. Sadik (2016). "Fluoride removal from drinking water using regenerated aluminium oxide coated media." Journal of Environmental Chemical Engineering (4).

[11] Sampat, P. (2000). "Deep Trouble:The Hidden Threat of Groundwater Pollution."

[12] Saxena, V. K. and S. Ahmed (2003). "Inferring the chemical parameters for the dissolution of fluoride in groundwater." Environmental geology 43.

[13] Salifu A., B. Petrusevski, K. Ghebremichael, R. Buamah, G. Amy (2012). "Multivariate statistical analysis for fluoride occurrence in groundwater in the Northern region of Ghana." Journal of Contaminant Hydrology 141: 34-44.

[14] Salifu A., B. Petrusevski, K. Ghebremichael, L. Modestus, R. Buamah, C. Aubry , G.L. Amy a,d,e (2013). "Aluminium (hydr) oxide coated pumice for fluoride removal from drinking water: Synthesis, equilibrium, kinetics and mechanism." Chemical Engineering Journal 228: 63-74.

[15] Salifu A., B. Petrusevski, E. Mwampashi, Iddi A.

[16] Eva Kumara, Mika Sillanpaa, Amit Bhatnagara (2011) *Fluoride removal from water by adsorption—A review.* Chemical Engineering Journal 171:811– 840.

[17] Msilama, I.P. (2014) Fluoride removal from drinking water using low cost adsorbents: Aluminum oxide coated charcoal (AOCC). MSc thesis, UNESCO-IHE, Delft, The Netherlands

[18] Petrusevski B (2016) Removal of Arsenic and Fluoride UNESCO-IHE, UNESCO-IHE.

[19] Nan Chen, Zhenya Zhang, Yingnan Yang, Norio Sugiura (2016). "Preparation and Characterization of Porous Granular Ceramic Containing Dispersed Aluminum and Iron Oxides as Adsorbents for Fluoride Removal from Aqueous Solution." Journal of hazardous materials

[20] Uwamariya, Valentine. (2013). “Adsorptive Removal of Heavy Metals from Groundwater by Iron Oxide Based Adsorbents.”

[21] J Skopp - 2009 - Derivation of the Freundlich adsorption isotherm from kinetics Journal of chemical education, ACS Publications