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UofKEJ Vol. 12 Issue 1 pp. 6- 9 (February 2022)

UNIVERSITY OF KHARTOUM ENGINEERING JOURNAL (UofKEJ)

Incorporation of Fluoride into Coating Process of Aluminium Oxide Coated Charcoal to Enhance Its Adsorption Capacity

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Abstract*:* Fluoride removal from water is one of the topics that researchers have discussed frequently in the recent period. Many techniques were invented; however; adsorption is considered the most preferred one due its high efficiency low cost. Aluminum Oxide Coated Charcoal AOCC is the one of the most promising fluoride adsorbent. Different researchers found that; AOCC are not only recovering its adsorption capacity after regeneration; but amazingly the adsorption capacity is further increase. The aim of this study is to investigate the reason behind the enhancement of AOCC adsorption capacity after regeneration and to optimize its coating process. Different coating conditions were applied then batch experiments were performed to determine the isotherms and kinetics of fluoride adsorption onto AOCC. Moreover, different techniques were used to characterize the adsorbent such as SEM, EDX and pH point of zero charge methods. The results show that incorporation of fluoride into coating process resulted in formation of aluminum hydroxide precipitates inside the charcoal pores. This precipitated aluminum hydroxide particles lead to enhance the specific surface area and increase the aluminum contents in adsorbent which consequently improve fluoride adsorption capacity.

Keywords*: fluoride removal, coating modification.*

1. INTRODUCTION

Water is essential material for human being. It is important for body biochemical functions, domestic use, personal hygiene and economic development. However, some elements in water could negatively affect human health if it exceeds a certain concentrations. (Braune and Xu, 2010).

One of those elements is fluoride. Fluorine (F_2) is the first element of the halogens group with a molar mass of 37.99 g/mole and it is a yellow-green corrosive gas. Due to its high electronegativity and reactivity it cannot be found in elemental form in the nature. Fluoride F^- is fluorine anion which has small radius and high tendency to form a huge number of organic and inorganic compounds in air, water, soil, plants and animals. Most of fluorine compounds are very soluble in water, so fluoride almost found in ground and surface water as a completely dissociated fluoride ion (WHO, 2002)

Many areas around the world have high fluoride concentrations in groundwater. 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).

When fluoride concentration in drinking water is below WHO guidelines of less than 1.5 mg/l a then, it will be useful for human health. However, if it found in high concentration then it could cause serious problems for the human health.

Along with this line, Yiming et al. 2001 stated that, exposure to high concentrations of fluoride for long periods of time can cause many serious health problems for the human. They reported that, long-term fluoride exposure from drinking water containing >4.32 ppm increases the risk of overall bone fractures as well as hip fractures. Furthermore, when the concentration exceeds 10 mg/l, probably result in crippling skeletal fluorosis.

Therefore, water with high fluoride levels has to be treated to be safe for human consumption. Fawell et all, 2006 mentioned that; the main methods for fluoride removal from drinking water are membrane filtration, precipitation and adsorption.

Membrane technology is a very efficient even with very high fluoride concentrations. However, for economic and technical considerations this technique is not suitable for rural areas in developing countries.

Petrusevski, 2016 stated that, in contact precipitation method for fluoride removal; calcium and phosphate compounds are used to precipitate fluoride. Then, suitable filter media is used to remove fluoride precipitates. However, this technique requires a high qualified personnel and it could not performed in houses.

On the other hand, Adsorption considered as the most affordable technique to remove fluoride from drinking water comparing to other available techniques (Dava, 2015). However, to optimize the adsorption process; all factors affecting the process must be considered. William, 1987 concluded that the factors which affect the adsorption rate are: mixing efficiency, particle size and pulp density. While, the factors influencing the adsorption capacity are: the temperature, the ionic strength and pH value.

Different adsorbents could be used for fluoride removal. For example, aluminum compounds, clay, soils, calcium compounds, bone charcoal, etc. Aluminum hydroxide is widely used for fluoride adsorption due to its high efficiency. However Salifu, 2017 stated that aluminum oxide coated charcoal found to be the best adsorbent to remove fluoride from groundwater.This study aims to analyze all chemical, Physical and textural factors affecting fluoride adsorption from drinking water. Furthermore, investigate the interactions between all these factors.

1.1. Reverse osmosis

Reverse osmosis is very effective method for fluoride removal (Reddy V. et al). However, there are many drawbacks when using RO. Mandal S. (2013) stated that, when using RO for fluoride removal; many essential ions for human health will be removed. Consequently, re-mineralization is required to recover some important minerals. Also, pH of water will be decreased and need to be adjusted. Finally, the capital and operational cost is too high comparing with other different fluoride removal techniques.

1.2. Filtration

Many types of filters were investigated by researchers. Calcium sulfate filter, gypsum-bauxite- magnesite filter…etc. they are very effective in fluoride removal and cheap as well. Nevertheless, calcium and sulfate concentrations in water will increase dramatically (Fawell, 2006).

1.3. Nalgonda Technique

It is a technique whish established in India in order to be used for both house hold and community water treatment. Nalgonda is a process that uses aluminum sulfate for fluoride removal. So, it includes three steps; coagulation, flocculation and sedimentation (Salifu, 2017). Of course this technique is very effective for fluoride removal and affordable for developing countries. But, (Fawell, 2006) stated that, a high dose of aluminum sulfate usually required which may results in residual aluminum above the permissible limit.

1.4. Adsorption

There are three different types of adsorption: chemical, physical and ion exchange adsorption. Uwamariya, 2013 illustrated that, in the chemical adsorption, chemical bond links between adsorbent and adsorbate. While in the physical adsorption, the weak attraction force between molecules leads to attachment of adsorbate to the adsorbent. Whereas, exchange adsorption, in which different ionic charges attracted to each other through electrostatic force.

2. Factors affecting fluoride adsorption

2.1. Contact time

The contact time required to reach equilibrium in fluoride adsorption process is significantly influenced by the nature of the chemical reaction between fluoride and adsorbent surface and the structure of the adsorbent. In other words, if the adsorbent surface has compact crystalline structures; the transport time of the adsorbate to reach the adsorbent surface will be less than if the adsorbent has porous surface with intra-particle sites. Bazrafshan et al. (2016) stated that, at all initial fluoride concentration; the removal efficiency increased when the contact time increase.

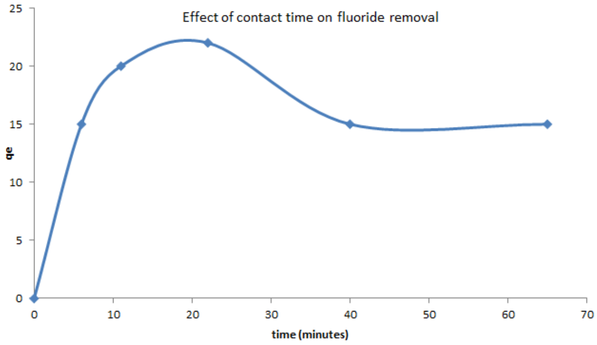

Fig. 1. Effect of contact time on fluoride removal [Source Mwangi C. et al. (2016)].

Mwangi C. et al. (2016) illustrated that, the fluoride adsorption rate increase with time until reach the maximum rate. Then, the adsorption rate decreases gradually until reach the equilibrium. The high adsorption rate at the beginning of the process attributed to high availability of surface area.

After available surface area has been saturated equilibrium will be established. Tripathy S. et al. (2006) whom used alum-impregnated activated alumina for fluoride adsorption also found that the fluoride removal rate increase with time until reach the maximum rate after that remain constant.

1.1. Co-ions

Dava (2015) stated that the concentration of co-ions such as chloride, bicarbonate, nitrate, phosphate and sulfate in the normal levels do not affect the adsorption of fluoride using aluminum oxide coated charcoal. However, when carbonate and phosphate present in high concentrations in groundwater they compete fluoride ions and reduce its adsorption capacity.

According to Pazi I. (2012) the increase of bicarbonate concentration from 260, 420 and 560 mg/l resulted in decrease in fluoride removal efficiency 67.9, 57.5 and 50.4% respectively. On the other hand, Salifu (2017) stated that phosphate is most competitive ions for fluoride in adsorption process when using granular aluminum coated bauxite.

As a matter of fact, the effects of co-ions on fluoride removal not only depend on the adsorbent type but also the pH of water. Nigussie W. et al. (2007) concluded that, the adsorption of bicarbonate may result in increase of pH in the water. Consequently, the fluoride adsorption capacity will decrease.

1.2. pH

Faust and Aly (1987) stated that, generally $[H]^+$ or $[H_3O]^-$ affect adsorption process by dissociation of functional groups on the adsorbent and adsorbate.The point of zero charge is the value pH at which the net surface charge of the adsorbent is equal to zero.

Sharma 2011 stated that, when the solution has pH less than the point of zero charge of the adsorbent; the surface of the adsorbent will be positively charged so the attraction of the negative charged ions such as fluoride will be increased. On the contrary, when the pH of the solution is more than the point of zero charge of the adsorbent, then the surface of the adsorbent will be negatively charged, so the negative charged ions like fluoride will be will be repelled from the absorption surface.

The similarity in the charge of fluoride and hydroxyl ions makes the impact of pH on fluoride removal from aqueous solutions significant. Faust and Aly, 1998 stated that, pH is not only determines the surface charge of the adsorbent, but also at low pH; the hydroxyl ions replace the fluoride ions in the adsorbent surface. Correspondingly, fluoride removal efficiency will be deteriorated. However, Bhatnagar (2011) illustrated that, in case that the aluminum hydroxides is the adsorbent, too low pH resulted in dissolution amorphous of aluminum hydroxide which lead to decrease in the fluoride adsorption efficiency. So, for every adsorbent there are a unique optimum range of pH has to be determined.

1.3. Temperature

The effects of temperature on fluoride adsorption differ from one adsorbent to another. It affects fluoride adsorption indirectly through altering the pH point of zero charge of the adsorbent. López et al. 2006 whom used aluminum oxide for fluoride removal stated that, when temperature goes up, proton desorption from adsorbent surface, consequently, the pH point of zero charge of the adsorbent goes down and fluoride removal efficiency decreases . Of course, the nature of the fluoride removal reaction (endothermic or exothermic) could determine the effect of temperature on fluoride removal efficiency. Zhang et al. 2012 reported that, the removal of fluoride using nano-particles hydroxyapatite is endothermic processes. Thus, the fluoride adsorption capacity of hydroxyapatite increases with temperature. On the other hand, Sujana et al. 1998 found that the fluoride adsorption efficiency using bauxite decrease with increasing temperature due to exothermic fluoride reaction occur in bauxite surfaces.

1.4. Initial fluoride concentration and adsorbent dose

Although high initial concentration of fluoride is good to provide an important driving force required to overcome the mass transfer resistance between the aqueous and solid phases, Kamathi Mwangi C. et al., (2016) found that the adsorption capacity of fluoride by using biomaterials; inversely proportional to fluoride initial concentration in the water. Various initial fluoride concentrations (10 – 100) mg/l were used under same conditions of pH, temperature, .etc. the Fig below illustrate the relation between fluoride initial concentration and removal capacity:

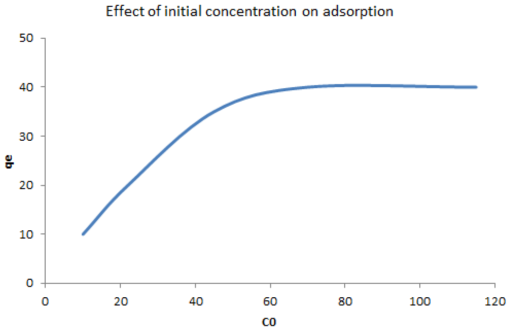

Fig. 2. Effect of initial fluoride concentrations on fluoride removal. [Source: Kamathi Mwangi C. et al., (2016)].

Along with this line Ly Y. et al. (2018) stated that increase in the fluoride initial concentration resulted in decrease of fluoride adsorption capacity. Along with this line, Mohammad and Majumder (2014) found that fluoride removal efficiency decreased when initial fluoride concentration increased. The main reason is due to saturation of active surface area and pore volume with fluoride. On the other hand, the initial fluoride concentration has no effect on the equilibrium time (Bazrafshan et al. 2016).

Fig 3 above illustrate that, when the initial fluoride concentration is increased, the fluoride removal percentage decreased. Conversely, when the initial fluoride concentration increased, the amounts of adsorbed fluoride also increase. On another study Malakootian, M. et al. 2001 reveled that, when fluoride initial concentration increased; fluoride removal efficiency decreased and adsorption capacity increased. On the other hand, when adsorbent dose increased the adsorption capacity increased too. However, the fluoride adsorption efficiency decreased.

Fig 4 below illustrate the relation between initial fluoride concentration, adsorbent dose and removal efficiency.

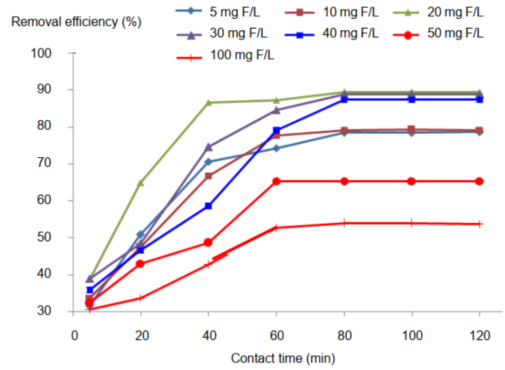

Fig. 3. Effect of initial fluoride concentration on the adsorption of F onto CuO nanoparticles (trend of F removal).

[Source (Bazrafshan et al. 2016)].

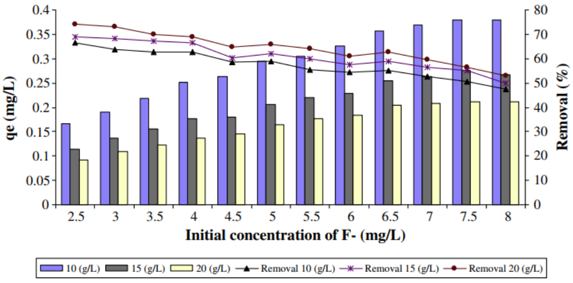

Fig. 4. Effect of contact time on adsorption capacity (3, 5, 8 mg F-/L, 20 g RSBE/L, pH=7)
[Source: Malakootian et al. (2011)].

1.1. Surface area, pore volume and pore size

Adsorption is a surface phenomenon. Armenante, 2009 illustrated that, the available surface area of the adsorbent is a key factor which determines the rate and extent of the adsorption. Sharma, 2014 stated that some small particles like activated carbon can possess large surface which is very effective to remove some charged contaminants present in drinking water. So, adsorption efficiency depends both on the available active surface area and pores volume which is necessary for molecules transport to the interior of particle pores.

Along with this line, Ying Li, et al. whom used water sludge in fluoride removal. They found that; after treatment of water sludge with hydrochloric acid the surface area and pore volume enhanced 6.82 and 7.93 times, respectively. On the other hand, the average pore size reduced from 8.9 to 3.2 nm. They concluded that, the adsorption capacity of water sludge treated with hydrochloric acid (HWS) increased due to increase in the surface area and pore volume. However, the reduction of pore size indicated that the adsorption potential in the micropores is very strong. Also, Tripathy et al. (2006) found that; when activated alumina impregnated with alum; amorphous aluminum hydroxide precipitate on the surface of activated alumina which leads to increase in surface area from 117 to 176 m^2/g. Consequently, fluoride adsorption capacity increased which indicate that the removal may not only adsorption but also simple surface precipitation.

In addition, Sandip et al. (2012) demonstrated that when adsorbent dose increase the fluoride removal increase too. However, after specific point the addition of adsorbent may decrease the fluoride removal, this is due to decreasing the effective surface area by covering of active sites when adsorbent dose is too high.

Dhongde V.et al. (2017) that used Zr-Al-Ca Nano-hybrid adsorbent for fluoride removal they noticed that; after fluoride been adsorbed the pore size of the adsorbent decreased while surface area and pore volume increased. As it is clear in the table below:

Source Dhongde V.et al. (2017)

Adsorbent	**Before Fluoride Adsorption**	**After Fluoride Adsorption**
Surface Area (m2/g)	252.4	278.2
Pore Size (Å)	16.36	15.20
Pore Volume (cm3/g-1)	0.322	0.331

This may be the explanation for the results reached by a number of researchers: Salifu A. (2017), Alhaj (2017) and Msilama (2014) where they found that the fluoride adsorption capacity increases after regeneration. Which mean that the enhancement of the surface area and pore volume was the main reason behind adsorption capacity improvement after adsorbent regeneration.

3. Conclusion

The factors affecting the fluoride adsorption process from water are multiple and overlapping. When any of these factors changed; its effect on all other factors must be considered. If temperature changed it will affect pH which will affect the carbonate concentration which is the most competitive co-ions for fluoride adsorption. Too much adsorbent dose may lead to decreasing of fluoride removal due to decreasing the effective surface area by covering the active sites.

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