Defluorination of Water Using Aluminium – Loaded Lemon Peelings Carbon as Modified Natural Adsorbents

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Declaration

I, Ssekitto Nathan, declare that this research work is my original work and has not been submitted for any award in any University or other institution of higher learning. The information derived from the literature has been fully acknowledged in the text by citation and a list of references provided.

Signature…………………………………. Date…11/04/2023……

Approval

This research project report has been submitted for examination with the approval of my supervisor.

Dr Egor Moses

Signature..Date.........11/04/2023

Dedication

I dedicate this project to my mother, Ms. Nagadya Christine for the support given to me throughout my life at secondary school and the university in terms of monetary support, emotional guidance, everlasting care and encouragement. I am eternally grateful for your contributions towards my life and pledge to forever have you at heart for the kindness, sacrifice, commitment and sincere support towards the better version of me.

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List of Acronyms and abbreviations

ALLPC	-	Aluminium Loaded Lemon Peelings Carbon
CDTA	-	Cyclohexanediaminetetraacetic acid
EC	-	Electro-Coagulation
ESI-MS	-	Electrospray Ionisation Mass Spectroscopy
FESEM	-	Field Emission Scanning Electron Microscopy
IQ	-	Intelligence Quotient
ISE	-	Ion Selective Electrode
NEERI	-	National Environmental Engineering Research Institute
NF	-	Nano Filtration
PTFE	-	Polytetrafluoroethylene
PXRD	-	Power X-ray diffraction
TDS	-	Total Dissolved Solids
TISAB	-	Total Ionic Strength Adjustment Buffer
UNBS	-	Uganda National Bureau of Standards
WHO	-	World Health Organisation
XPS	-	X-ray Photoelectron Spectroscopy

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Abstract

The contamination of groundwater and high concentrations of fluoride ions are major problems worldwide, causing diseases like dental and skeletal fluorosis; in the population that uses this water for their consumption and therefore, its removal from groundwater is a very important issue. This study was aimed at developing an inexpensive and effective adsorbent for removing fluoride ions from drinking water to the safety limit, 1.5 mg/L set by World Health Organization and Uganda National Bureau of Standards. Lemon peelings obtained from Nagongera market, Tororo district were impregnated with aluminium by subsequent carbonization, alkalinizing and treatment with aluminium chloride and effectiveness in adsorbing fluoride ions was confirmed by batch adsorption studies. The adsorption data were analyzed by Freundlich and Langmuir isotherms. The adsorption on the aluminium-loaded lemon peelings carbon (ALLPC) obeyed the pseudo second order kinetic model. The adsorption capacity ALLPC was studied with variation in size of adsorbent dose, size particles, pH, adsorbent dose and initial fluoride concentration. The extent of adsorption of fluoride ions by ALLPC adsorbent increased with increase in adsorbent dose, contact time and pH until an optimum value but decreased with the increase in particle size and initial fluoride concentration. In future, the potential ALLPC adsorbent can be used to design a household defluorination unit for effective and economical fluoride removal.

Chapter 1: Introduction

1.1 Background

Chemical contamination of water sources can be either caused naturally or caused by pollution from different sources (man-made). Man-made contamination can hopefully be identified and stopped, but the natural way is not easy and this can put communities into risks (Shorter, 2011). Chemical contamination generally occurs during the water cycle and one of the most well documented naturally occurring contaminants is fluoride which affects drinking water supplies in a number of countries (Jamode, Sapkal, & Jamode, 2004; Kimambo, Bhattacharya, Mtalo, Mtamba, & Ahmad, 2019). When water makes contact regularly with ores, minerals such as fluorite and weathering of rocks (for example shale, basalt, granite) consequently, high fluoride concentration may yield in water (Kimambo et al., 2019). Various industries are also involved in discharging of fluoride in water. These industries include; semiconductor manufacturing factories, pharmaceutical companies, beryllium extraction plants, aluminum smelters, fertilizer manufacturing, and mining industries and others (Paudyal et al., 2013).

Fluoride is the most electronegative and reactive element in the periodic table, occurring primarily as the fluoride ion (F^-) and at the level of 1.0 mg L^{-1} in the body enhances bone development and prevents dental carriers hence the growth and maintenance of healthy bones and teeth by displacing the hydroxide ions from hydroxyapatite, the principal mineral constituent of teeth and bones, to form the fluorapatite, which is harder and tougher than hydroxyapatite.

$$\mathrm{Ca_5(PO_4)_3OH_{(S)} + F^-{}_{(aq)} \rightarrow Ca_5(PO_4)_3F_{(S)} + OH^-{}_{(aq)}} \qquad (1)$$

The maximum tolerance limit of fluoride in drinking water specified by the World Health Organization (WHO) is 1.5 mg L^{-1} , but a lower concentration is recommended for children and even though the highest fluoride concentration in drinking water is 1.5 mg L^{-1} , in many tropical countries, where there is a high sweat loss and a high intake of water due to the hot weather, such an upper limit is unsuitable (Rajkumar et al., 2019) therefore even if the upper limit according to the WHO in the temperate regions is 1.5 mg/L, some areas have their upper limits varying for example, in South Africa, the upper limit is 0.75 mg/L, in India, it is 1 mg/L and in some parts such as Nakuru of Kenya, the upper limit is 3 mg/L and in Uganda, it is 0.6 mg/L.

References

Amor, Z., Bariou, B., Mameri, N., Taky, M., Nicolas, S., & Elmidaoui, A. (2001). Fluoride removal from brackish water by electrodialysis. *Desalination, 133*(3), 215-223. doi:https://doi.org/10.1016/S0011-9164(01)00102-3

Aoudj, S., Khelifa, A., Drouiche, N., & Hecini, M. (2015). Development of an integrated electro-coagulation–flotation for semiconductor wastewater treatment. *Desalination and Water Treatment, 55*(6), 1422-1432. doi:https://doi.org/10.1080/19443994.2014.926462

Bhatnagar, A., Sillanpää, M., & Witek-Krowiak, A. (2015). Agricultural waste peels as versatile biomass for water purification–A review. *Chemical engineering journal, 270*, 244-271. doi:https://doi.org/10.1016/j.cej.2015.01.135

Bhise, R., Patil, A., Raskar, A., Patil, P., & Deshpande, D. (2012). Removal of colour of spent wash by activated charcoal adsorption and electrocoagulation. *Research Journal of Recent Sciences, 2277*, 2502. doi:http://www.isca.me/rjrs/archive/v1/i6/12.ISCA-RJRS-2012-145%20Done.pdf

Chan, C. K. (2011). *Thermo Scientific Orion Star A214 Benchtop and Star A324 Portable pH/ISE Meter Reference Guide* (1st ed. Vol. 1). Singapore: Thermo Fisher Scientific Inc. .

Chikuma, M., Okabayashi, Y., Nakagawa, T., Inoue, A., & Tanaka, H. (1987). Separation and determination of fluoride ion by using ion exchange resin loaded with alizarin fluorine blue. *Chemical and pharmaceutical bulletin, 35*(9), 3734-3739. doi:https://doi.org/10.1248/cpb.35.3734

Crini, G., Lichtfouse, E., Wilson, L. D., & Morin-Crini, N. (2019). Conventional and non-conventional adsorbents for wastewater treatment. *Environmental Chemistry Letters, 17*(1), 195-213. doi:https://hal.archives-ouvertes.fr/hal-02082916/document

Diawara, C. K. (2008). Nanofiltration process efficiency in water desalination. *Separation & purification reviews, 37*(3), 302-324. doi:https://doi.org/10.1080/15422110802228770

Dissanayake, C., & Chandrajith, R. (2019). Fluoride and hardness in groundwater of tropical regions-review of recent evidence indicating tissue calcification and calcium phosphate nanoparticle formation in kidney tubules. *Ceylon Journal of Science, 48*(3), 197-207. doi:http://doi.org/10.4038/cjs.v48i3.7643

Dubey, S., Agarwal, M., & Gupta, A. (2018). Experimental investigation of Al-F species formation and transformation during coagulation for fluoride removal using alum and PACl. *Journal of Molecular Liquids, 266,* 349-360. doi:https://doi.org/10.1016/j.molliq.2018.06.080

Egor, M., & Birungi, G. (2020). Fluoride contamination and its optimum upper limit in groundwater from Sukulu Hills, Tororo District, Uganda. *Scientific African, 7*, e00241. doi:https://doi.org/10.1016/j.sciaf.2019.e00241

Emmanuel, A., & Emmanuel, E. (2021). Chemical Pollution of Drinking Water in Haiti: An Important Threat to Public Health. *Environmental Health*, 147. doi:http://dx.doi.org/10.5772/intechopen.97766

Fawell, J., Bailey, K., Chilton, J., Dahi, E., & Magara, Y. (2006). *Fluoride in drinking-water*: IWA publishing.

Guth, S., Hüser, S., Roth, A., Degen, G., Diel, P., Edlund, K., . . . Grune, T. (2021). Contribution to the ongoing discussion on fluoride toxicity. *Archives of Toxicology*, *95*(7), 2571-2587. doi:https://link.springer.com/article/10.1007/s00204-021-03072-6

Hamdi, N., & Srasra, E. (2007). Removal of fluoride from acidic wastewater by clay mineral: Effect of solid–liquid ratios. *Desalination, 206*(1-3), 238-244. doi:https://doi.org/10.1016/j.desal.2006.04.054

Hussein, I. A. (2017). *Comparative study between bentonite and mica on deflouridation of drinking water in Hai district of Tanzania.* The University of Dodoma, Retrieved from http://hdl.handle.net/20.500.12661/526

Jamode, A., Sapkal, V., & Jamode, V. (2004). Defluoridation of water using inexpensive adsorbents. *Journal of the Indian Institute of Science, 84*(5), 163. doi:http://journal.library.iisc.ernet.in/index.php/iisc/article/download/2375/2426

Junlian, Q. I. A. O., Zimin, C. U. I., Yuankui, S. U. N., Qinghai, H. U., & Xiaohong, Q. U. A. N. (2014). Simultaneous removal of arsenate and

fluoride from water by Al–Fe (hydr)oxides. *Frontiers Environ.*

Sci. Eng. , *2*(8), 169–179.

Kariyanna, H. (1987). *Geological and geochemical environment and causes of fluorosis—possible treatment—a review*. Paper presented at the Proceedings seminar on role of earth sciences in environment, Bombay.

Kimambo, V., Bhattacharya, P., Mtalo, F., Mtamba, J., & Ahmad, A. (2019). Fluoride occurrence in groundwater systems at global scale and status of defluoridation–state of the art. *Groundwater for Sustainable Development, 9*, 100223. doi:https://doi.org/10.1016/j.gsd.2019.100223

Littleton, J. (1999). Paleopathology of skeletal fluorosis. *American Journal of Physical Anthropology: The Official Publication of the American Association of Physical Anthropologists, 109*(4), 465-483. doi:https://doi.org/10.1002/(SICI)1096-8644(199908)109:4%3C465::AID-AJPA4%3E3.0.CO;2-T

Maheshwari, R. (2006). Fluoride in drinking water and its removal. *Journal of Hazardous materials, 137*(1), 456-463. doi:https://doi.org/10.1016/j.jhazmat.2006.02.024

Majewska-Nowak, K., Grzegorzek, M., & Kabsch-Korbutowicz, M. (2015). Removal of fluoride ions by batch electrodialysis. *Environment Protection Engineering, 41*(1). doi:http://dx.doi.org/10.5277/epe150106

Malago, J., Makoba, E., & Muzuka, A. (2017). Fluoride levels in surface and groundwater in Africa: a review. *American Journal of Water Science and Engineering, 3*(1), 1-17. doi:10.11648/j.ajwse.20170301.11

Manna, S., Roy, D., Adhikari, B., Thomas, S., & Das, P. (2018). Biomass for water defluoridation and current understanding on biosorption mechanisms: A review. *Environmental Progress & Sustainable Energy, 37*(5), 1560-1572. doi:https://doi.org/10.1002/ep.12855

Meenakshi, S., & Viswanathan, N. (2007). Identification of selective ion-exchange resin for fluoride sorption. *Journal of Colloid and Interface Science, 308*(2), 438-450. doi:https://doi.org/10.1016/j.jcis.2006.12.032

Miya, K. S., & Jha, V. K. (2020). Determination of Fluoride in Various Samples Using a Fluoride Selective Electrode. *Journal of Analytical Sciences, Methods and Instrumentation, 10*(4), 97-103. doi:https://doi.org/10.4236/jasmi.2020.104007

Mohapatra, M., Anand, S., Mishra, B. K., Giles, D. E., & Singh, P. (2009). Review of fluoride removal from drinking water. *Journal of environmental management, 91*(1), 67-77. doi:https://doi.org/10.1016/j.jenvman.2009.08.015

Mulugeta, E., Zewge, F., Johnson, C. A., & Chandravanshi, B. S. (2015). Aluminium hydro (oxide)–based (AO) adsorbent for defluoridation of drinking water: Optimisation, performance comparison, and field testing. *Water SA, 41*(1), 121-128. doi:https://doi.org/10.4314/wsa.v41i1.15

Ndiaye, P., Moulin, P., Dominguez, L., Millet, J., & Charbit, F. (2005). Removal of fluoride from electronic industrial effluentby RO membrane separation. *Desalination, 173*(1), 25-32. doi:https://doi.org/10.1016/j.desal.2004.07.042

Paudyal, H., Pangeni, B., Inoue, K., Kawakita, H., Ohto, K., & Alam, S. (2013). Adsorptive removal of fluoride from aqueous medium using a fixed bed column packed with Zr (IV) loaded dried orange juice residue. *Bioresource technology, 146*, 713-720. doi:https://doi.org/10.1016/j.biortech.2013.07.014

Pillai, P., Dharaskar, S., Pandian, S., & Panchal, H. (2021). Overview of fluoride removal from water using separation techniques. *Environmental Technology & Innovation, 21*, 101246. doi:https://doi.org/10.1016/j.eti.2020.101246

Rajkumar, S., Murugesh, S., Sivasankar, V., Darchen, A., Msagati, T., & Chaabane, T. (2019). Low-cost fluoride adsorbents prepared from a renewable biowaste: syntheses, characterization and modeling studies. *Arabian Journal of Chemistry, 12*(8), 3004-3017. doi:http://dx.doi.org/10.1016/j.arabjc.2015.06.028

Said, M., & Machunda, R. L. (2014). Defluoridation of water supplies using coconut shells activated carbon: batch studies. *International Journal of Science and Research (IJSR), 3*(7), 2327-2331. doi:https://www.researchgate.net/profile/Said-Mateso/publication/264420519_Defluoridation_of_Water_Supplies_Using_Coconut_Shells_Activated_Carbon_Batch_Studies/links/53dd3e0f0cf2cfac99291444/Defluoridation-of-Water-Supplies-Using-Coconut-Shells-Activated-Carbon-Batch-Studies.pdf

Schneiter, R. W., & Middlebrooks, E. J. (1983). Arsenic and fluoride removal from groundwater by reverse osmosis. *Environment International, 9*(4), 289-291. doi:https://doi.org/10.1016/0160-4120(83)90087-9

Shorter, J. (2011). *Fluoride in groundwater: Investigating the cause, scale, effect and treatment of fluoride in drinking water in Northern Tanzania.* Newcastle University, Retrieved from http://hdl.handle.net/10443/1245

Singh, J., Singh, P., & Singh, A. (2016). Fluoride ions vs removal technologies: a study. *Arabian Journal of Chemistry, 9*(6), 815-824. doi:https://doi.org/10.1016/j.arabjc.2014.06.005

Singha, B., Naiya, T. K., kumar Bhattacharya, A., & Das, S. K. (2011). Cr (VI) ions removal from aqueous solutions using natural adsorbents–FTIR studies. *Journal of Environmental Protection, 2*(06), 729. doi:10.4236/jep.2011.26084

Sundaram, C. S., & Meenakshi, S. (2009). Fluoride sorption using organic–inorganic hybrid type ion exchangers. *Journal of Colloid and Interface Science, 333*(1), 58-62. doi:https://doi.org/10.1016/j.jcis.2009.01.022

Talat, M., Mohan, S., Dixit, V., Singh, D. K., Hasan, S. H., & Srivastava, O. N. (2018). Effective removal of fluoride from water by coconut husk activated carbon in fixed bed column: Experimental and breakthrough curves analysis. *Groundwater for Sustainable Development, 7*, 48-55. doi:https://doi.org/10.1016/j.gsd.2018.03.001

Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., & Yang, Z. (2015). Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere, 125*, 70-85. doi:https://doi.org/10.1016/j.chemosphere.2014.12.058

Thergaonkar, V., & Nawalakhe, W. (1971). Activated magnesia for fluoride removal. *Ind. J. Environ. Health, 16*, 241-243.

Waghmare, S. S., & Arfin, T. (2015). Fluoride removal from water by various techniques. *Int. J. Innov. Sci. Eng. Technol, 2*(3), 560-571. doi:http://www.ijiset.com/