



University of Venda

School of Environmental Sciences  
Department of Hydrology and Water Resources

DEFLUORIDATION OF GROUNDWATER USING VERMICULITE MODIFIED WITH  
HEXADECYLTRIMETHYLAMMONIUM: A CASE STUDY OF SILOAM VILLAGE,  
LIMPOPO PROVINCE, SOUTH AFRICA

BY

OLOGUNDUDU, TAYO OLADIPO

Student No: 14009804

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Supervisor  
Prof J.O. Odiyo

Co-supervisor  
Prof G.E. Ekosse

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## ABSTRACT

High fluoride in groundwater, above the World Health Organisation's (WHO) standard value of 1.5 mg/L, is a global phenomenon that has led to health complications such as dental and skeletal fluorosis. This occurs mostly in rural communities where groundwater is the only source of drinking water. Many methods, including adsorption, precipitation, ion-exchange, reverse osmosis and electrodialysis, have been employed in defluoridation. However, some of these methods are expensive, ineffective and are not applicable in rural communities. Siloam Village in Limpopo Province of South Africa, is a rural area which relies on groundwater for household use due to inadequacy of alternative sources. Fluoride is present in groundwater in Siloam Village up to 5.6 mg/L, which is much higher than the WHO and the South African Department of Water Affairs and Forestry's (DWAF) standards of 1.5 and 1 mg/L, respectively. This research is aimed at defluoridation of groundwater to permissible limits in Siloam Village using materials and methods that incorporate a combination of cost and efficiency. To this end, vermiculite, a naturally available clay mineral with the largest deposit in the world at Phalaborwa in Limpopo Province, was modified with hexadecyltrimethylammonium, an organic cation and used as an adsorbent for defluoridation.

Laboratory simulated fluoride solution (8 mg/L) was used for this study. Thereafter groundwater samples were taken from Siloam Village to test the proposed defluoridation method on actual field samples. The physicochemical properties of the groundwater samples such as pH, EC and temperature were measured at the point of sampling. Adsorption isotherms such as Langmuir and Freundlich were used to determine the adsorption capacity and the nature of adsorption, while the mechanism was investigated by the pseudo first and second order models. X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) and fourier transform infra-red (FTIR) were used to characterise the adsorbent to recognise the properties of modified vermiculite (HDTMA-VMT) responsible for defluoridation alongside any apparent changes from the original material due to modification. Experimental parameters such as contact time (5-70 minutes), adsorbent dosage (0.2-2 g), pH (2-10), adsorbate concentration (5-100 mg/L) and temperature (25-55°C) were optimised to determine the best conditions that facilitate fluoride removal using the adsorbent.

Concentrations of the organic cation equivalent to 50 (0.0393 M), 100 (0.0788 M) and 200% (0.1575 M) of vermiculite's cation exchange capacity (CEC) were used to modify the clay mineral. However, the adsorbent obtained from this approach showed low fluoride removal potential ( $\leq 13\%$ ). Thus, it was necessary to increase the concentrations of the modifying agent to 0.2, 0.3 and 0.4 M. Unmodified vermiculite was also used for fluoride sorption studies, serving as the control (Control-VMT) to accurately determine the efficiency of HDTMA-VMT.

The results showed that 0.2 M modification approach coupled with surface pH reduction to pH of 1.5, gave better fluoride removal (>13%) and was maintained throughout the study. Optimisation conditions for the maximum fluoride removal using HDTMA-VMT include: 2 g adsorbent dosage, pH 6.5, 70 minutes contact time and 25°C. The point-of-zero-charge for HDTMA-VMT was determined to be 6.4, which could enhance removal due to its positivity, while that of the Control-VMT was estimated at 9.7, a rather alkaline pH which cannot facilitate adsorption. The adsorption conformed to both Langmuir ( $R^2= 0.8902$ ) and Freundlich ( $R^2= 0.9985$ ) isotherms, with an adsorption capacity of 2.37 mg/g and fluoride removal of approximately 50% using HDTMA-VMT. The Control-VMT, however, showed negligible removal within acceptable pH range of potable water. Study of the kinetics showed conformity to the pseudo second order model, which implies a case of chemisorption as the mechanism of fluoride removal. This occurs by electrostatic attraction between the positively charged adsorbent and the negatively charged fluoride. FTIR analysis also reveals that the  $CH_3$  and  $CH_2$  bonds introduced to vermiculite by the addition of hexadecyltrimethylammonium were responsible for the adsorption while the XRF shows a percentage gain of fluoride by HDTMA-VMT after defluoridation.

The use of HDTMA-VMT for defluoridation of groundwater from Siloam Village showed a removal efficiencies of 22 and 20% for the two sampling points (GW 1 and GW 2), respectively, while the Control-VMT showed 0% removal. The reduction in percentage removal was attributed to the alkaline pH of field water coupled with competition for adsorbent site by other anionic components. It can be deduced from this study that the use of HDTMA-VMT for defluoridation has shown potential which can be developed by additional research into a domestic defluoridation unit. This can be effective for reducing the fluoride in groundwater to less detrimental levels especially in areas where fluoride levels range between 2-8 mg/L, such as Siloam Village. \*