Contents

Development of a tea waste-based mixture for the removal of fluoride in water: A case study with selected concentrations of fluoride in water

A V P S Buddhima[1], D T Jayawardana [1,2*], N U S Dissanayake [1], B M Gunathilake[1], P L Herath[1]

[1]University of Sri Jayewardenepura, Faculty of Applied Sciences, Department of Forestry and Environmental Science, Gangodawila, Nugegoda, Sri Lanka.

[2]Center for Forestry and Environment, Faculty of Applied Sciences, Department of Forestry and Environmental Science, Gangodawila, Nugegoda, Sri Lanka.

ABSTRACT

The main objective of this study is to investigate the sorption behavior of fluoride in tea waste under various fluoride concentrations in water in Sri Lanka to study the fluoride removal from drinking water. The physicochemical characteristics of tea waste were investigated using SEM, AAS, BET, and FTIR analysis. The results obtained by batch experiments showed that the maximum percentage removal efficiency of 42.58±0.97 was at pH 6, after 20 min of contact time, and with an adsorbent dose of 1.5 g. The adsorption equilibrium isotherms followed by the Langmuir model, and the reaction obeyed the pseudo-second-order model. Phosphate ions have shown maximum influence on fluoride removal by the tea waste-laterite mixture. A mixture containing 65% tea waste and 35% laterite showed the highest removal efficiency with a maximum adsorption capacity of 0.0216 mg/g. Finally, a fluoride removal setup was prepared and the filtering performance of the tea waste-based mixture was studied under selected influent fluoride concentrations of 1.5 ppm, 2.0 ppm, and 2.5 ppm, respectively. The results of this experiment showed that each filtering set-up with different influent concentrations had significant fluoride removal efficiency to the WHO drinking water quality standard limit of 1.5 ppm. The optimum fluoride removal happened at pH6 in both batch experiments and filtering set-up experiments. Therefore, the material can be applied for fluoride removal without changing the normal pH of potable groundwater.

Keywords: *tea waste, laterite, fluoride, sorption*

Corresponding author – Email: *daham@sci.sjp.ac.lk*

INTRODUCTION

Fluorine is the most electronegative element that occurs naturally. Fluoride is one of the most abundant anions in drinking water and can be either beneficial or harmful to human health, depending on the concentration and amount consumed (Cai *et al*., 2015). Fluoride has a beneficial effect on teeth at low concentrations, but excessive fluoride can be harmful. The majority of fluoride in the human body is ingested through drinking water (Jayarathne and Jayawardana, 2018). According to the WHO, the standard fluoride concentration in drinking water ranges from 0.5 to 1.5 mg/L (WHO, 2011). Higher fluoride levels in potable water in hot tropical lands where people consume a large amount of water can lead to excessive fluoride intake (Chandrajith et al., 2012).

Defluoridation techniques are used to reduce fluoride levels in drinking water. Precipitation and coagulation, membrane separation, ion exchange, and adsorption are some of the primary defluoridation techniques used (Jagtap et al., 2012). Even though most defluoridation methods are commercially available, removing fluoride from water is not always simple or inexpensive. Attempts to develop a method of defluoridation that can be sustained under varying social, financial, environmental, and technical constraints have not been fully successful (Brunt et al., 2004). Therefore, the development of cost-effective, easy-to-handle, and quick defluoridation methods is in high demand in developing countries like Sri Lanka. Adsorption is generally regarded as an appropriate technique for small community water sources compared to other methods due to its simplicity of design, ease of operation, availability of a diverse range of adsorbents, and low operating and investment costs (Bhatnagar and Sillanpää, 2011).

Recent increase in consumption of tea worldwide have resulted in large quantities of tea waste (Tsubaki and Azuma, 2013), which generates a significant amount of tea-based organic waste. As per findings, Turkey disposes of about 30,000 tons of tea factory waste in the small bays that surround the Black Sea (Yagmur et al., 2008).Thus, production of such a large amount of waste alone from the tea sector would inevitably contribute to environmental problems associated with its inappropriate disposal (Hussain et al., 2018).

Little work has been done so far to test the use of tea waste in the defluoridation of drinking water (Cai et al., 2015). There are no studies done on the use of tea waste for sorption experiments in Sri Lanka (Chandrajith et al., 2020). The objective of study is to effectively use tea waste for potential applications by studying the sorption behaviour of fluoride in tea waste under selected water types and developing tea waste-based amendments to remove fluoride.

MATERIALS AND METHODS

Materials

Tea waste was collected from households and washed with boiling water several times until the supernatant solution remained colorless (Karthik and Suresh, 2019). The washed tea waste was oven-dried at 105 °C until tea waste got dried. Then the dried tea waste was grounded and sieved in a 0.5 mm US standard sieve. The laterite soil obtained from the southwestern part of Sri Lanka was washed several times using distilled water to remove impurities. Then the sample was air-dried for around 24 hours to remove moisture and soil samples were ground with the motor and the pestle. Finally, the ground samples were sieved using a US standard sieve of 0.5 mm. prepared tea waste powder and laterite powder were placed in zip lock bags to reduce moisture loss and contamination. Groundwater samples were randomly collected from Kalutara and Colombo districts in the western province, and samples were taken as composite samples. Nitrate, sulphate, chloride, and phosphate solutions were prepared by dissolving sodium nitrate ($NaNO_3$), sodium sulphate (Na_2SO_4), sodium fluoride (NaF), respectively and potassium phosphate dibasic anhydrous (K_2HPO_4) in distilled water. All chemicals and solvents used during experiments were of analytical grade quality.

Physico-chemical analysis of tea waste

X-ray Fluorescence (XRF) analysis: The powdered laterite samples were initially analyzed for major and trace elements by X-ray fluorescence spectrometry (RIX 2000). The sample was split and oven-dried for 48 hours at 160 °C. Under a force of 200 kN for 60 seconds, powdered samples (< 63 µm) were compressed into briquettes (Nayanthika et al., 2018).

Fourier-Transform Infrared spectroscopy (FT-IR) analysis: FT-IR analysis was performed to investigate the chemical bandings of all filter media before and after filtration. Small amounts (2–5 mg) of samples were placed directly on the crystal and operated by the machine with the assistance of the staff.

SEM (Scanning electron micrograph) and EDX (Energy-dispersive X-ray spectroscopy): The test was carried out utilizing double-sided conductive carbon tape of gold-sputtered ground soil samples mounted on the SEM sample holder. At a steady current of 25 mA, gold sputtering of ground soil was achieved (Nayanthika et al., 2018).

Atomic absorption spectroscopy (AAS): There can be chemical changes occur and elements readily available in the samples can be leached to the solution during the experiment. An elution test was carried out and the filtrate was acidified using concentrated HCl for preservation. The prepared samples were analyzed to determine element concentrations.

Determination of the textural properties of mixtures: The textural properties of the studied samples were determined from the adsorption and desorption isotherms. The powdered sample was analyzed for specific surface area and pore size distributions by N_2 adsorption at 77 K using the Autosorb IQ-MP (1 Stat.) Viton BET surface area analyzer (Gibson *et al.,* 2020). The pore size distribution was obtained from the adsorption isotherm using the BJH (Barrett- Joyner-Halenda) method (Barrett et al., 1951).

Determination of the pH (pzc) of tea waste

For the determination of the pH value at the point of zero charges of tea waste, solutions of 50 ml 0.1 M NaCl were taken, and the initial pH (pH_i) of solutions was adjusted between 2 and 10 by the addition of 0.1 M HCl and 0.1 M NaOH. After pH adjustment, 0.05 g of tea waste was added to the solutions, and the suspension was shaken at a speed of 120 rpm at room temperature. After 24 hours, the solutions were filtered by a 0.45 µm cellulose acetate membrane, and the final pHs (pH_f) of the filtrates were measured. The difference between the initial and final pH values ($\Delta pH = pH_i - pH_f$) was plotted versus pH_i. The pH at which $\Delta pH = 0$ was considered the pH value at the point of zero charges (Hafshejani et al., 2016).

Investigation of possible sorption behavior of different fluoride concentrations with the tea waste in selected water type under common salinity /hardness

Step 01- Groundwater samples were collected from the districts of Colombo and Kalutara. Then, tea waste (TW) was added to the collected groundwater samples, maintaining a tea waste: groundwater ratio of 1:200 (g: ml). The mixture was shaken at 120 rpm at 25 °C at room temperature for 1 hour. The solid phase was separated using centrifugation at 4000 rpm for 10 minutes. Then, solutions were filtered by millex-GP syringe filter unit pore size 0.45 µm. The concentration of remaining fluoride was determined in supernatants by the Hach DR900 Multiparameter Portable Colorimeter. The percentage removal efficiency was calculated using equation 1 (Hafshejani et al., 2016).

Step 02- Fluoride concentrations in collected groundwater samples were adjusted between 0.31 mg $L^{-1}$and 11.1 mg L^{-1}. To investigate the potential sorption behavior of tea waste in groundwater under low to high fluoride concentrations. The required amounts of material were then added to the fluoride level-adjusted groundwater samples and the procedure in step 01 was repeated.

Determination of the optimum mixing ratio of tea waste and laterite

Tea waste and laterite powder were combined at various mass percentages of tea waste, ranging from 50% to 100% while maintaining the overall mass constant at 1 g. A series of fluoride solutions (C_0 = 2 mg L^{-1}) were added with the prepared mixtures keeping a ratio of [m:V] = [1:50]. The mixtures were then shaken for 1 hour with an agitation speed of 120 rpm at room temperature. The solid phase was separated by centrifugation at 4000 rpm for 10 min. The solutions were filtered by a millex-GP syringe filter unit pore size of 0.45 µm. The concentration of remaining fluoride was determined in supernatants by the Hach DR900 Multiparameter Portable Colorimeter. The percentage removal efficiency was calculated using equation (1) and the amount of fluoride absorbed per unit weight of adsorbent (qe in mg g^{-1}) was calculated as equation (2).

$$\text{Percentage removal Efficiency} = \frac{(C_0\text{-}C_e)\times 100}{C_0} \quad (1)$$

$$\text{Adsorption capacity} = \frac{(C_0\text{-}C_e)\times V}{m} \quad (2)$$

Where C_0 is the initial fluoride concentration and C_e is the equilibrium concentration of fluoride in solution (mg L^{-1}), V is the volume of solution (L), and m is the mass of the tea waste and laterite (g) (Hafshejani et al., 2016, Viglašová et al., 2018).

Batch Experiments of Fluoride

The effect of adsorbent dosage on fluoride adsorption was studied by adjusting the adsorbent dosage from 0.5 g to 10.0 g with an initial fluoride concentration of 2 mg L^{-1}. Then TWL65 mixture (tea waste 65% and laterite 35%). The influence of contact time on adsorption experiments was investigated. The mixture was kept for different time intervals from 5.00 minutes to 6.00 hours while shaking under 120 rpm in the mechanical stirrer to determine the optimum contact time for fluoride removal. The pH of the synthesized solution was adjusted to 6.00 in both experiments.

The effect of adsorbent dosage on fluoride adsorption was studied by adjusting the solution pH from pH 2-11 by using 0.1 M HCl and 0.1 M NaOH at optimum with an initial fluoride concentration of 2 mg L^{-1} with optimum dosage and optimum contact time. Throughout the experiment, required amount of material was added to the solution, maintaining a 1:200 (g: ml) ratio of the TWL65 mixture and the fluoride solution. The mixture was shaken at 120 rpm at 25°C at room temperature. The solid phase was separated by centrifugation at 4000 rpm for 10 min. The solutions were filtered by millex-GP syringe filter unit pore size 0.45 µm. The concentration of remaining fluoride was determined in supernatants by the Hach DR900 Multiparameter Portable Colorimeter.

Adsorption Kinetic Studies of fluoride by TW65

Kinetic adsorption experiments were conducted with a series of solutions with an initial fluoride concentration of 2 mg L^{-1}, optimum pH, and optimum adsorbent dosage, at room temperature of 25°C by varying the contact time with an agitation speed of 120 rpm. After the predetermined time interval was completed, the solids phase was removed from the solutions by filtration using 0.45 µm cellulose acetate membrane filters, and fluoride concentrations were analyzed. The dynamics of the fluoride adsorption process by TWL65 were evaluated with the pseudo-first-order (Eq. (3)) (Lagergren, 1898), pseudo-second-order (Eq. (4)) (Ho and McKay, 1999) kinetic models.

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (3)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \qquad (4)$$

Where q_t and q_e are the amounts of nitrate ions adsorbed on the modified biochar (mg g^{-1}) at time t and equilibrium time, respectively; k_1 is the rate constant of the pseudo-first-order (min^{-1}), k_2 is the rate constant of the pseudo-second-order (g mg^{-1} min^{-1}).

Adsorption Isotherms of fluoride by TW65

Equilibrium adsorption experiments were conducted using a series of solutions with initial fluoride concentrations of 1.5–3.5 mg L^{-1} with an optimum solution pH and optimum adsorbent at room temperature 25 °C. The mixtures were shaken at 120 rpm, and after equilibration, samples were filtered by 0.45 µm cellulose acetate membrane filters and were analyzed by the HACH DR900 Multiparameter Portable Colorimeter for the determination of residual fluoride concentration. The Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906) and Temkin (Kinniburgh, 1986) models were applied to fit the equilibrium data. Each isotherm model was expressed by relatively certain constants, which characterized the surface properties and indicated the adsorption capacity of this material.

Effect of co-existing (competing) anions on fluoride removal by TW65

The fluoride adsorption potential of the mixture TWL65 was also investigated in the typical presence of co-existing (competing) anions (e.g., phosphate, sulfate, and nitrate) in real groundwater. Experiments were conducted by adding varying concentrations of co-existing anions (5-50 mg L^{-1}) in a fluoride solution with a fixed fluoride concentration of 2 mg L^{-1}, optimum pH, optimum contact time and optimum adsorbent dosage. The mixtures were shaken at a speed of 120 rpm at a room temperature of 25 °C. Then the solid phase was separated from the solution by filtration using a millex-

GP syringe filter unit pore size 0.45 µm. The concentration of remaining fluoride was determined by the Hach DR900 Multiparameter Portable Colorimeter.

Fluoride removal study with TW65

A simple fluoride removal setup was designed to study the effect of feeding volume on fluoride removal efficiency and changes in pH of effluent solutions using transparent plastic pipes with a 3.5 cm diameter and a cross-sectional surface area of 38.5 cm^2. The height of the pipes used to prepare filter columns was 20 cm. Prepared three different influent fluoride solutions (1.5 ppm, 2.0 ppm, and 2.5 ppm) were used for filter from each filter setup. The influent laboratory-prepared fluoride solution was entered into the filter at the top and effluent was collected from the bottom of the columns of each filter (Chathuranga et al., 2015). Each column was filled with 100 g of TWL65 filter media with a sand layer about 1 cm in height at the bottom.

Analysis of Data

All analyses were performed using IBM SPSS Statistics 18.

RESULTS AND DISCUSION

Physico-chemical analysis of tea waste and laterite

The composition of the soil samples used was determined using an XRF analysis.

Table 1: Composition of raw laterite

	Sample 1	Sample 2	Sample 3	Average	Min	Max	SD
Minerals/wt %							
SiO_2	44.6	44.3	44.8	44.6	44.3	44.8	0.252
Al_2O_3	32.9	33.5	33	33.1	32.9	33.5	0.321
Fe_2O_3	19.3	18.8	18.9	19.0	18.8	19.3	0.265
TiO_2	2.31	2.34	2.33	2.32	2.31	2.34	0.015
K_2O	0.171	0.168	0.162	0.167	0.162	0.171	0.005
CaO	0.078	0.07	0.085	0.078	0.07	0.085	0.008
Elements/wt %							
Fe	64.8	64.6	65.8	65.1	64.6	65.8	0.643
Al	16.3	15.8	15.8	16.0	15.8	16.3	0.289
Si	14.9	15.6	14.7	15.1	14.7	15.6	0.473
Ti	1.91	1.91	1.90	1.9	1.87	1.91	0.023
Zr	1.00	0.98	1.00	1.0	0.984	1.00	0.009

Tb	0.26	0.19	0.30	0.3	0.196	0.347	0.076
Co	0.18	0.20	0.20	0.2	0.181	0.201	0.010
Gd	0.17	0.16	0.00	0.2	0.164	0.175	0.008
K	0.13	0.13	0.10	0.1	0.129	0.131	0.001
V	0.08	0.08	0.10	0.1	0.085	0.088	0.002

There were 33 elements and compounds found in laterite (Table 1).

Fe was the most common element in all three samples, accounting for 65. 1±0.643 % of the total mass. Aside from that, Al and Si were plentiful. When it comes to the compounds discovered by XRF analysis, SiO_2 is the most abundant of all three analyzed samples. High levels of Al_2O_3 and Fe_2O_3 were also found. TiO_2, CaO, and K_2O are among the other compounds discovered (Nayanthika et al., 2018).

Elution analysis was carried out for tea waste to find readily available metal ions that can be leached into the solution. The elements which can be leached to the filtrates were checked through atomic absorption spectroscopy (Table 2).

Table 2: Elements detected in the elution analysis of tea waste

Constituents determined	Element concentration (ppm)
Fe	0.11
Mg	8.6
Na	12.6
Mn	0.3
Al	<0.1
K	3.3
Ca	2.7

According to the results obtained, Na, Mg, K, Fe, Mn, Al, and Ca were found, and these elements were present at ppm level. All elements were present in ppm levels that were highly below the WHO drinking water quality guidelines (WHO, 2011).

SEM observed the surface topography of the tea waste.

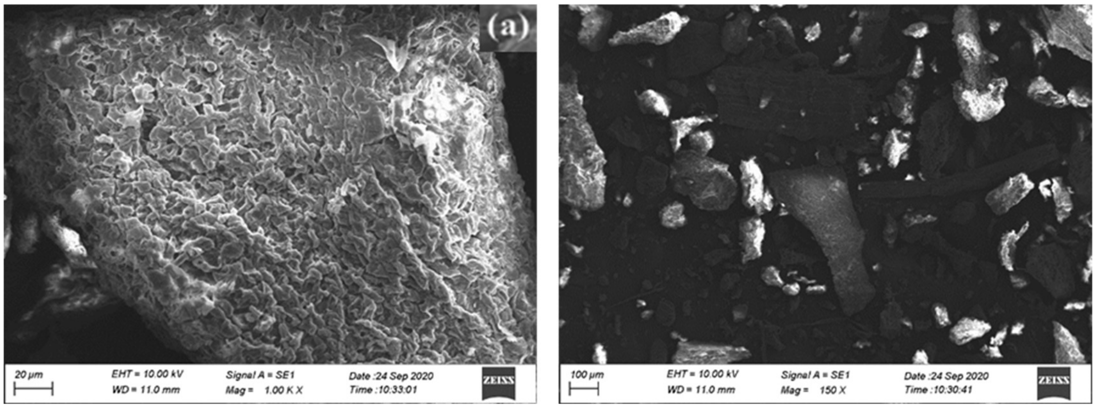

Figure 1: SEM images of tea waste (a), (b) at higher magnification

The surface of the tea waste was rough (Bansal et al., 2020) and had tiny pores, and the adsorbent surface was irregular and porous (Fig. 1). Thus, the surface of tea waste would facilitate the adsorption of fluoride ions onto tea waste (Mondal, 2017).

BET analysis was performed to study the surface area, total pore volume, and average pore radius of the TW and TWL65 mixture. The BET surface area was higher in the TWL65 mixture than in the TW, which is relatively higher than other common-plant-based adsorbents (Bakar et al., 2016).

The average pore radii of TW and TWL65 recorded were 3.3077 nm and 8.9620 nm, respectively, which fall within the range of mesoporous pore size within 2–50 nm. The N_2 adsorption/desorption isotherm exhibits the type IV behaviour for TWL65 (Fig.2), which is characteristic of mesoporous structure based on the IUPAC classification.

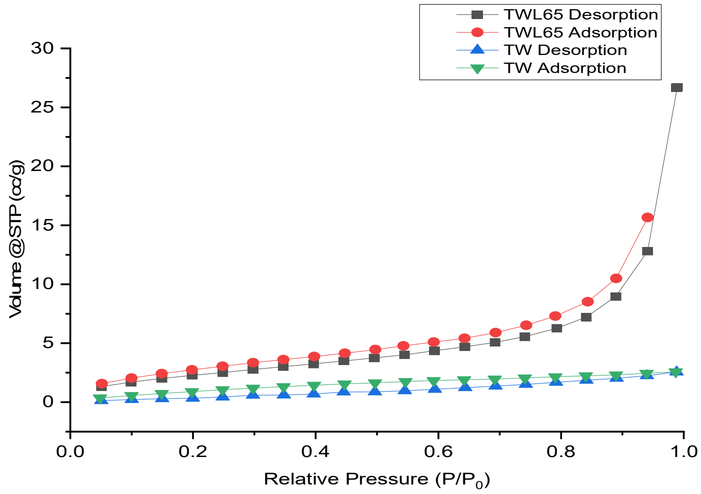

Figure 2: Low-temperature nitrogen adsorption and desorption isotherms of TW and TWL65 samples

The main advantages of mesoporous materials are narrow pore size distributions and high surface areas, simple organic functioning strategies, biocompatibility, and low toxicity (Wu and Zhao, 2011). The applicability of both blends for the study is thus confirmed. Points of zero charge (pHpzc) are the pH at which the adsorbent's net surface charge is zero. The difference between the initial and final pH values (ΔpH = pHi − pHf) was plotted versus pHi.

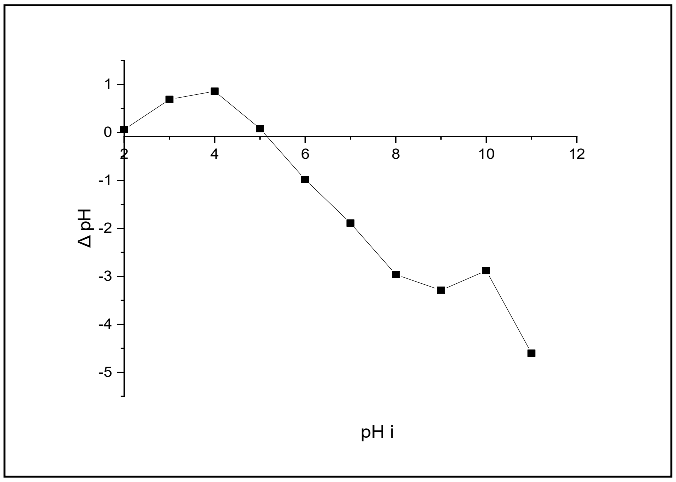

Figure 3: The difference between the initial and final pH values

The pH at which ΔpH = 0 was considered as the pH value at the point of zero charges (Wu and Zhao, 2011). The results of this experiment show that the pHpzc of tea waste is about 5.10 (Fig. 3).

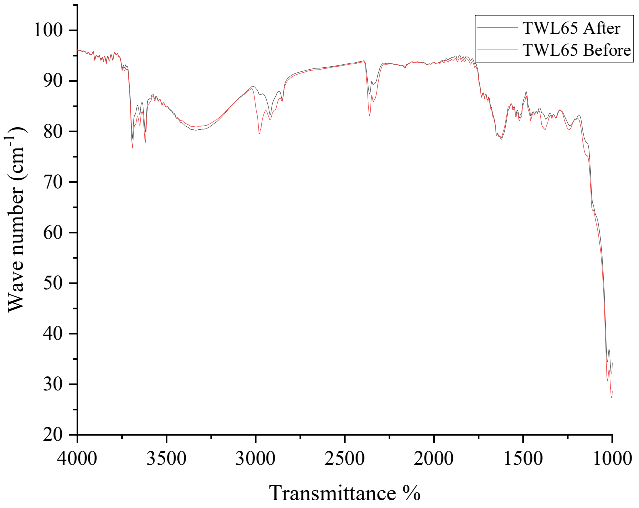

Figure 4: FTIR spectra of TWL65 before and after fluoride adsorption

Before and after fluoride adsorption, FTIR spectra were obtained for TW and TWL65 (Fig.4). The broad and intense absorption single band at around 3332 cm^{-1} correspond to O–H stretching vibrations caused by inter and intermolecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols, and carboxylic acids found in pectin, cellulose, and lignin, indicating the presence of "free" hydroxyl groups on the adsorbent surface (Wu and Zhao, 2011). The symmetric and asymmetric C–H stretching vibration of aliphatic acids is responsible for the peak at 2920 cm^{-1}. The peak at 1616 cm^{-1} is caused by asymmetric stretching vibrations of C=O, while an aromatic compound group causes the peak at 1515 cm-^{1} (Bansal et al., 2020). However, in the TW mixture, distinct changes are not noted between the spectra before and after fluoride adsorption onto tea waste. This indicates that the main structures of both soil mixtures were not altered due to fluoride adsorption.

Sorption properties of fluoride by tea waste under selected water types in the typical salinity/hardness range

Step1- After adding tea waste to the fluoride non-adjusted groundwater samples, diverse fluoride removal behaviors were observed as shown in Fig.5a.

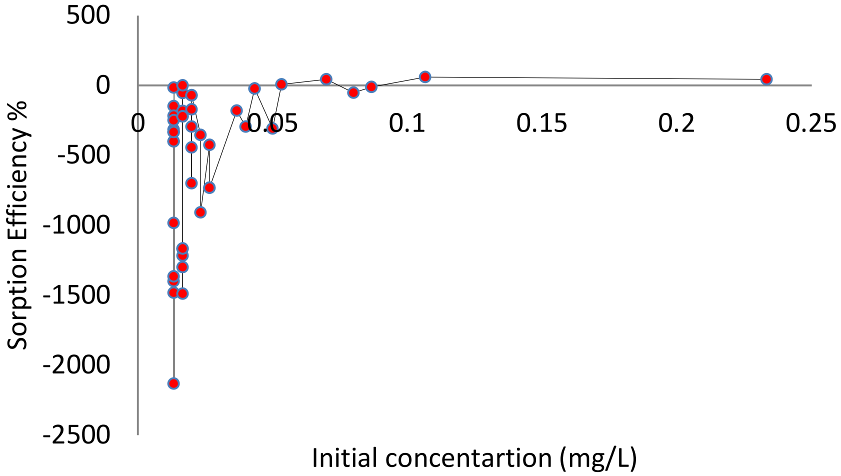

Figure 5(a): Variation of fluoride sorption efficiency with changes in initial fluoride concentration (mg L^{-1}) of groundwater samples

Both the sorption and leaching behavior of fluoride by tea waste could be observed during the experiments. Favorable (positive) sorption efficiencies were interpreted as fluoride removal from the solution, whereas negative sorption efficiencies were interpreted as fluoride leaching into the solution. Step 2- Fluoride concentrations in collected groundwater samples were adjusted to align with fluoride levels in water in Sri Lanka from <0.01 mg/L to 8.00 mg/L(Bansal et al., 2020), to further investigate the potential sorption behavior of tea waste in groundwater under low to high fluoride concentration range as the experimental procedure outlined in section 2.4 (step 02). According to the initial fluoride concentration of water samples, both the sorption and leaching behavior of fluoride by tea waste could be identified when tea waste was added to fluoride-adjusted and non-adjusted groundwater samples (Fig.5b).

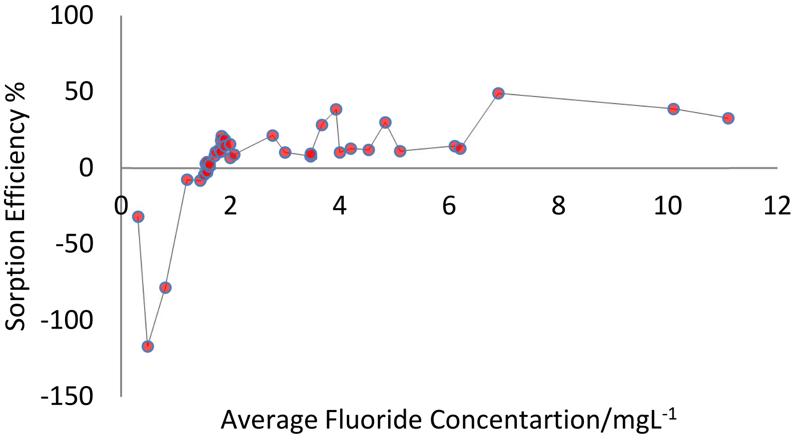

Figure 5(b): Variation of fluoride sorption efficiency with initial fluoride concentration (mg L^{-1}) of adjusted groundwater samples

During the sorption studies, higher fluoride levels in water resulted in fluoride sorption, whereas lower fluoride levels in water resulted in fluoride leaching by tea waste. Thus, behavior of fluoride sorption by tea waste varies depending on the fluoride concentration in the water. Similar sorption behavior was observed in tea leaves as mentioned in (Malde et al., 2006), which indicated that fluoride is easily released from tealeaves in low-fluoride water and tealeaves may release or absorb fluoride, depending on the fluoride content of water.

Determination of the optimum mixing ratio of tea waste and laterite

The fluoride removal efficiency is the highest when TWL65 is used, including 65% of tea waste and 35% of laterite powder. The lowest removal efficiency was seen in TW (100% tea waste), which was made of 100% tea waste powder. As the highest removal efficiency (40.83 ±1.607) % was recorded in TWL65 (65% of tea waste and 35% laterite powder), it was considered the optimum mixture and was used to carry out further studies (Table 3).

Table 3: Results of optimum mixing ratio

Tea waste percentage/%	Remaining fluoride concentration/mg L^{-1}	Percentage removal efficiency/%	Adsorption capacity/ mg g^{-1}
50	1.24±0.075	40.33±3.753	0.087±0.004
55	1.44±0.020	30.50±1.000	0.072±0.001
60	1.32±0.154	34.50±7.697	0.080±0.008
65	1.23±0.032	40.83 ±1.607	0.769±0.002
70	1.41±0.174	32.00±8.718	0.077±0.009
75	1.68±0.030	18.50±1.500	0.043±0.002
80	1.54±0.026	25.50±1.323	0.060±0.001
90	1.62±0.129	21.67±6.449	0.049±0.006
100	1.77±0.096	14.00±4.822	0.014±0.005

Batch Experiments of Fluoride

When the adsorbent dose of tea waste increases, the percentage of removal was also increased, and the highest adsorption efficiency was achieved at 1.5 g with the removal efficiency of 40.77±5.19% (Fig. 6a).

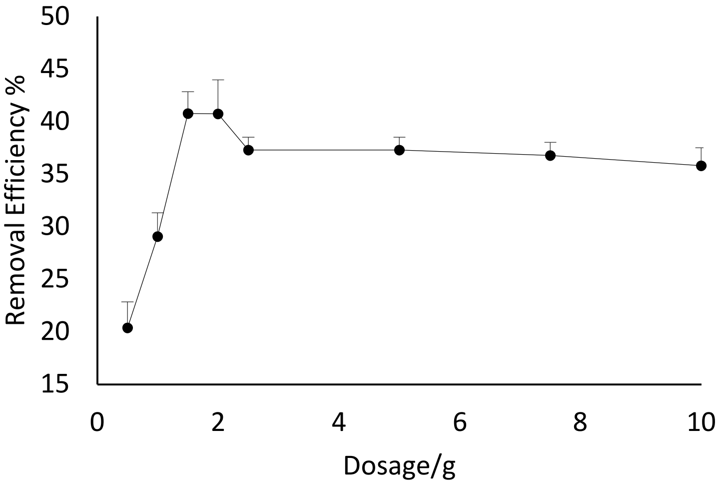

Figure 6(a): Variation of fluoride removal efficiency with changes of TWL65-mixture dosage

Further increase in adsorbent dosage beyond 1.5 g did not significantly affect the fluoride adsorption efficiency, and with further increase in adsorbent dose, the adsorption efficiency remained constant. Due to the increasing number of accessible active sites of the adsorbent, the removal efficiency is commonly increased by increasing the amount of adsorbent dose. The adsorption capacity, however, remains constant after a certain adsorbent dose (Pooresmaeil et al., 2018). The adsorption potential of TWL65 for removing fluoride was found to be rapid in the early stages of contact time.

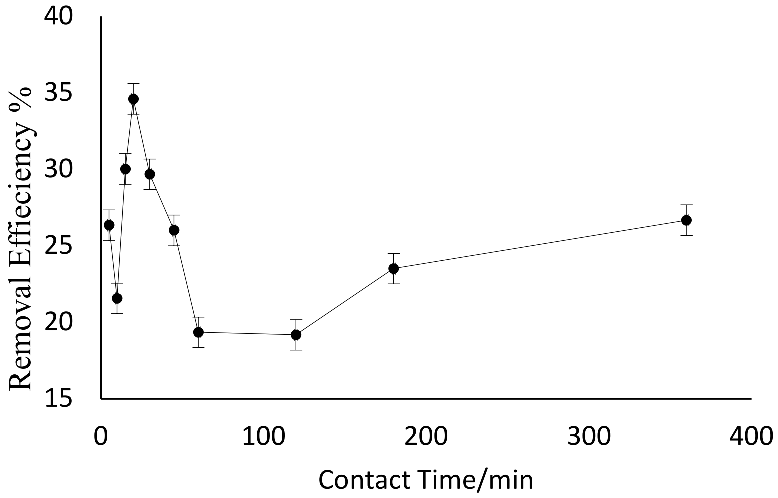

Figure 6(b): Time-dependent variation in removal fluoride efficiency for TWL65

The rate of adsorption decreases with time after 20 minutes, and the adsorption mechanism reaches equilibrium within 20 minutes. According to (Pooresmaeil et al., 2018), this observation may be explained by a larger number of active sites on TWL65 for fluoride ion adsorption in the early stages. The adsorption efficiency increased as the aqueous phase pH values increased from 2 to 11 (Fig. 6c).

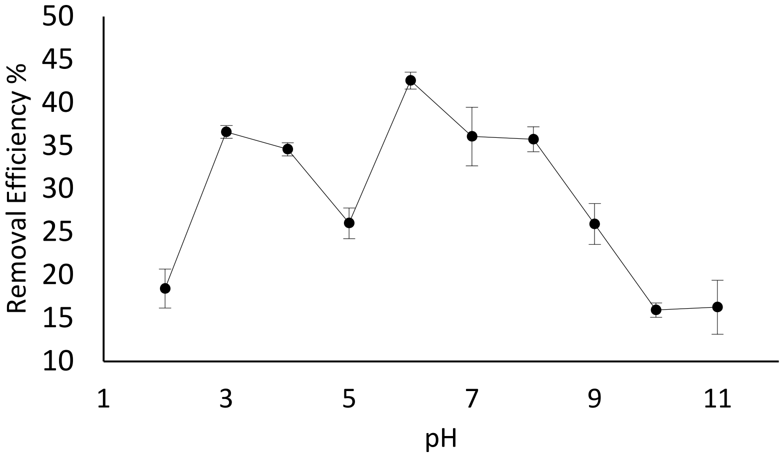

Figure 6(c): Variation of fluoride removal efficiency with changes in pH for TWL65 mixture

Initially, the percentage of fluoride ions removed increased rapidly with the increasing pH of the solution, with pH 6 being the optimal pH. A further increase in pH results in a significant decrease in the adsorption percentage. This could be because of the electrostatic repulsion between the oppositely charged adsorbate and adsorbent (Al-Othman et al., 2012).

Adsorption kinetic studies of fluoride by TW65

Table 4: Kinetic parameters of fluoride adsorption by TWL65

Kinetic Model	Parameter	Value
Pseudo first order	R^2	0.4650
	K_1 (min^{-1})	0.0015
	$q_{e\ (cal)}$ ($mg\ g^{-1}$)	0.0216
	$q_{e\ (exp)}$ ($mg\ g^{-1}$)	5.65×10^{-5}
Pseudo second order	R^2	0.9950
	K_2 ($g\ mg^{-1}\ min^{-1}$)	24.136
	$q_{e\ (cal)}$ ($mg\ g^{-1}$)	0.0216
	$q_{e\ (exp)}$ ($mg\ g^{-1}$)	0.0164

According to the Table 4, the q_{cal} values calculated from the pseudo-second-order model is 0.0216 mg g^{-1} which is close to the experimental values q_{exp} value 0.0164 $mg\cdot g^{-1}$ than the pseudo-first-order model. These findings confirmed the applicability of pseudo-second-order kinetic model to determine the rate of reaction. (Smitha et al., 2017).

Adsorption isotherms studies of fluoride by TW65

To investigate the interaction of fluoride with the surface of TWL65, adsorption isotherms were plotted. The Langmuir isotherm model (Langmuir, 1916) has a higher R^2 value (0.92529) compared to the Freundlich isotherm model value of R^2 -0.88853 and the Temkin isotherm model value of R^2 -0.77121 (Table 5).

The adsorption of fluoride data was well represented in the Langmuir model, which indicates that the adsorption mechanism follows the monolayer adsorption behavior. The adsorbent has active sites with uniform energy on the surface of the adsorbent. Based on the linear regression coefficient, the model that best fits for TWL65 was the Langmuir adsorption isotherm model.

Table 5: Langmuir, Freundlich and Temkin isotherm parameters for adsorption of fluoride on TWL65

Isotherm	Parameter	Value
Langmuir	R^2	0.92529
	q_{max}	0.01708
	K_L	0.44602
Freundlich	R^2	0.88853
	n	0.36023
	K_F	0.01196
Temkin	R^2	0.77121
	B_T	9.37952
	K_T	1.00173

Table 6: pH variation of effluent with feeding volume of influent solutions (1.5 ppm, 2.00 ppm and 2.5 ppm)

	Influent (Fl^-) concentrations		
	1.5 ppm	**2.0 ppm**	**2.5 ppm**
	pH	**pH**	**pH**
Max	6.5	5.6	5.2
Min	5.9	6.25	5.73
Mean	6.15	6.15	6.15

Effect of competing ions on fluoride removal by TW65

It was found that the removal efficiency of TWL65 towards fluoride was reduced due to the presence of co-existing (phosphate, nitrate, and sulfate) in the water. Nitrate and sulfate have nearly identical effects on fluoride adsorption, which showed removal efficiency ranging between 27.77± 0.555% to 48.23± 7.692% in the presence of nitrate and between 33.33± 3.469% to 42.40±0.320% in the presence of sulfate. Phosphate ions have shown maximum effects on the adsorption of fluoride, and the removal efficiency varied between 0.555± 0.555 to 44.31± 3.239% (Fig. 7).

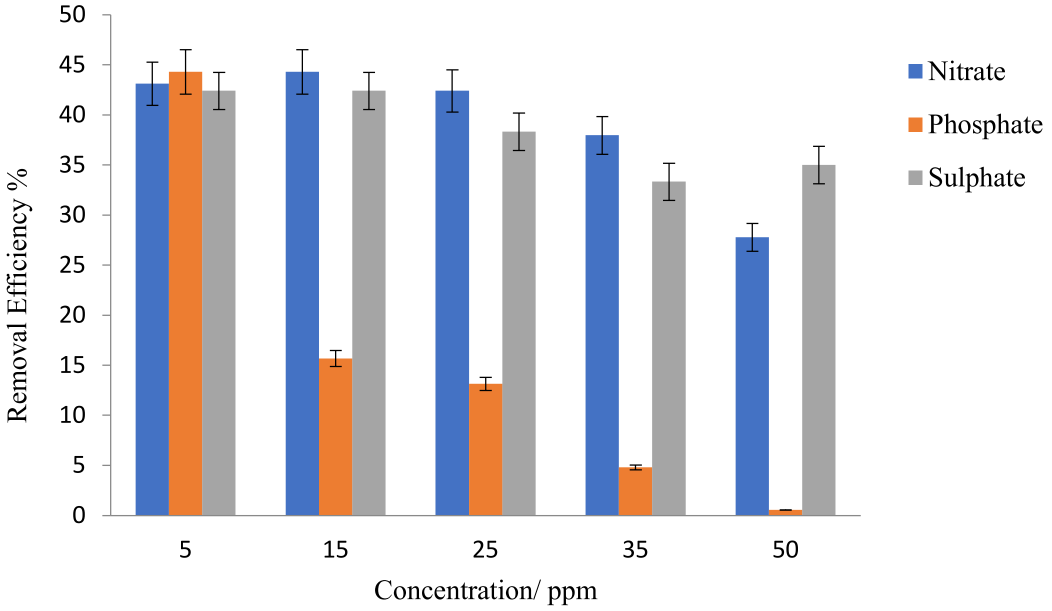

Figure 7: Effect of competing anions on the adsorption capacity of TWL65 for fluoride adsorption

The decrease in fluoride removal in the presence of phosphate could be attributed to the high affinity of adsorbent for carbonate and phosphate ions and their competition for active binding sites with fluoride (Chen et al., 2011). The fluoride removal efficiency decreased as the concentration of the competing ion increased. It could be explained by the fact that in multi-element solutions, the electrostatic interaction of co-existing anions with adsorption sites of TWL65 mixture was much stronger than the electrostatic interaction of fluoride ions species.

Effluent fluoride concentration variations with feeding volume and fluoride removal efficiencies under 1.5 ppm, 2.0 ppm, and 2.5 ppm influent fluoride concentrations

Fluoride concentrations in the effluent dropped as the feeding volume increased, and fluoride removal efficiency increased gradually in the initial stage of the filtering process in all fluoride removal set-ups with 1.5 ppm, 2.0 ppm, and 2.5 ppm influent fluoride concentrations as shown in fig.8.

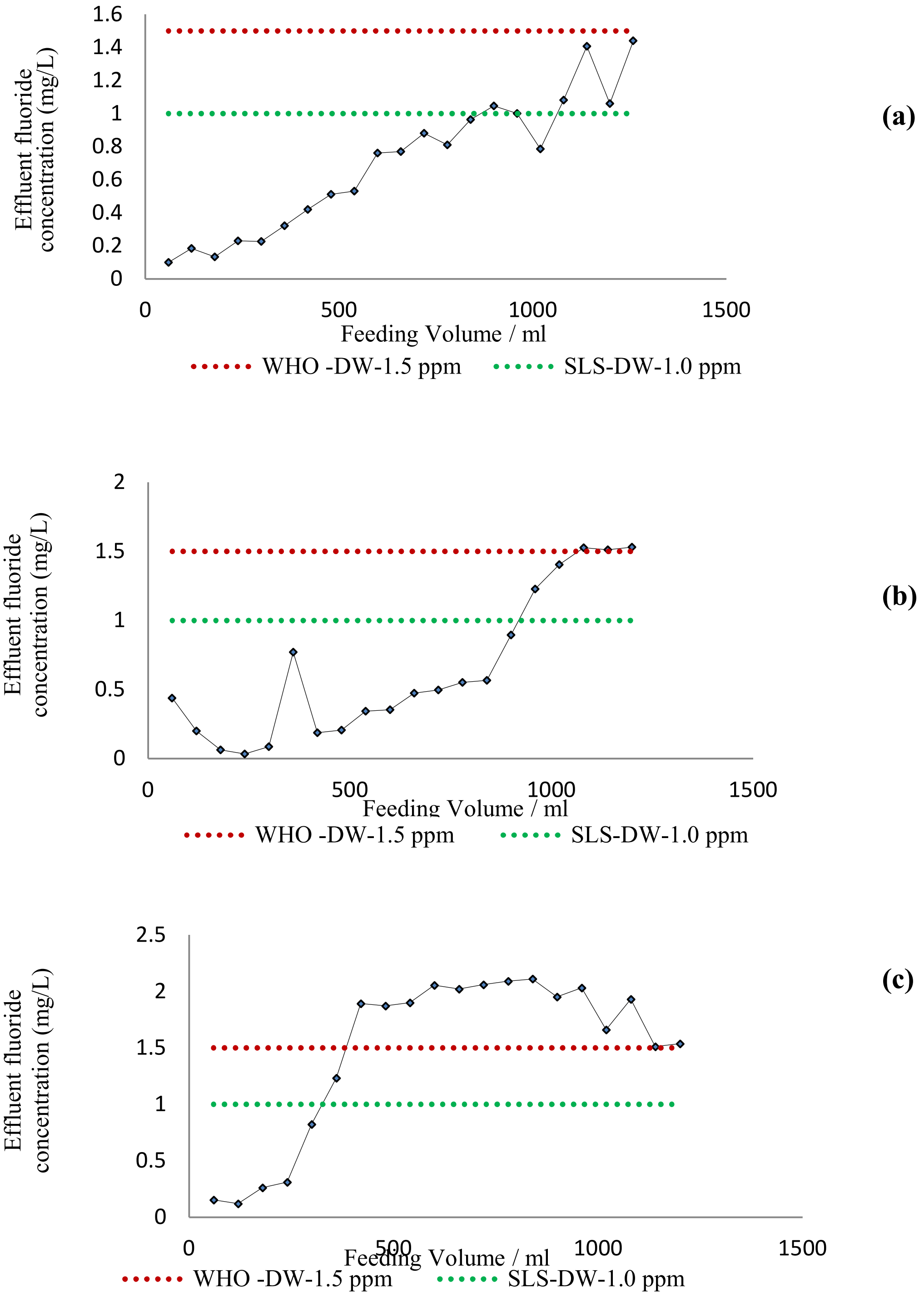

Figure 8: Fluoride concentration variation with feeding volume of influent solution (1.5 ppm) (a), Fluoride concentration variation with feeding volume of influent solution (2.0 ppm) (b) and Fluoride concentration variation with feeding volume of influent solution (2.5 ppm) (c)

When feeding more volume, the effluent fluoride concentration decreased, than the initial stage of the filtering process. Similar fluoride removal trends were observed in the study conducted on the development of activated iron oxide soil pellets to study the filtering efficiency of fluoride ions in aqueous fluoride solutions (Jayarathne and Jayawardana, 2018). However, when more volume is added, time passes and the available sites are decreased, while the effluent fluoride concentration increased. In all three setups with different influent fluoride concentrations, fluoride removal efficiencies were found to be closer or lower than the WHO drinking water quality standards level for fluoride of 1.5 ppm (WHO, 2011) and Sri Lankan drinking water standards level (Institute, 2013) for fluoride of 1 ppm. When the feeding volume was increased, the pH values in the filtrates varied, but the pH values did not differ significantly from the initial values of the influent solutions in all three fluoride removal setups (Table 6). The mean pH values of the filtrates were lower than the maximum permissible pH level of the drinking water quality standard in Sri Lanka, which is 6.5-8.5 (Institute, 2013).

CONCLUSIONS

The study was planned to investigate the sorption behavior of tea waste with dominant harmful fluoride concentrations and finally, a novel adsorbent was introduced by amending laterite to tea waste. The initial sorption behavior of tea waste with different fluoride levels in groundwater concluded that fluoride leaches from tea waste with lower fluoride levels in the water, while tea waste absorbs fluoride when the fluoride concentration is high in water. Thus, it is vital to examine the chemical kinetics of fluoride adsorption by tea waste with the necessary amendments to reduce possible desorption for the effective use of tea waste. In this experiment, laterite powder was discovered to be a suitable amendment. Thus, TW65 (65% tea waste:35% laterite) an be used to remove fluoride from water while maintaining the normal pH of potable groundwater. In batch experiments, fluoride removal was highest around pH6, whereas the influent fluoride solution at pH6 produced better filtering performances in fluoride removal experiments using a simple fluoride removal setup. The addition of laterite to tea waste inhibited fluoride leaching from tea waste into the water. Therefore, tea waste and laterite mixture can be introduced as an eco-friendly adsorbent for removing fluoride from portable groundwater under natural pH conditions.

ACKNOWLEDGEMENT

We extend our gratitude to the Department of Forestry and Environmental Sciences staff for granting support. Our special thanks to the Central Instrumental Center, Faculty of Applied Science University of Sri Jayewardenepura (USJP), Sri Lanka. This study was conducted under the AHEAD ICE grant.

REFERENCES

1. Munajad, A. and Subroto, C., 2018. Fourier transform infrared (FTIR) spectroscopy analysis of transformer paper in mineral oil-paper composite insulation under accelerated thermal aging. *Energies*, *11*(2), p.364.
2. Barrett, E.P., Joyner, L.G. and Halenda, P.P., 1951 The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *Journal of the American Chemical society*, *73*(1), pp.373-380.
3. Bakar, A., Koay, Y., Ching, Y., Abdullah, L., Choong, T., Alkhatib, M., Mobarekeh, M. and Mohd Zahri, N., 2016' Removal of fluoride using quaternized palm kernel shell as adsorbents: Equilibrium isotherms and kinetics studies', *BioResources*, 11(2), pp. 4485–4511. doi: 10.15376/biores.11.2.4485-4511.
4. Baral, S. S., Das, S. N. and Rath, P. 2006 'Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust', *Biochemical Engineering Journal*, 31(3), pp. 216–222. doi: 10.1016/j.bej.2006.08.003.
5. Bansal, M., Patnala, P.K. and Dugmore, T., 2020. Adsorption of Eriochrome Black-T (EBT) using tea waste as a low cost adsorbent by batch studies: A green approach for dye effluent treatments. *Current Research in Green and Sustainable Chemistry*, *3*, p.100036.
6. Bhatnagar, A. and Sillanpää, M., 2011. A review of emerging adsorbents for nitrate removal from water. *Chemical Engineering Journal*, *168*(2), pp.493-504.
7. Brunt, R., Vasak, L. and Griffioen, J. 2004 'Fluoride in groundwater: Probability of occurrence of excessive concentration on global scale', *International Groundwater Resources Accessment Centre, UNESCO.*, pp 20.
8. Cai, H., Chen, G., Peng, C., Xu, L., Zhu, X., Zhang, Z., Dong, Y., Shang, G., Ke, F., Gao, H. and Wan, X., 2015 'Enhanced removal of fluoride by tea waste supported hydrous aluminium oxide nanoparticles: Anionic polyacrylamide mediated aluminium assembly and adsorption mechanism', *RSC Advances*, 5(37), pp 29266–29275. doi: 10.1039/c5ra01560j.
9. Chandrajith, R., Padmasiri, J., Dissanayake, C. and Prematilaka, K., 2012 'Spatial distribution of

fluoride in groundwater of Sri Lanka', *Journal of the National Science Foundation of Sri Lanka*, 40(4), pp. 303–309. doi: 10.4038/jnsfsr.v40i4.5044.

10. Chandrajith, R., Diyabalanage, S. and Dissanayake, C. B. 2020 'Geogenic fluoride and arsenic in groundwater of Sri Lanka and its implications to community health', *Groundwater for Sustainable Development*, 10(March), pp. 100359. doi: 10.1016/j.gsd.2020.100359.
11. Chathuranga, W. G., Silva, N. C. D., Chaminda, T., Ellawala, C. and Kawakami, T. 2015' Removal of Fluoride , Hardness and Heavy Metals in Ground Water using Chicken Bone Char', pp. 271–276.
12. Chen, N., Zhang, Z., Feng, C., Zhu, D., Yang, Y. and Sugiura, N., 2011 '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*, 186(1), pp. 863–868. doi: 10.1016/j.jhazmat.2010.11.083.
13. Dissanayake, C. B. 1996 'Water quality and dental health in the Dry Zone of Sri Lanka', *Geological Society Special Publication*, 113(113), pp. 131–140. doi: 10.1144/GSL.SP.1996.113.01.10.
14. Divband, L., Hooshmand, A., Ali, A., Soltani, A., Abbasi, F., Bhatnagar, A., 2016. Removal of nitrate from aqueous solution by modified sugarcane bagasse biochar. *Ecol. Eng.* 95, pp. 101–111.
15. Freundlich, H.M.F., 1906. Over the adsorption in solution. *J. Phys. Chem*, 57(385471), pp.1100-1107.
16. Hussain, S., Anjali, K., Hassan, S. and Dwivedi, P., 2018 'Waste tea as a novel adsorbent: a review', *Applied Water Science*, 8(6), pp.1-16. doi: 10.1007/s13201-018-0824-5..0
17. Ho, Y. S. and McKay, G. 1998 'A Comparison of chemisorption kinetic models applied to pollutant removal on various sorbents', *Process Safety and Environmental Protection*, 76(4), pp. 332–340. doi: 10.1205/095758298529696.
18. Jayarathne, S. V. A. A. L., Chandrajith, R. and Weerasooriya, R. 2014' Removal of fluoride from aqueous solutions using natural apatite : a laboratory simulation', 18, pp. 9537.
19. Jagtap, S., Yenkie, M.K., Labhsetwar, N. and Rayalu, S., 2012. Fluoride in drinking water and defluoridation of water. *Chemical reviews*, *112*(4), pp.2454-2466.
20. Jayarathne, A. and Jayawardana, D., 2018. Development of Activated Iron Oxide Soil Pellets to Study the Filtering Efficiency of Fluoride Ions in Aqueous Fluoride Solutions. *23rd International Forestry and Environment Symposium,* 28, pp.101.
21. Karthik, K. Y. and Suresh, S. 2019 'Defluoridation of Water Using Activated Coffee Husk and Activated Tea Waste', (July), pp. 1592–1599.

22. Kinniburgh, D.G., 1986. General Purpose Adsorption Isotherms 895–904.Langmuir, I., 1916. The constitution and fundamental properties of solid and liquids. Part I. *J. Am. Chem.* 252, pp. 2221–2295.
23. Lagergren, 1898. About the theory of so-called adsorption of soluble substances S Zur Theorieder Sogenannten. K. Sven. Vetensk. sakademiens Handl. 24, 1–39.
24. Lengauer, C.L., Viglašová, E., Galamboš, M., Danková, Z., Krivosudsky, L., Hoodnowotny, R., Soja, G., Rompel, A., Matík, M., Brianc, J., 2018. Production, characterization and adsorption studies of bamboo-based biochar / montmorillonite composite for nitrate removal. *Waste Manag*. 79, pp. 385–394.
25. Lin, D., Wu, F., Hu, Y., Zhang, T., Liu, C., Hu, Q., Hu, Y., Xue, Z., Han, H. and Ko, T., 2020 'Adsorption of Dye by Waste Black Tea Powder: Parameters, Kinetic, Equilibrium, and Thermodynamic Studies', *Journal of Chemistry*, pp.1-13. doi: 10.1155/2020/5431046.
26. Nayanthika, I., Jayawardana, D., Bandara, N., Manage, P. and Madushanka, R., 2018. Effective use of iron-aluminum rich laterite-based soil mixture for treatment of landfill leachate. *Waste Management*, 74, pp.347-361.
27. Mahdavinia, G. R. and Mosallanezhad, A. 2016 'Facile and green rout to prepare magnetic and chitosan-crosslinked κ-carrageenan bionanocomposites for removal of methylene blue', *Journal of Water Process Engineering*, 10, pp. 143–155. doi: 10.1016/j.jwpe.2016.02.010.
28. Mitra, S., Thakur, L.S., Rathore, V.K., 2015. Removal of Pb (II) and Cr (VI) by laterite soil from synthetic waste water : single and bi-component adsorption approach. Desalin. Water Treat. 3994. https://doi.org/10.1080/19443994.2015.1088806.
29. Mondal, N.K., 2017. Natural banana (Musa acuminate) peel: an unconventional adsorbent for Removal of fluoride from aqueous solution through batch study. *Water Conservation Science and Engineering*, *1*(4), pp.223-232
30. Peng, C., Yan, X. B., Wang, R. T., Lang, J. W., Ou, Y. J., & Xue, Q. J. (2013). Promising activated carbons derived from waste tea-leaves and their application in high performance supercapacitors electrodes. *Electrochimica Acta*, *87*, 401-408.
31. Pooresmaeil, M., Mansoori, Y., Mirzaeinejad, M. and Khodayari, A.L.I., 2018. Efficient removal of methylene blue by novel magnetic hydrogel nanocomposites of poly (acrylic acid). Advances in Polymer Technology, 37(1), pp.262-274.
32. Renuka, P. and Pushpanji, K. 2013 'Review on Defluoridation Techniques of Water', *The International Journal of Engineering And Science (IJES)*, 2(3), pp. 86–94.

33. Sri Lankan Standard Institute. 2013. SLS standard 614:2013. Colombo : Sri Lankan Standard Institute.
34. Smitha, T., Santhi, T., Prasad, A., & Manonmani, S. 2017 'Cucumis sativus used as adsorbent for the removal of dyes from aqueous solution', *Arabian Journal of Chemistry*, 10, pp. S244–S251. doi: 10.1016/j.arabjc.2012.07.030.
35. Thommes, M. 2015 'Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)', *Pure and Applied Chemistry*, 87(9–10), pp. 1051–1069. doi: 10.1515/pac-2014-1117.
36. Tsubaki, S. and Azuma, J. ichi 2013' Total fractionation of green tea residue by microwave-assisted alkaline pretreatment and enzymatic hydrolysis', *Bioresource Technology*, 131, pp. 485–491. doi: 10.1016/j.biortech.2013.01.001.
37. Vithanage, M. and Bhattacharya, P., 2015. Fluoride in the environment: sources, distribution and defluoridation. *Environmental Chemistry Letters*, *13*(2), pp.131-147.WHO, 2011. Edition, F.,Guidelines for drinking-water quality. *WHO chronicle*, *38*(4), pp.104-108.
38. Wu, Z., Zhao, D., 2011. Ordered mesoporous materials as adsorbents. Chem. Commun. 47, pp. 3332–3338.