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## Research Article

# Remediation of Soils Contaminated by Fluoride Using a Fermentation Product of Seaweed (*Eucheuma cottonii*)

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This study investigated the efficacy of fermented seaweed (*Eucheuma cottonii*) on the remediation of fluoride-contaminated soil. The soil was amended with either 1.25, 3.0, or 5.0% (*w/w*) fermented seaweed (FSW), parallel with the controls (0%). The amendment improved the physicochemical properties of the soil particularly pH regulated from strong alkaline (9.3) to neutral (7.0) which is essential for germination, crop growth, and yield. The amount of water soluble-fluoride (Ws-F) dropped from  $81.7 \pm 3.1$  mg/kg to  $42.7 \pm 2.4$ ,  $33.7 \pm 1.2$ ,  $19.6 \pm 0.9$ , and  $12 \pm 1.3$  mg/kg following 0, 1.25, 3, and 5% amendment dosage, respectively. Most of the Ws-F was converted into exchangeable fluoride (Ex-F) and to fluoride-bound to iron and manganese (Fe/Mn-F). Furthermore, the amendment also enhanced microbial mass and diversity in the soil. The FSW contains organic acids which participate in ionic bonding with the multivalent cations in the soil. The formed compound participates in ion exchange with clay or with anionic adsorption to positively charged clay sites at the edges. This interaction is further essential for enhancing the fluoride holding capacity of the soil. The use of seaweed reduced the bioavailability of fluoride in the agricultural soils and had positive effects on promoting soil fertility. However, further studies to observe its effects on crop performance is of significance.

## 1. Introduction

Fluorine is the 13<sup>th</sup> most abundant element on the Earth's crust. It is released into the soil naturally over weathering and volcanic activities but also anthropogenically through human activities particularly, industrialization and agricultural practices [1, 2]. Fluorine possesses a strong electronegative property and is therefore very reactive. Because of this property, it rarely exists as a fluorine element, but rather as a fluoride ion [1,3]. Ingestion of low fluoride concentrations is recommended by the World Health Organization (WHO) for stronger bones and teeth; nonetheless, ingestion of high fluoride concentrations leads to a condition called fluorosis which rests as a global problem [2–5].

Although the WHO recommends fluoride consumption to not exceed 1.5 mg/day, it remains extensively hard to

maintain this low ingestion level because of the presence of multiple exposure sources [6, 7]. Most countries, for example, fluoridate their drinking water to the recommended level, but foods, drinks, dental products, and even inhalation represent other significant sources of fluoride exposure [8, 9]. With multiple exposure sources, the majority of the population remains subject to higher levels of fluoride daily. Animals and their products have also been found to contain fluorinated compounds acquired from their diet [2, 3, 9]. The greater part of the fluoride found in the food has its origin back in the soil and hence, we must find ways to control the bioavailable amount of fluoride in the soil.

Bioadsorption is one of the most important techniques for the removal of environmental contaminants. It has advantages of abundance, cost-effectiveness, eco-friendly, and efficiency [10, 11]. Seaweed is amongst the biomasses

fitted for their use as bio-adsorbents. The seaweed improves important soil properties such as soil organic matter (SOM), pH, microbial diversity, and nutrient composition and is therefore used as a natural fertilizer worldwide [11–13]. Seaweed also contains polysaccharides, proteins, and sulfate which act as the binding sites for ions present in the soil solution. The polysaccharides undergo other chemical transformations which additionally alter their chemical interaction with the soil elements [11, 14, 15]. Because of these properties, seaweed has been successfully investigated and used for remediation of soils contaminated with heavy metals [14, 15], however, not yet been investigated for anionic species particularly, fluoride in the soil. This study, therefore, examines the efficiency of fermented seaweed (*Eucheuma cottonii*) in reducing the amount of bioavailable fluoride in the soil while monitoring its impact on the soil's physical, chemical, and microbial properties.

## 2. Materials and Methods

**2.1. Soil Sampling and Analysis.** The composite soil samples were collected from agricultural fields located along the slopes of Mount Meru, Arusha, Tanzania, ( $3^{\circ}10'35''$  S  $36^{\circ}51'35''$  E) at a vertical profile of 0–20 cm. The composite samples were packed in plastic bags and brought to the laboratory. The samples were further air-dried and sieved to pass through a 2 mm sieve to remove debris and plant materials and then stored in containers that were cleaned with nitric acids before analysis.

**2.2. Seaweed Sampling and Preparation.** The seaweed used was *Eucheuma cottonii* collected from the Tanga region, Tanzania. The seaweed samples were brought to the laboratory where it was cleaned thoroughly with distilled water, sun-dried, then powdered using an electric grinder. Afterward, the 500 g of the seaweed powder was transferred to a container where it was mixed with the inoculum (anaerobic sludge from the septic tank), distilled water, and 100 ml molasses. The molasses contains high quantities of sucrose and fructose which is an easily available food source for the anaerobic biomass. Subsequently, 4 ml of iodoform was added to prevent the methanogenesis process from taking place, thereby encouraging acidogenesis and acetogenesis processes [16]. After mixing, the container was closed to stimulate the fermentation process. The container was kept in a shaker (110 rpm) at  $37^{\circ}\text{C}$ , free from light until the seaweed was entirely soft (5 weeks). The now fermented seaweeds were oven-dried at  $50^{\circ}\text{C}$  to obtain a hard solid which was again milled into a fine powder.

**2.3. Experimental Set-Up.** The soil samples (1 kg) were packed into the experimental pots and then mixed thoroughly with either 1.25, 3, or 5% (*w/w*) of the fermented seaweed powder (FSW) equivalent to the control samples labeled 0%. Thereafter, the soil was humified to 70–75% saturation and incubated in a shaded area, at room temperature ( $24 \pm 3^{\circ}\text{C}$ ). The first soil sample was collected within 24 h of inoculation, and the fluoride fractions, as well as pH,

were measured and quantified. The incubation process continued for 4 months while sampling and analysis were conducted every 30 days. The monitored parameters were pH, soil organic matter (SOM), cation exchange capacity (CEC), electrical conductivity (EC), fluoride fractions (water-soluble (Ws-F), exchangeable fluoride (Ex-F), fluoride-bound to iron/manganese (Fe/Mn-F), organic matter bound-fluoride (Or-F), and residual-fluoride (Res-F)), phosphorus (P), nitrogen (N), and the exchangeable bases (calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), potassium ( $\text{K}^{+}$ ), and sodium ( $\text{Na}^{+}$ )). Each treatment was replicated three times and the experiment was conducted in a completely randomized design.

**2.4. Analysis.** The hydrometer method was used to measure the soil particle size distribution. The content of SOM was calculated using the loss-on-ignition (LOI) method. An electrical conductivity meter and pH meter were used to measure the electric conductivity (EC) and pH. The cation exchange capacity (CEC) was measured using the barium chloride-triethanolamine method (pH 8.2). The water absorption capacity was measured by the centrifugation method [17]. The specific surface area of the soil was determined using the ethylene glycol monoethyl ether (EGME) method according to the procedures by Yukuksen and Kaya [18]. The exchangeable bases were quantified using the atomic absorption spectrophotometer (AAS) and the X-ray fluorescence (XRF) was used to analyze the total elemental composition. Total fluoride was determined according to McQuaker and Gurney's (1977) procedure [19]. Sequential extraction of fluoride was conducted as per our previous study [20]. In short, 2.5 g of the soil sample was placed into a 50 mL centrifuge tube and various species of fluoride were extracted by adding 25 ml of the extracting solutions as shown in Table 1.

Gas chromatography (GC) was used to analyze the amount of volatile fatty acids (VFAs) present in the fermentative sap using the flame ionization detector (FID). For analysis, the samples were collected from the fermented sap and then centrifuged at 1,500 rpm for 10 minutes to obtain a clear liquid. The liquid was acidified to pH 1.8 with formic acid. Due to analytical limitations, the VFA results were given as the total volatile fatty acids (TVFAs) expressed as g acetic acid/l (gAc/l). The C: N ratio of the seaweed was measured using the CHNS analyzer and the rest of the analyses were carried out as the soil samples. All the chemicals used were of analytical grade and distilled water was used throughout.

**2.5. Adsorption Experiment.** The adsorption experiment was conducted in batch at room temperature  $24 \pm 3^{\circ}\text{C}$ . The experimental soil (5 g) was mixed with different concentrations of fluoride (25, 50, 100, 200, and 300 mg/l) together and 50 ml of 0.01 mol/l  $\text{CaCl}_2$  solution. Thereafter, 62.5 mg FSW was added and the mixture was kept shaking in a shaker at 110 rpm for 72 h. After 72 h the mixture was centrifuged and the amount of fluoride remaining in the supernatant was measured potentiometrically. The amount of fluoride

TABLE 1: Extraction processes of various fluoride fractions in the soil.

Fluoride species	Extraction process
Water-soluble fluoride (Ws-F)	Distilled water Shake for 30 min at 60°C
Exchangeable-fluoride (Ex-F)	1 mol/L MgCl <sub>2</sub> Shake for 1 h at 25°C
Fe/Mn bound fluoride (Fe/Mn-F)	0.04 mol/L NH <sub>4</sub> .HCl Shake for 1 h at 60°C
Organic matter-bound fluoride (Or-F)	Step 1: 3 ml of 0.02 mol/l HNO <sub>3</sub> + 10 ml 30% H <sub>2</sub> O <sub>2</sub> Step 2: 12 ml of 3.2 mol/L NH <sub>4</sub> acetate Shake for 30 min at 25°C
Residual fluoride (Res-F)	Tot-F minus the above for species of fluoride

absorbed by the soil ( $q_e$ ) was determined as a difference between the initial concentration ( $C_0$ ) and the final concentration ( $C_e$ ) using the following equation:

$$q_e = \left( \frac{C_0 - C_e}{W} \right) V, \quad (1)$$

where  $q_e$  is fluoride adsorbed by the soil (mg/g),  $C$  is concentration (mg/l),  $W$  is weight of the soil (kg), and  $V$  is the volume of the solution (l).

To further understand the adsorption behavior of fluoride to the FSW, the experimental data were fitted on the Langmuir (1), Freundlich (2), and Temkin (4) models.

$$\frac{1}{q_e} = \frac{1}{k_L Q_{\max}} \cdot \frac{1}{C_e} + \frac{1}{Q_{\max}}, \quad (2)$$

$$\log q_e = \log k_f + \frac{1}{n \log C_e}, \quad (3)$$

$$q_e = \frac{RT}{b_T \ln A_T} + \frac{RT}{b_T} \ln C_e, \quad (4)$$

where  $q_e$  is the amount of fluoride adsorbed by the soil (mg/g),  $C_e$  is the fluoride concentration at equilibrium (mg/l),  $k_L$  is the Langmuir constant representing the maximum adsorption capacity (l/mg),  $Q_{\max}$  is the maximum fluoride concentration adsorbed by the soil (mg/g),  $k_f$  is the Freundlich constant, and  $1/n$  is the adsorption intensity. The value of  $1/n$  defines as to whether the adsorption process is favorable ( $0.1 < 1/n < 0.5$ ) or unfavorable ( $1/n > 0.5$ ) [21].  $R$  is the universal gas constant (8.314 J/mol·K),  $T$  is the temperature (K),  $A_T$  is the Temkin isotherm equilibrium binding constant (l/g), and  $b_T$  is the Temkin isotherm constant.

**2.6. Analysis of the Microbial Community.** The soil microorganisms were quantified by the agar plate dilution method [22]. Bacteria were cultured using a buffered peptone enrichment medium and later transferred to the nutrient agar where it was subcultured into blood agar and MacConkey agar. The Sabouraud dextrose agar was used for culturing fungi, and starch casein agar (SCA) was used for culturing actinomycetes.

**2.7. Statistical Analysis.** The statistical analysis was conducted using Microsoft Excel. The ANOVA tests were conducted using XLSTAT and the significant difference

between the means of the control and the treatments was identified using the Tukey's multiple pairwise comparison tests at a significance level of 5%. The values presented are the mean of the three replicates  $\pm$  standard error. Fluoride was determined as fluoride concentration =  $C \times (V/1000) \times (1000/W)$ , where  $C$  is the concentration measured reading in mg/kg,  $V$  is the volume of the extracted solution (ml), and  $W$  is the amount of the soil used (kg).

### 3. Results and Discussion

**3.1. The Fermentation Process.** The FSW had a water absorption capacity of  $2.7 \pm 0.3$  g/g. The dried seaweed comprised 59% carbohydrate, 4.6% cellulose, 3.3% lignin, 0.9% lipids, 6.7% protein, 23.1% total organic carbon (TOC), 1.2% nitrogen (N), and 19.3 C/N ratio. The TVFAs in the FSW were 0.3 gAc/l and its pH stood at 5.9. The amount of phosphorus (P), potassium (K), calcium (Ca), and sodium (Na) were 4.1, 3.7, 14.7, and 21.0 mg/kg, respectively. The amount of nitrogen in the fermented fertilizer was observed to be decreased (3 mg/kg) compared to the dried seaweed (16.4 mg/kg). The nitrogen loss could be attributed to nitrate conversion to ammonium and other gaseous forms of nitrogen wasted by volatilization during drying [20].

The anaerobic biomass converts the insoluble high molecular weight organic compounds (HMWOCs) such as polysaccharides, proteins, and lipids which are the main components in the seaweed into soluble low molecular weight organic compounds (LMWOCs) like monosaccharides, amino acids, and other simple organic compounds which exists as a source of energy and carbon to the other group of microorganisms [16, 23]. The simple organic acids produced are further assimilated to produce short-chain organic acids like acetic acid, propionic acids, butyric acids, and alcohols which can either be fatty acids (VFAs), amino acids, or simple sugars as shown in Equations (3)–(10) [16, 24]. These processes are accountable for the 0.3 gAc/l TVFAs obtained.

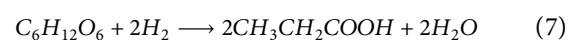
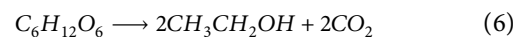
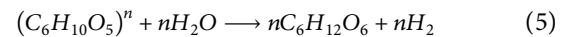
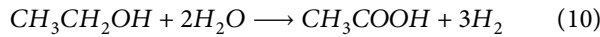
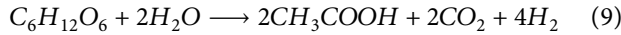
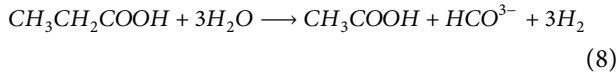
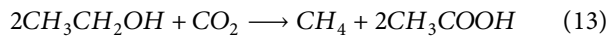
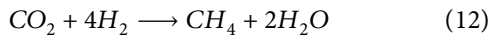
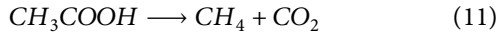


TABLE 2: The influence of fermented seaweed (FSW) amendment on selected soil properties at the end of the experimental phase (120th day).

Soil texture (%)	Soil		Soil + FSW (120th day)		
	Initial %	0%	1.25%	3%	5%
sand	68 ± 1	67 ± 1	65 ± 3	62 ± 3	55 ± 5
Silt	21 ± 4	20 ± 1	21 ± 6	21 ± 3	22 ± 3
Clay	11 ± 2	13 ± 2	14 ± 2	17 ± 4	23 ± 6
Water absorption (gH <sub>2</sub> O/g soil)	0.02 ± 0.1	0.02 ± 0.1	0.06 ± 0.1	0.17 ± 0.1	0.23 ± 0.1
pH	9.3 ± 0.0	8.9 ± 0.3	7.8 ± 0.1	7.4 ± 0.1	7.0 ± 0.0
CEC (meq/100 g)	32.8 ± 0.9	30.5 ± 0.5	34.5 ± 1.7	35.3 ± 1.7	37 ± 1.3
Phosphate (PO <sub>4</sub> <sup>3-</sup> ) (mg/kg)	17.2 ± 0.4	15.8 ± 2	12.5 ± 0.4	14.0 ± 0.9	16.4 ± 0.8
Exchangeable bases (mg/kg)					
Na <sup>+</sup>	8.48 ± 1.7	6.09 ± 1.9	12.8 ± 0.2	13.4 ± 3.3	14.3 ± 1.3
Ca <sup>2+</sup>	4.63 ± 0.3	4.66 ± 2.1	5.1 ± 0.5	4.7 ± 0.6	5.8 ± 0.9
Mg <sup>2+</sup>	2.03 ± 0.7	1.57 ± 0.6	2.5 ± 0.3	2.9 ± 0.4	3.2 ± 1.6
K <sup>+</sup>	7.37 ± 1.8	7.68 ± 2.3	10.5 ± 0.8	11.6 ± 3.5	13 ± 2.8
Electrical conductivity (EC) (μs/cm)	453.9 ± 2.3	451 ± 1.6	444 ± 1.3	443 ± 0.4	440 ± 2
Soil organic matter (SOM) (%)	2.5 ± 0.1	2.6 ± 0.4	3.5 ± 0.6	4.2 ± 0.3	5.4 ± 0.3



The use of iodoform prohibited the acetic acid conversion (Equations (11)–(13)) into methane but promoted the accumulation of TVFAs as reported by Jung et al. (2015) [25].



The addition of low molecular weight organic acids (LMWOAs) into the soil plays an important role in the chemical, physical, and biological properties of the rhizosphere [26]. Its alteration of the soil's rhizosphere accelerates the bioavailability of soil carbon and micronutrients for plant utilization but also alters the behavior of contaminants. The organic acids react with the metal found in the rhizosphere and free up the held nutrients for plant utilization. The fermentation process could therefore be the best alternative to speed up the action of organic fertilizer in the soil since the decomposition of HMWOCs to the LMWOCs is a slow process and could take ages.

**3.2. Soil Physicochemical Analysis before and after FSW Amendment.** The FSW amendment revealed a positive influence on the soil properties as presented in Table 2. The amount of water absorption capacity, clay content, SOM, CEC, and exchangeable bases increased after the amendments, whereas the soil pH of each treatment decreased. The impact of FSW on the soil quality was directly related to the amendment dosage such that the higher the dosage, the higher its impact on the soil quality parameters.

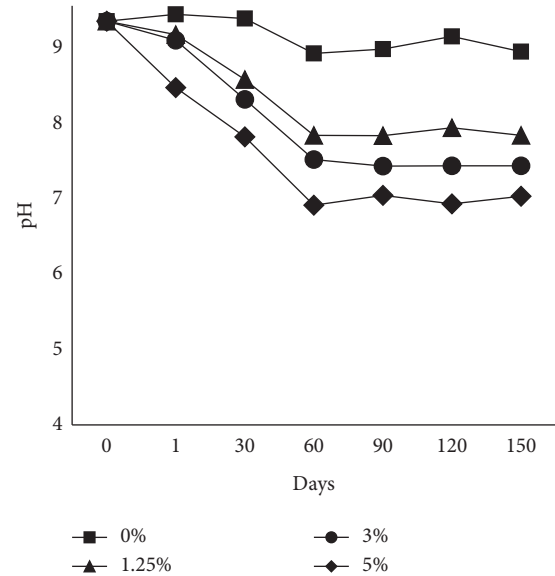
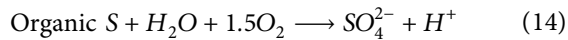


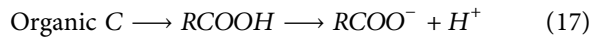
FIGURE 1: The impact of fermented seaweed (FSW) on the pH of the soil.

**3.3. The Impact of FSW on pH of the Soil.** The influence of the amendments on the pH of the soil is presented in Figure 1. The initial pH of the soil was  $9.3 \pm 0.0$ . There was no statistically significant change in the pH of the control samples throughout the experiment except for the 60th day when pH dropped to  $8.9 \pm 0.3$  and remained fairly constant thereafter. In the first 24 h, pH dropped from  $9.3 \pm 0.0$  to  $9.1 \pm 0.2$ ,  $9.0 \pm 0.1$ , and  $8.4 \pm 0.0$  following, 1.25, 3, and 5% amendment dosages, respectively. The pH continued to drop from  $9.3 \pm 0.0$  to  $7.8 \pm 0.1$ ,  $7.4 \pm 0.1$ , and  $7.0 \pm 0.0$  correspondingly, by the 120th day. The pH drop indicates that the process responsible for its behavior was progressing slowly and attained stability on the 60th day. There was a significant pH difference ( $p < 0.05$ ) between the treatments and the control. Even though the pH amongst treatments was significantly different, the 3 and 5% amendments were not statistically different ( $p > 0.05$ ) throughout the experiment.

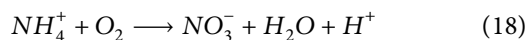
The pH influence most of the soil's biogeochemical properties. It controls the interaction, translocation, transformation, and the fate of different elements in the soil, including contaminants. It is therefore the mastermind behind the behavior and property of the soil [27]. In the soil, pH is lowered by the processes that release hydrogen ions ( $H^+$ ). Sulfur (S), nitrogen (N), and carbon (in the form of organic compounds) in the FSW undergo oxidation and decomposition reactions in the soil releasing the  $H^+$  responsible for soil acidification. Sulfur is oxidized by the soil microorganisms into  $SO_4^{2-}$  and  $H^+$  ions (Equation 14).



The  $H^+$  responsible for acidification is also released during the microbial decomposition of organic matter introduced by the FSW. When soil microorganisms decompose organic matter, they release  $CO_2$  which dissolves in water to produce carbonic acid ( $H_2CO_3$ ). The carbonic acid further dissociates into  $H^+$  and  $HCO_3^-$  (Equation (15) and (16)). The same soil microorganisms also release organic acids during the decomposition of organic matter found abundantly in the organic compounds although this is a slow process (Equation 17).



Furthermore, the pH drop observed could have been contributed by the nitrification process where  $NH_4^+$  is oxidized to  $NO_3^-$  and  $NO_2^-$  (Equation 18). The influence of nitrogen on pH could be more complicated because of the neutralization by the ammonification process which precedes nitrification and the denitrification process coming after nitrification.



Although both of the aforementioned processes contribute to acidification, the most obvious reason is the introduction of the FSW already loaded with the low pH LMWOAs. The decomposition of organic compounds into organic acids by the soil microorganisms could have also contributed to the acidification shown by the slow pH drop. The acidification is beneficial for regulating the strong alkaline property of the soil since most plants grow well at pH 6.5 to 7.5. Although, the behavior of pH observed could be different in the field where there are plants because plants assimilate  $NO_3^-$ , carbon, and  $SO_4^{2-}$  and release the  $OH^-$  which could neutralize the released  $H^+$ .

**3.4. The Adsorption Isotherms of Fluoride to the Soil System after the Amendment.** The adsorption isotherms are important in providing evidence of the adsorption behavior and capacity, surface properties, and the binding affinity of the adsorbent (Figure 2). These understandings reveal the

action mechanism of the amendments in the soil and their interaction with the targeted contaminant. In this study, three theoretical models were used to understand the interaction behavior of fluoride with the FSW amended soil, Langmuir, Freundlich, and Temkin. Langmuir isotherm works in an assumption that adsorption takes place at a homogeneous surface inside the adsorbent and once a fluoride ion occupies that particular site no other fluoride ion can be adsorbed (monolayer adsorption). Alternatively, Freundlich isotherms adopt a heterogeneous surface of the adsorbent and interaction between the adsorbed molecules (multilayer adsorption). The Temkin isotherm describes that as the adsorbent surface coverage increases, the adsorption heat of molecules decreases linearly. In this case, the adsorption is dictated by the uniform distribution of the binding energies to the maximum binding energy.

Table 3 represents the calculated isotherm parameters of the three models. When comparing the  $r^2$  values of the three models, Temkin's model provided the best fit (0.996) for the adsorption data from the experiment. High  $r^2$  represents the strong interaction between the fluoride ions and the reactive groups in the FSW. According to Temkin's model, the  $A_T$  value describes the affinity of the adsorbent to soil ions. The  $A_T$  value for this study was extremely high (1.9222 L/g), which indicates a high affinity of fluoride ions to the FSW. The slightly positive value of  $b^T$  (0.040) also indicated that this process is exothermic.

The value of  $b$  (1,567 mg/g) in the Langmuir isotherm describes the maximum capacity of fluoride in the soil after the amendment. The study by Abasiyan et al. (2019), reported that the amount of  $b$  was higher in the soil compared to the same adsorbent in the water system [28]. The high adsorption in the soil is accounted for the presence of other adsorbents containing a variety of functional groups such as carboxyl, phenolic, and carbonyl which interact and bind with the target ions in the soil.

### 3.5. The Impact of FSW Amendment on the Behavior of Fluoride Fractions in the Soil

**3.5.1. Direct Impact of FSW on Fluoride Fractions.** The four fractions of fluoride were monitored throughout the experiment and the results are presented in Figure 3. The amendments decreased the amount of water-soluble fluoride (Ws-F) from  $81.7 \pm 3.1$  mg/kg to  $42.7 \pm 2.4$ ,  $33.7 \pm 1.2$ ,  $19.6 \pm 0.9$ , and  $12 \pm 1.3$  mg/kg following 0, 1.25, 3, and 5% dosages, respectively. The 5% amendment could reduce the amount of Ws-F below the recommended level of 16.4 mg/kg [2]. Unlike Ws-F, the amount of exchangeable-fluoride (Ex-F) and fluoride-bound to iron and manganese (Fe/Mn-F) increased following the FSW amendment. The Ex-F increased from  $5.5 \pm 0.1$  mg/kg to  $14.8 \pm 0.7$ ,  $19.1 \pm 2$ ,  $20.3 \pm 0.8$ , and  $21 \pm 1.6$  mg/kg subsequent to 0, 1.25, 3, and 5% amendments. The Fe/Mn-F increased from  $8.7 \pm 0.1$  mg/kg to  $16.3 \pm 3.5$ ,  $24.4 \pm 2$ ,  $24.8 \pm 2.1$ , and  $25.7 \pm 1$  succeeding 0, 1.25, 3, and 5% amendment which is the lesser bioavailable form compared to the abovementioned two. There was no observed impact of the amendments on the amount of fluoride-bound to organic matter (Or-F).

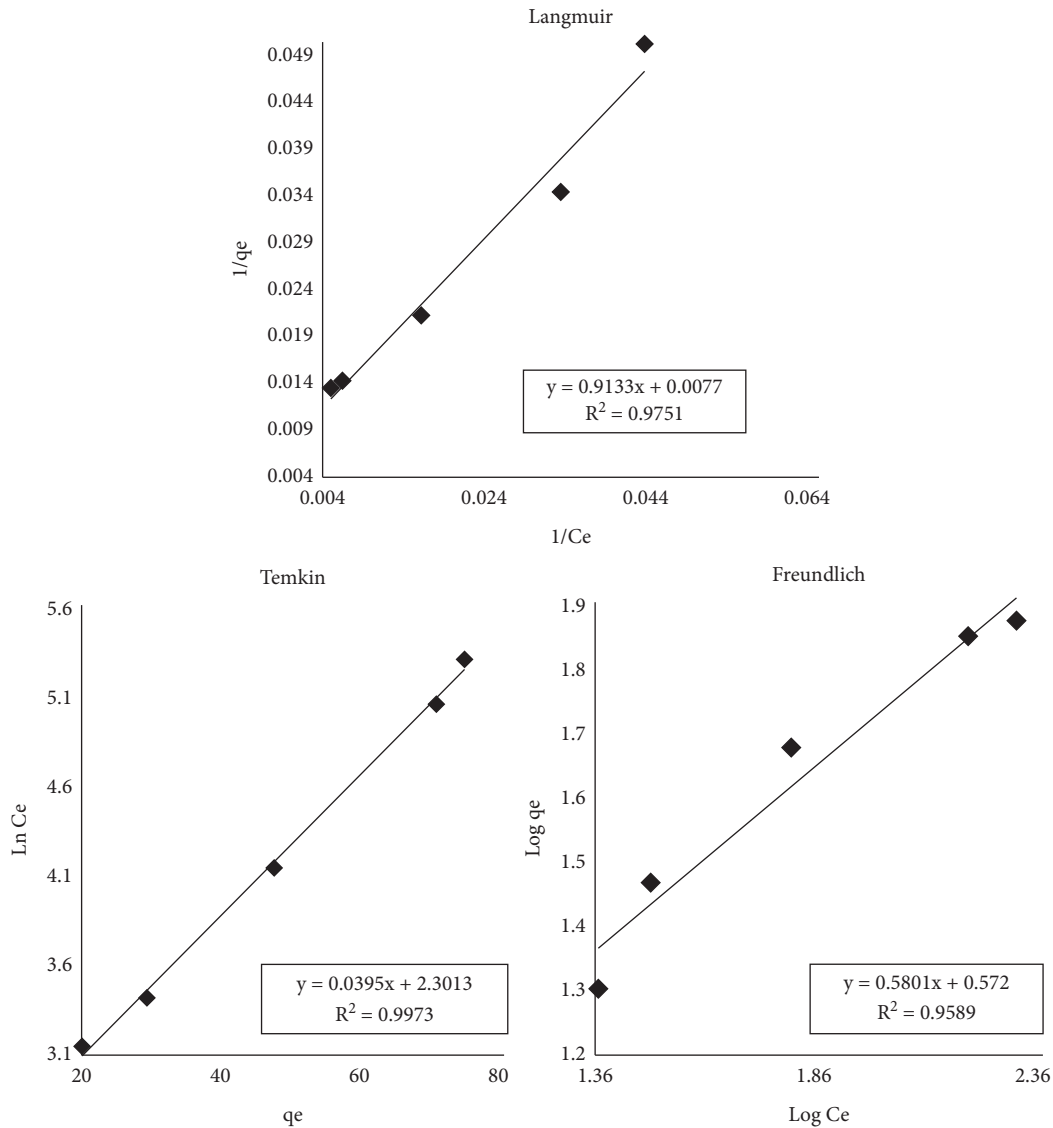


FIGURE 2: The adsorption isotherms of fluoride to the soil following the FSW amendment.

TABLE 3: Isotherm parameters for the adsorption of fluoride in the soil succeeding fermented seaweed (FSW) amendment at 1.25% amendment dosage (62.5 mg FSW).

Parameters	Langmuir	Freundlich	Temkin
b (mg/g)	1567		
$K_L$ (L/mg)	0.009		
$r^2$	0.967		
$1/n$		0.58	
$k_f$		3.733	
$r^2$		0.959	
$b_T$ (J/mol)			0.040
$A_T$ (L/g)			$1.92^{22}$
$r^2$			0.996

There was a significant difference ( $p < 0.05$ ) in the amount of Ws-F observed between 0, 1.25, and 3% to that of 5% amendment within the first 24 h of the incubation. The

amendment dosage was inversely proportional to the amount of Ws-F in the soil such that, as the dosage increased, the amount of Ws-F in the soil decreased. Within 30-day incubation, the amount of Ws-F was significantly different ( $p < 0.05$ ) between the treatments and the control (0%). The significant difference between 1.25 and 3% to the 5% amendment was also noticed but the two (1.25 and 3%) were not significantly different ( $p > 0.05$ ) up until the 60th day. From the 60th day to the 120th day, there was a significant difference in the amount of Ws-F among all treatments.

The organic matter comprises functional groups (-COOH and -OH) which participate in the replacement reactions with the fluoride ions in the soil. The direction of the reaction depends on the pH and the amount of either  $F^-$  or  $OH^-$  present in the soil solution. At high pH, the  $F^-$  replaces the  $OH^-$ , which reduces the number of  $F^-$  present in the soil solution interface. If the pH of the soil is high, the

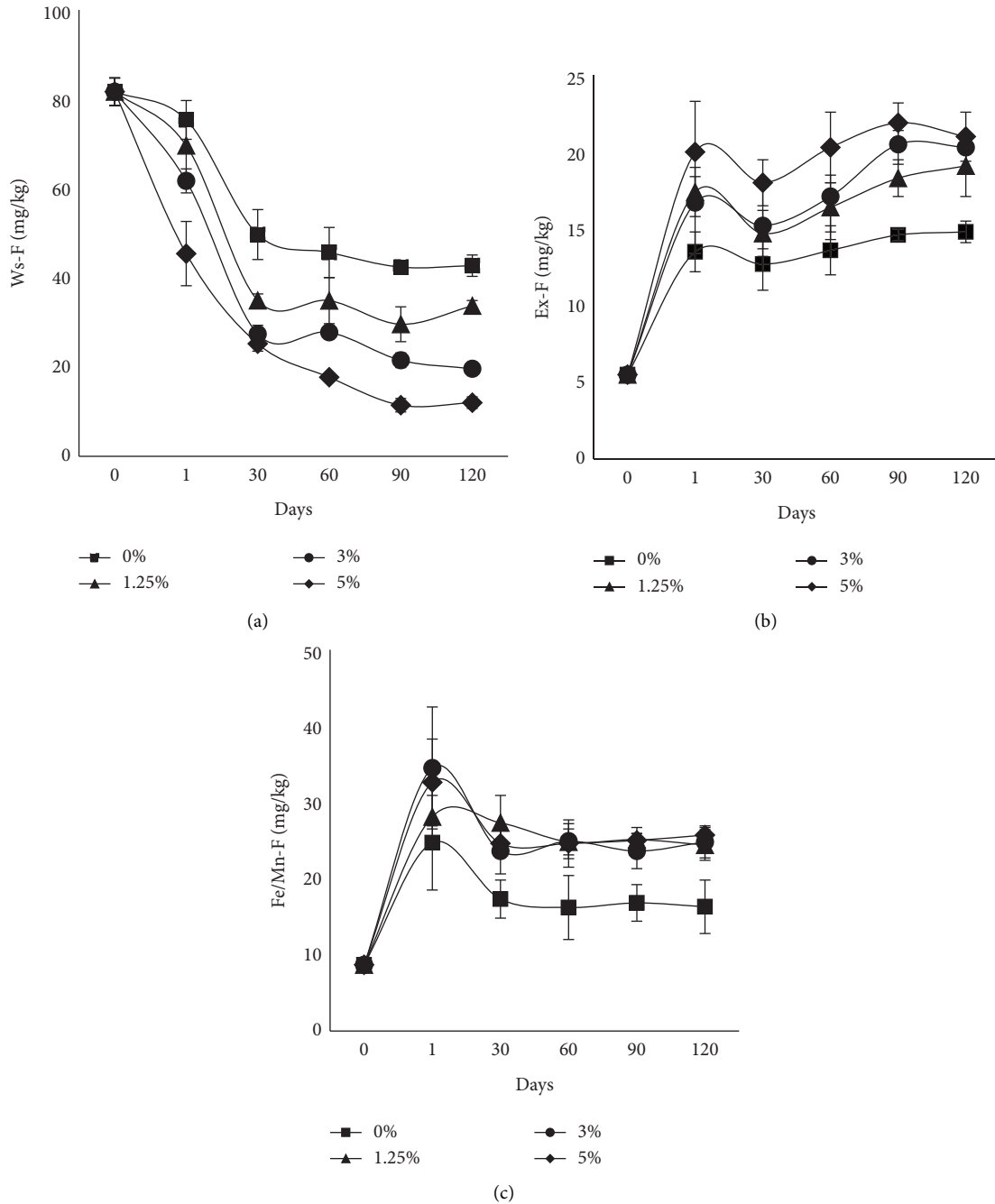
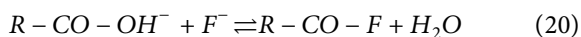
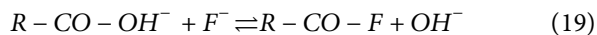


FIGURE 3: The impact of fermented seaweed (FSW) amendment on fluoride fractions of the soil (a) water soluble-fluoride (Ws-F), (b) exchangeable-fluoride (Ex-F), and (c) fluoride-bound to iron/manganese (Fe/Mn-F).

released  $\text{OH}^-$  increases. The increase in the  $\text{OH}^-$  further replaces the  $\text{F}^-$  until an equilibrium is established (Equation 19). But at neutral to low pH, the  $\text{H}^+$  reacts with the  $\text{OH}^-$  to form  $\text{H}_2\text{O}$  (Equation 20).



Both HMWOCs and LMWOCs act as binding sites for soil ions. Their binding capacity depends on their length,

linearity, flexibility, the number of  $-\text{OH}$  groups, and the number of acid groups ( $-\text{COOH}$ ) [29]. The binding capacity is also catalyzed by the multivalent ions in the soil which react with the negatively charged acidic functional groups of the organic acids creating a positively charged compound that further reacts with the clay. In both neutral and alkaline soils, the multivalent ions involved in these reactions are  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  [30]. Therefore, the organic compounds containing acid groups particularly the carboxylic groups ( $-\text{COOH}$ ) and hydroxyl groups ( $-\text{OH}$ ) participates in ionic binding with the multivalent cations which then participate



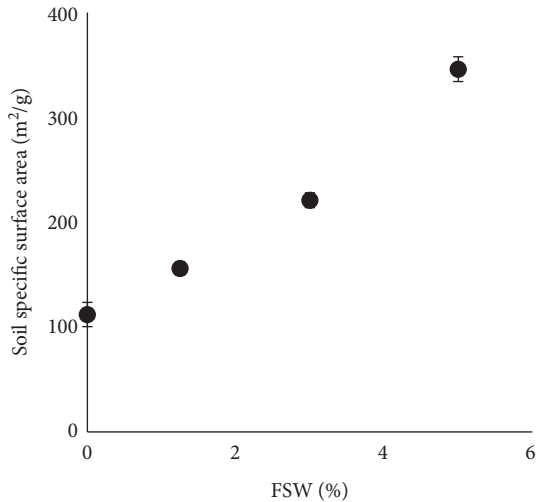


FIGURE 4: A scatter diagram showing a linear relationship between the FSW and the specific surface area of the soil at the 120th day.

in the ion exchange sites on clay or with anionic adsorption to positively charged clay sites at the edges (Equations (21)–(23)) [15, 29]. This could be a complex way through which fluoride is adsorbed into the organic compounds of the FSW introduced into the soil.

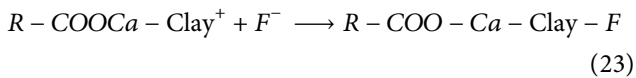
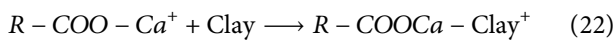
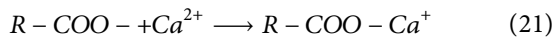


Figure 4 presents the influence of amendments on the specific surface area of the soil. The addition of FSW into the soil increased the specific surface area of the soil significantly ( $p < 0.05$ ) by 28.2, 49.3, and 67.6% succeeding 1.25, 3, and 5% amendment, respectively. Most of the fluoride ions in the soil are attached to the solid phase of the soil, therefore higher solid surface of the soil will likely hold more fluoride ions. The amendments increased the solid phase of the soil which provided the soil with an extra surface for fluoride ions to attach.

**3.5.2. The Indirect Impact of FSW on the Bioavailability of Fluoride in the Soil.** The FSW also acts indirectly through the alteration of the soil properties. Apart from binding with the soil ions, the application of FSW reduced the bioavailability of fluoride in the soil indirectly by converting most of the  $\text{Ws-F}$  to either  $\text{Ex-F}$ ,  $\text{Fe/Mn-F}$ , or  $\text{Res-F}$  and also through pH change. The FSW had an observable impact on the pH of the experimental soil. The pH was reduced from strong alkaline (pH  $9.3 \pm 0.0$ ) to  $7.8 \pm 0.1$ ,  $7.4 \pm 0.1$ , and  $7.0 \pm 0.0$  succeeding the amendments which is in contrast to the control samples upheld at pH  $8.9 \pm 0.3$ . The pH which remains an important soil property controls the soil's chemical reactions and the activity of soil microorganisms.

Among the chemical reactions' that pH controls, is the sorption and desorption of fluoride in the soil. At high pH, the fluoride attached to either clay particles, SOM, exchangeable bases, or other multivalent elements is easily replaced by the  $-\text{OH}$  ions accumulated on the soil solution interface. As the pH drops, the amount of  $-\text{OH}$  ions in the soil solution interface decreases reducing its competition with fluoride ions on the solid phase of the soil which results to more fluoride being held by the soil. The  $\text{Ex-F}$  is bound to the exchangeable bases ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$ , and  $\text{Na}^{+}$ ) in the soil which are sensitive to pH changes, whereas the  $\text{Fe/Mn-F}$  representing fluoride-bound to Fe, Mn, and aluminum (Al) exist in their stable forms (unreactive) at high pH and become reactive (unstable) as pH drops [20]. Therefore, as pH drops, they easily react with the soil's anionic species particularly fluoride which is strong electronegative.

**3.6. The Impact of FSW Amendment on the Bacteria, Fungi, and Actinomycetes in the Soil.** The soils treated with the FSW revealed significantly higher quantities of bacteria as compared to those found in the control group (Figure 5). The number of bacteria increased by a factor of  $1 \pm 7.2$ ,  $1.9 \pm 4.3$ ,  $3.0 \pm 9.0$ , for 1.25, 3, and 5% amendment dosage, respectively. The increase is equivalent to 47.4 and 66.7% increment. The addition of 5% FSW was also observed to increase the amount of fungus in the soil by a factor of  $1.6 \pm 9.9$ , whereas 3 and 1.25% amendments did not reveal a statistically significant difference to that of the control group. Furthermore, 3% FSW reduced the number of actinomycetes in the soil by a factor of  $1.3 \pm 8$ , and 5% FSW increased the number of actinomycetes by a factor of  $1.7 \pm 17$  and there was no significant difference on the impact of 1.25% amendment dosage to that of the control group. The increase in the number of bacteria, fungi, and actinomycetes was directly proportional to the amendment dosage. Gram stain was performed and the result obtained was Gram-positive rods in the chain for *Bacillus subtilis* was dominant.

The soil microorganisms play an important role in guaranteeing nutrient cycling for plants, preserving the soil quality, remediating, and stabilizing the general functioning of the soil system. The addition of FSW transformed the microbial structure of the soil by enhancement of the magnitude of bacteria, fungus, and actinomycetes. Studies have reported an increase in microbial quantities in the soil following the amendments. Wang et al. (2017) reported an increase of both bacteria and fungi resulting from seaweed fertilizer addition [13]. The results were later confirmed by another study investigating the response of soil microorganisms to seaweed fertilizer application [12]. Although our results are analogous to these studies, an increment in fungi and actinomycetes could only be observed at 5% FSW amendment but not for 1.25 and 3% amendments. Amending the soil with FSW promotes bacterial growth and diversity through modification of the moisture-holding capacity of the soil, supplementation of essential nutrients for microbial consumption, and adjusting the pH of the soil but the same factors could be the main reason for the

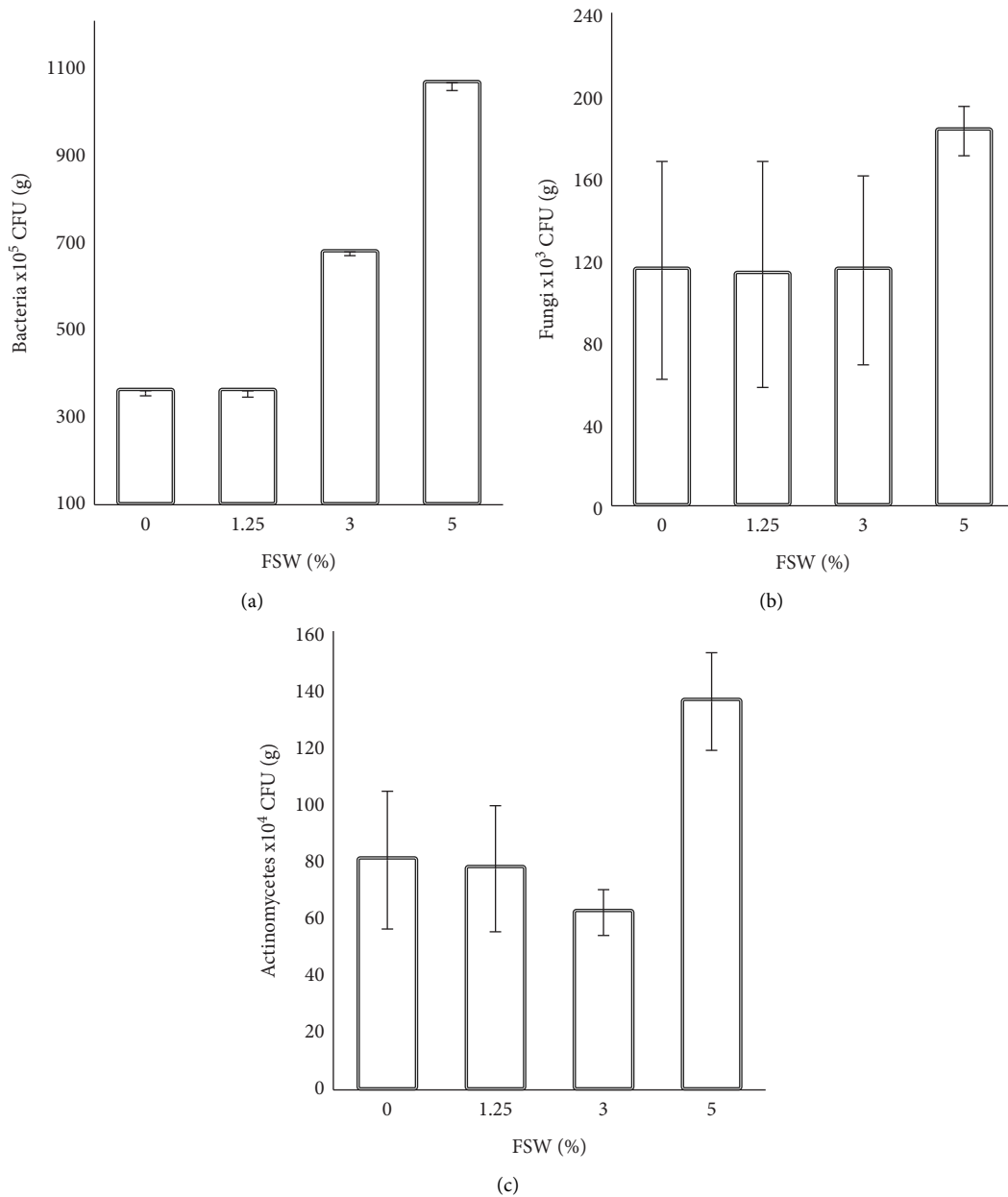


FIGURE 5: The impact of amendment of different concentrations of the fermented seaweed (FSW) on microbial quantity on the soil (a) bacteria, (b) fungi, and (c) actinomycetes.

increase and decrease in the number of fungi and actinomycetes observed.

#### 4. Conclusion

This study investigated the efficiency of fermented seaweed (FSW) on reducing the amount of bioavailable fluoride in the soil. The amendment reduced the amount of water soluble-fluoride (Ws-F) from  $81.7 \pm 3.1$  mg/kg to  $42.7 \pm 2.4$ ,  $33.7 \pm 1.2$ ,  $19.6 \pm 0.9$ , and  $12 \pm 1.3$  mg/kg following 0, 1.25, 3, and 5% amendment dosage, respectively. Fluoride adsorption fitted best with the Temkin model and the remaining Ws-F in the soil was converted into either exchangeable-fluoride (Ex-F) or fluoride-bound to iron and manganese (Fe/Mn-F). The application of FSW improved the water

absorption capacity, pH, microbial quantity, and nutrient retention of the soil. The study recommends to further investigate the impact of FSW application on crop germination and development.

#### Data Availability

The data used in this study are available from the corresponding author on request.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest whatsoever in publishing this article.

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