

Synthesis And Characterization Of Struvite By Aqueous Precipitation Using Wastewater And Hot Spring Water

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Abstract

Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a phosphate mineral that has recently become a prudent venture for many researchers due to its nutritional value to plants in the field of agriculture. The cost of production of this mineral heavily relies on the cost of the magnesium source used. In this study, hot spring water was investigated as a potentially cheaper natural source of magnesium ions while sewage wastewater was used as a source of phosphate and ammonium ions for the struvite synthesis. The synthesized struvite composite was then characterized using X-ray fluorescence (XRF), X-ray diffraction (XRD), and Scanning electron microscope (SEM). The precipitate purity and phosphorous recovery were analysed. XRF results showed that synthesized struvite majorly consisted of magnesium oxide and phosphorous oxide. XRD analysis showed the presence of orthorhombic crystalline phases between 4-9 degrees (2θ) with struvite peaks at 2θ values 15.8, 20.9 and 46.3 which matched struvite ICDD card information. SEM revealed irregular, crystalline, and rod-like morphological structures that were consistent with those identified in the literature. The synthesized composite contained a percentage purity of 68.61% and phosphorous recovery of 76.15%. The presence of phosphorous and nitrogen in the struvite which is plant macronutrients makes the composite potential fertilizer for agricultural applications.

Keywords: Characterization, Hot spring water, Struvite, Synthesis, Wastewater

Date of Submission: 16-07-2024

Date of Acceptance: 26-07-2024

I. Introduction

Struvite is a biogenic mineral with a solubility of 0.2 g/L in water and is composed of magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$)^[1] (Barak & Stafford, 2006). Its prevalence in various habitats and its usefulness as a resource have drawn a lot of interest. Struvite can be applied at high rates as a slow-release fertilizer without harming plant roots, and it is a very effective source of phosphorus, magnesium, and nitrogen for plants^{[2][3]}. The synthesis of magnesium ammonium phosphate hexahydrate (MAP), commonly referred to as struvite, has drawn a lot of attention in the last 10 years for the recovery of both nitrogen and phosphorus from wastewater effluents^[4]. This has created new opportunities to find more environmentally friendly ways to get phosphorus for agriculture than the existing practice of mining phosphorous rocks. Magnesium ions control the process of struvite formation and their quantity needs to be slightly above the stoichiometric amount for struvite crystals^[5]. Siciliano *et al.*^[6] observed that the commonly used artificial magnesium sources for struvite precipitation are magnesium oxide, magnesium hydroxide, magnesium sulphate, and magnesium chloride, which are expensive thus making the entire process costly. Brye *et al.*^[7] in their literature survey observed the use of natural sources of magnesium i.e. magnesite, bittern, seawater, and wood ash as they are cost-effective. Magnesite is a natural magnesium source containing 98% magnesium carbonate^[8]. It is a low-solubility mineral rock of high abundance in nature which requires pre-treatment by acids before being used. But despite lowering the cost of struvite production, it faces the disadvantage of leaving a carbon footprint causing environmental pollution. Sea water contains 146 kg/m³ of Mg²⁺ making it a potential magnesium source^[6]. A comparative study involving the use of seawater and magnesium chloride to precipitate struvite from urine has been done^[9]. Large crystals of struvite were produced when magnesium chloride was used compared to seawater. The latter also produced quality struvite of high purity while the former produced impure struvite because it had low ion activities^[10]. Bittern as a waste stream from brine production is another natural source of magnesium that has been used in the struvite precipitation process^[11]. Thus its availability relies on the brine production process. Struvite has been synthesized using different magnesium sources. However, these sources face different demerits which remain hindrances in the cost of the struvite precipitation process. Cheaper and readily available magnesium sources are therefore needed to lower the cost of production. A study done by Yoshiike^[12] in Japan revealed that hot spring water contains a substantial amount of magnesium. Therefore this study thrived to synthesize struvite composite using hot spring water from Lake Bogoria in Kenya as a source of magnesium and wastewater as a source of phosphate and ammonium ions.

II. Materials And Methods

Reagents and materials

All chemicals used in the synthesis were of analytical grade manufactured by Sigma Aldrich Company. 2M NaOH was used to raise the pH of the mixture, 2M HCl was used to lower the pH of the mixture, Distilled water, hot spring water as a source of magnesium, and sewage wastewater as a source of ammonium and phosphate ions.

Collection and pre-treatment of hot spring water and sewage wastewater

Hot spring water was obtained from Lake Bogoria, in Kenya, and transported to Kibabii University Chemistry laboratory, filtered, and then stored at 4°C in clean stoppered containers. Sewage wastewater was collected from the Kibabii sewage wastewater treatment plant located in Kibabii University, in Bungoma County, Kenya, filtered to remove solid suspensions, and then stored in clean stoppered plastic bottles at 4°C^[13] to prevent any further degradation.

Apparatus and Instrumentation

The apparatus used was an electromagnetic stirrer (79-1 Magnetic stirrer with hot plate- Griffchem) for uniform mixing of the mixture, a pH Meter (210 Benchtop pH/mV meter) to determine the pH of solutions, 0.45 µm Filter paper, Beakers, 250 mL Measuring cylinder, Thermometer, 500 mL conical flasks, stopwatch and 1000 mL Volumetric Flask apparatus. The instrumentations used were: UV-Vis spectrometer (UV-1650pc) used for phosphate analysis in wastewater and hot spring water, XRF (S1 Titan) used to determine the mineral composition of struvite, XRD (XRD, Rigaku Ltd, Japan) to determine the crystallinity of struvite, SEM (TESCAN Vega TC, Czech Republic) used to determine structural morphology of struvite, Discreet Analyzer (Thermo 200 Series) used in nitrogen content determination in wastewater and spring water. ICP- OES (Inductively coupled Atomic Plasma-ICAP) was used for magnesium content determination in hot spring water and wastewater and Micro-Kjeldahl for determination of nitrogen amount in struvite.

Determination of levels of magnesium ions in spring water and sewage wastewater

2.0 mL of concentrated nitric (V) acid and 1.0 mL of hydrogen peroxide were added to 5.0 mL of water sample. The mixture was then transferred into a Teflon vessel, closed, and placed into a microwave oven. A pressure of 35 bar was applied with a four-step digestion at temperatures indicated in Table 2.1.

Table 2.1: Digestion steps for samples for magnesium content determination.

Series	1	2	3	4
Temperature(°C)	100	160	180	100
Time(Minutes)	10	10	10	10
Transition time (Minutes)	5	3	3	3

The digested sample was transferred to a 50 mL volumetric flask and set to final volume using de-ionized water. Magnesium content was determined by the use of ICP-OES (Inductively coupled Atomic Plasma-ICAP).

Phosphate ion analysis in wastewater and hot spring water

10 mL of each sample was transferred to a 100 mL conical flask. The volume was then adjusted to 40 mL by dilution using distilled water. To the 40 mL, 4.0 mL of ammonium molybdate–sulphuric (VI) acid solution was added followed by 0.1g of ascorbic acid. This mixture was stirred and heated to boiling point for 1 minute, cooled, transferred to 50 mL calibration flask then set to final volume using de-ionized water. Finally, the absorbance of the mixture was read on the UV-vis spectrophotometer (UV-1650pc) at 820 nm. Blank test was performed on the reagents using distilled water as the sample.

Determination of amount of nitrogen in wastewater and spring water by colorimetric method

The sample was digested for 1.5 hours at 120°C using potassium persulphate in an autoclave to convert organic nitrogen to nitrates. Nitrate was then reduced to nitrite and quantified colorimetrically in a Discreet Analyzer (Thermo 200 series) using sulfanilamide- α -naphthyl-ethylenediamine dihydrochloride.

Synthesis of Struvite composite

The procedure was adopted from Sutiyono *et al.*^[14] with slight modification. 50 mL of wastewater was mixed with varied volumes of Hot spring water ranging from 10-120 mL to optimize the amount of Mg²⁺ ions required to synthesize the maximum yield of the struvite. In each series, the mixture's pH was adjusted using 2M

NaOH and 2M HCl to pH 10. The mixtures were then stirred at 200 rpm for 70 minutes at a temperature of 30°C and the precipitated deposit dried at room temperature for 48 hours before analysis.

Characterization of struvite

The struvite composite was characterized using X-ray fluorescence (S1 Titan) to determine the chemical composition [15], the Micro-Kjeldal method was used to determine total nitrogen content, Scanning Electron Microscope (TESCAN Vega TC, Czech Republic) was used to study the structural morphology of struvite and X-Ray Diffraction (XRD, Rigaku Ltd, Japan) to determine the crystallinity of the struvite composite.

Determination of purity of the struvite precipitate

The purity of the struvite precipitate recovered from the process was calculated using Equation 2.1 [16].

$$\text{Precipitate purity \%} = \left(\frac{\text{Mass of struvite in precipitate}}{\text{Total mass of precipitate}} \right) \times 100\% \dots\dots\dots 2.1$$

0.5g of struvite (total mass of the precipitate) was measured and analysed for phosphorus and magnesium using XRF analysis and ammonium ions content was determined by the Micro-Kjeldahl methods respectively. The mass of struvite in the precipitate was calculated from the results obtained.

Phosphorus Recovery

The phosphorous concentration was determined using the UV-Vis spectrometer model (UV-1650pc). Phosphate recovery percentage from struvite precipitation process was calculated from Equation 2.2 [10].

$$P \text{ recovery \%} = \left(\frac{P_{\text{initial}} - P_{\text{final}}}{P_{\text{initial}}} \right) \times 100\% \dots\dots\dots 2.2$$

The solution mixture which gave optimal yield was used to calculate the phosphorus recovery percentage.

III. Results And Discussions

Spring water and wastewater analysis for struvite ions

Determining the concentration of struvite ions (Magnesium, ammonium, and phosphate ions) for struvite synthesis was done in triplicate. The results in Table 3.1 show that spring water and wastewater contained 546.60±44.9 and 3.413±0.35 mg/L of Mg²⁺ respectively. The presence of Mg²⁺ in both wastewater and spring water made the two materials appropriate ingredients for synthesizing struvite composite. The high amount of Mg²⁺ ions in hot spring water could be a result of the surrounding rocks. The major cations such as Mg, generally originated from mother rocks of the hot spring [8].

Table 3.1: Spring water and wastewater composition

	Spring water Mean ±SD (mg/L)	Wastewater Mean ±SD (mg/L)
Mg ²⁺ ions	546.60 ± 44.9	3.413 ± 0.35
PO ₄ ³⁻	83.67 ± 16.13	237.60 ± 65.50
Total Nitrogen	74.40 ± 21.30	76.60 ± 16.51

The phosphorous concentration was determined using the UV-Vis spectrometer model (UV-1650pc). The method included two steps: the photo-oxidation of phosphorus to form orthophosphate ions, and their quantification by UV-visible spectrophotometry. The results in Table 3.1 show the amount of phosphates in spring water and wastewater studied were 83.67±16.13 and 237.60±65.50 mg/L respectively. The high levels of phosphates in wastewater could have resulted from human excreta and phosphorus-containing household detergents [17]. Both spring water and wastewater contain PO₄³⁻, which makes them suitable for struvite synthesis. The total nitrogen content was analysed colorimetrically. Total nitrogen concentrations of 74.40±21.30 and 76.60±16.51mg/L in hot spring water and wastewater respectively were observed. This wastewater contained notable nitrogen compounds making it a raw material for struvite synthesis [18]. The presence of nitrogen in spring water and wastewater makes them important resources for struvite synthesis.

Optimization of hot spring water in precipitation of struvite

The aqueous precipitation method was used to synthesize struvite for it is environmentally friendly and cost-effective [19]. The optimal conditions used were pH 10 and a temperature of 30°C to minimize the formation of other magnesium compounds which would have competed the struvite formation process [11]. Figure 3.1 shows the amount of struvite precipitated in relation to amount of magnesium and spring water used.

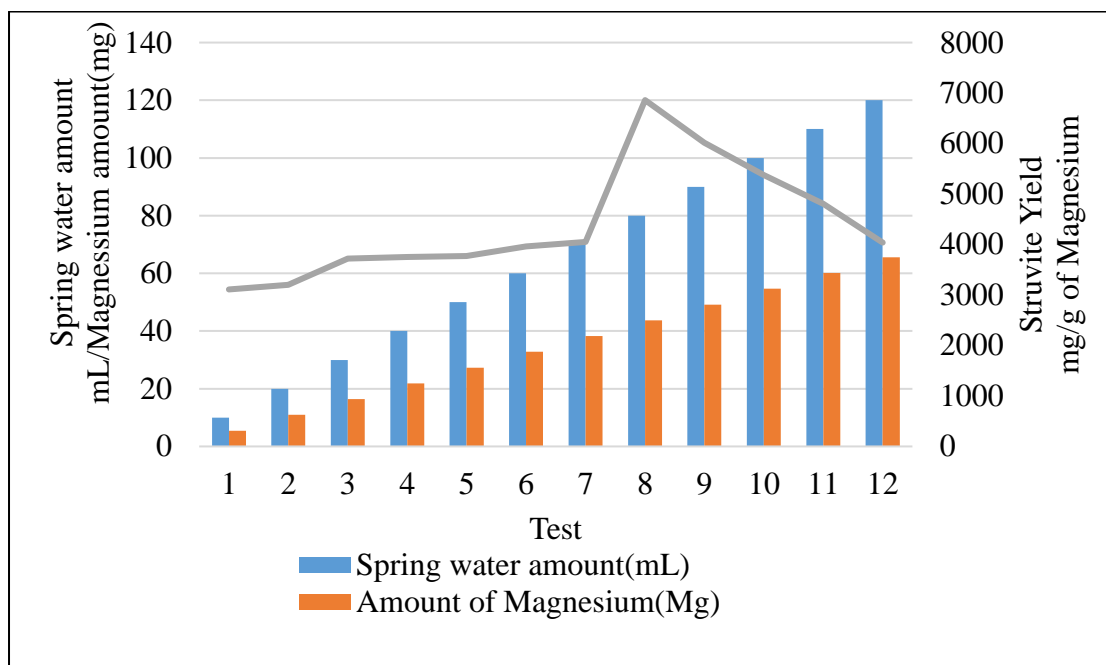


Figure 3.1: Struvite yield in relation to amount of magnesium and spring water used.

From Figure 3.1, it can be observed that the amount of magnesium increased drastically when the volume of spring water was varied from 10 mL to 120 mL. It can also be noted that struvite yield increased significantly with the addition of spring water from 10 mL to 80 mL to wastewater. The increase could be attributed to increased magnesium ion concentration which reduced the adhesion of the crystals on the walls of the reactor vessel [20]. This implied that magnesium ions concentration controls the struvite precipitation process i.e. more magnesium amount gives a larger amount of the struvite precipitate up to a certain limit [21]. A maximum struvite yield of 6860.6 mg/g of magnesium was noted when 80 mL of spring water was added to 50 mL of wastewater. But beyond 80 mL of spring water struvite yield decreased drastically because the excess magnesium would combine with non-struvite ions to form non-struvite compounds.

Chemical composition analysis of the struvite

This study used X-ray fluorescence (XRF) spectroscopy which is a widely recognized, highly reliable, and commonly utilized technique for ascertaining the primary elemental compositions of solid sample materials. Table 3.2 shows the percentage of chemical composition. The major composition identified from the struvite composite were MgO (70.94±2.793%), P₂O₅ (14.919±0.094%), S (2.737±0.043%), Cl (1.469±0.003%), K₂O (1.459±0.018%), CaO (6.212±0.027%) and Fe (1.381±0.010%).

Table 3.2: Analysis of struvite composite using XRF

Oxide/Element	Mean percentage composition Mean±SD (%)
MgO	70.94±2.793
P ₂ O ₅	14.919±0.094
S	2.737±0.043
Cl	1.469±0.003
K ₂ O	1.459±0.018
CaO	6.212±0.027
Ti	0.176±0.010
Mn	0.099±0.005
Fe	1.381±0.010
Cu	0.005±0.000
Zn	0.039±0.001
Sr	0.040±0.001
Y	0.020±0.001
Nb	0.013±0.001
Sn	0.478±0.056
Hg	0.159±0.000

From Table 3.2, it is clear that MgO and P₂O₅ dominated the composition of the struvite with 70.94% and 14.919% of the struvite precipitate respectively. These results are similar to those reported by Mavhungu *et al.* [22] where the dominant compounds were MgO and P₂O₅ with 32.40% and 40.14% respectively although their synthesized precipitate had a lesser percentage of magnesium oxide. Calcium amount was quite significant in this study because high concentrations of magnesium are usually accompanied by high amounts of calcium. The mineral contained 3.6% of ammonium ions amount as analysed by the micro Kjeldahl method because nitrogen being a low atomic number element could not be detected by the XRF analysis.

Results on purity of the struvite precipitate

The precipitate was found to have 3.6% ammonium ions (from Micro-Kjeldahl method), 42.564% magnesium ions (from XRF results), 13.238% phosphate ions (from XRF results), and 10.09% water of crystallization (from XRF results). From these results, the percentage purity of the struvite precipitate obtained was calculated as shown in Table 3.3 using equation 2.1.

Table 3.3: Precipitate purity

Total mass of struvite precipitate (g)	1.0
Mass of struvite in the precipitate (g)	0.6949
$Precipitate\ purity\ \% = \left(\frac{Mass\ of\ struvite\ in\ precipitate}{Total\ mass\ of\ precipitate} \right) \times 100\%$	69.49%.

It could be seen that the purity of the precipitate was lower because magnesium ions were used in excess thus introducing more foreign ions in form of impurities [23].

Phosphorus Recovery

The amount of phosphorus recovered was calculated using Equation 2.1. During struvite synthesis, 50 mL wastewater and 80 mL of hot spring water gave optimal yield of struvite. P(initial) and P(final) were 202.7 mg/L (initial phosphate concentration of 50 mL of wastewater) and 48.35 mg/L (final phosphate concentration of filtrate after adding 80 mL of spring water to 50mL of wastewater) respectively. A percentage of 76.15 phosphorous recovery was achieved. The recovery was effective for the percentage was above 65% [10].

SEM analysis of the struvite composite

The morphological properties of the prepared material were examined using SEM (model TESCAN Vega TC, Czech Republic). Figure 3.2 shows the morphological properties of the synthesized material.

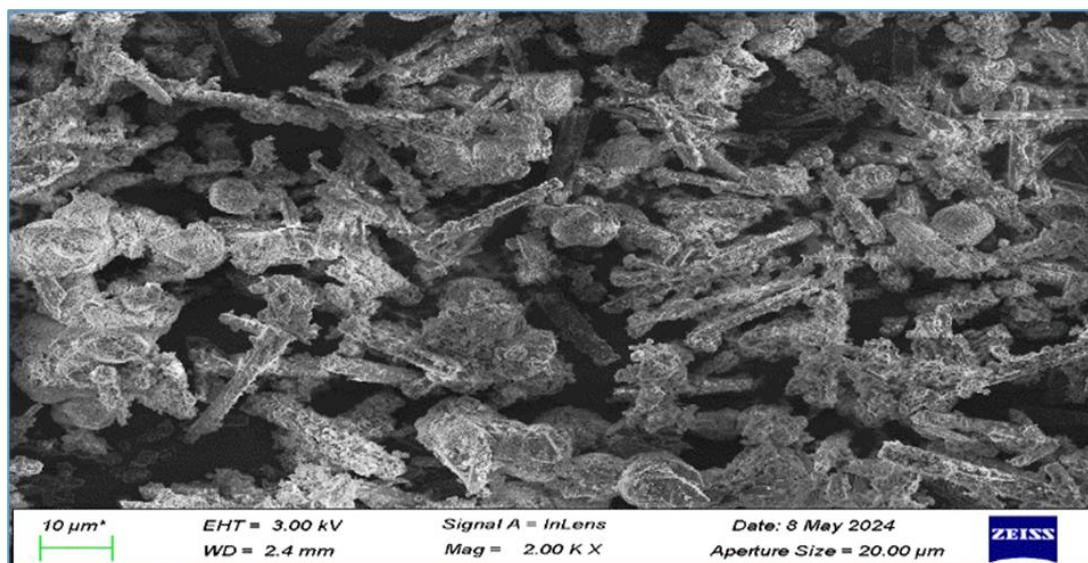


Figure 3.2: SEM micrographs of prepared material) at Magnification 2.00kx

The micrographs revealed rod-like, prismatic elongated irregular crystal structures at magnifications of 2.00kx. These morphologies are in tandem with those reported by Bouropoulos *et al.* [24] where struvite was presented as rod-like elongated prismatic crystals.

XRD analysis of struvite

The amorphous and crystal phases of the struvite samples were qualitatively determined using the X-ray Diffraction method. The crystal structure of the prepared material was assigned to orthorhombic crystal by the ICDD card number 01-090-2334 with a space group of Pmn21. Figure 3.3 represents the diffractogram of the synthesized material.

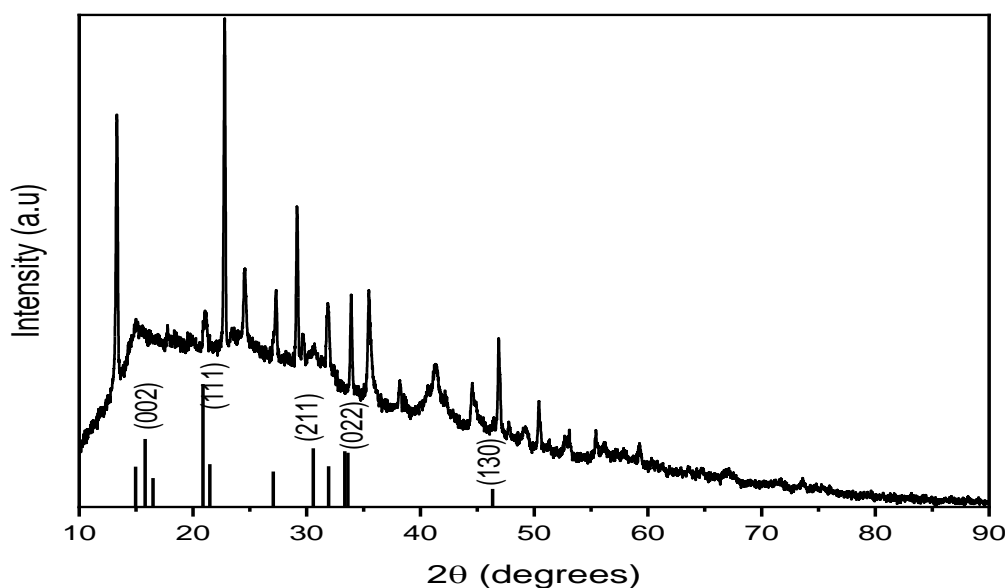


Figure 3.3: XRD diffractogram of the struvite composite

From Figure 3.3, the intensity of the material is plotted along the ordinate with 2θ being on the abscissa. The angle 2θ values ranged between 4-90 degrees. Various crystalline phases were observed at angles (215.8, 20.9, and 33.4 representing struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) crystalline phases [25]. XRD revealed that struvite dominated the composite under optimal conditions during the synthesis process. The peaks at angle (2θ) 30.6 and 46.3 represented dolomite ($\text{CaMg}(\text{CO}_3)_2$) and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) crystalline phases respectively. The presence of these phases could have been attributed to the presence of Ca^{2+} , Mg^{2+} , CO_3^{2-} and PO_4^{3-} in spring water which combined to form the compounds [26]. The struvite composite had a crystal size of 12.321 μm which was obtained using the Scherrer formula. The Sharp peaks observed revealed the crystallinity of the synthesized material. Because of this, the material was considered to be crystalline.

IV. Conclusions

This study has shown that the precipitation of struvite from hot spring water as a source of magnesium ions and sewage wastewater as a source of ammonium and phosphate ions was viable at pH of 10 and a temperature of 300C. XRF analysis confirmed the dominance of magnesium and phosphorous in the material and Micro-Kjeldahl method revealed a significant amount of nitrogen in the precipitate. SEM analysis revealed rod-like needle shaped morphological properties which were similar to those obtained in literature. XRD results revealed that the prepared material was struvite as the processed information matched the information on the struvite ICDD card. The struvite percentage purity of 68.61% was achieved. The use of hot spring water led to 76.15% phosphorous recovery from wastewater in the form of struvite. The presence of nitrogen and phosphorous which are key primary macronutrients and magnesium which is a secondary macronutrient makes the struvite composite a potential inorganic fertilizer.

Credit author statement

Edith Nasambu: Writing - original draft, Writing- Reviewing and Editing, Francis Maingi: Conceptualization, methodology review & editing, Supervision, Linda Ouma: Conceptualization; methodology, review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.