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Research Article

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# Fluoride Sorption Using Zirconium ion-impregnated Macadamia Nutshell-Derived Biochar from Aqueous Solution: Adsorption Isotherms and Kinetic Modeling

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# Abstract

Zirconium ion-impregnated macadamia nutshell biochar (ZMNB) was synthesized and tested for its fluoride sorption capacity by exploiting batch experiments. Four temperatures (300, 400, 500, and 600 °C) were used to pyrolyze the macadamia nutshells to yield macadamia nutshell biochar (MNB) which was separately impregnated with Zr (IV) aqueous solution. Both non-modified and chemically modified MNB were assessed by X-ray diffraction (XRD), attenuated total reflection Fourier Transform Infra-red (ATR-FTIR), field emission scanning electron microscope-energy dispersive X-ray (FESEM-EDS), thermogravimetric analysis, and Brunauer-Emmett-Teller (BET) surface area analyzer. The sequence of F<sup>-</sup> adsorption capacities for the synthesized biosorbents was ZMNB 300 > ZMNB 400 > ZMNB 500 > ZMNB 600, which revealed the influence of pyrolysis temperature on sorption process. ZMNB 300 had a maximum percentage fluoride removal effectiveness of 99.05% using 1.0 g L<sup>-1</sup> adsorbent lot, at neutral pH for an interaction period of 1 h. The adsorption studies suited perfectly with the pseudo-second-order kinetic model and the linear Langmuir isotherm, affirming a chemisorption process. Thermodynamic studies revealed that the calculated  $\Delta G^\circ$  value (-5.593 kJ mol<sup>-1</sup>) ascribed the rapidity and spontaneity of the sorption action,  $\Delta H^\circ$  value (30.102 kJ mol<sup>-1</sup>) elucidated the endothermic, irreversible and chemisorption process whereas the  $\Delta S^\circ$  value (118.55 J mol<sup>-1</sup> K<sup>-1</sup>) signified the F<sup>-</sup> adsorption's random trait on the solid or liquid interface of the ZMNB 300. Results from the sorption experiments using fluoride-contaminated natural water removed the F<sup>-</sup> ions below the curbed WHO standard (1.5 mg L<sup>-1</sup>) for drinking water and therefore, a potential material for practical applications.

## 1. Introduction

Globally, there is a significant water quality issue with fluoride pollution in groundwater. Fluoride makes up 0.08% of the Earth's crust and it's also the 13th top-tier affluent species [1]. It naturally leaches traces of F<sup>-</sup> ions from its containing minerals under favorable conditions into the groundwater. In addition, anthropogenic sources like industrial discharge with fluoride-containing substances contaminate surface water [2]. These sources expose human bodies to F<sup>-</sup> accumulation through food and water consumption [3], hence endangering human health. Therefore, high fluoride concentration in drinking water warrants its decontamination due to its profound environmental problems that causes irreversible health effects on humans. Water for domestic use has been limited to 1.5 mg L<sup>-1</sup> by WHO for its safe consumption by human and animals [4] beyond which it may result into health issues in humans and animals. Whilst fluoride plays a beneficial role in the proper enamel and bone formation in children at low amounts (0.5 to 1.5 mg L<sup>-1</sup>) [5], it, however, causes detrimental health effects to humans when persistently consumed for a long time at various elevated concentrations [6, 7]. In addition, excessive exposure to F<sup>-</sup> can lead to non-fluorosis effects in humans such as thyroid gland function interference, osteoporosis, nervous system, kidney, endocrine disruptor, insulin resistance in diabetic patients, [1], structural changes, growth retardation, children's intelligent quotient reduction, and death allied cases if ingested at concentrations > 250 mg L<sup>-1</sup> over an extended duration [8, 9].

Globally, approximately 300 million humans in 30 countries consume fluoride-containing water with levels exceeding  $1.5 \text{ mg L}^{-1}$  [10]. Majority of this human population are mostly found in the five classified global fluoride belts [1, 11]. The East African Rift Valley (EARV) is amongst these clustered belts within which countries like Ethiopia, Kenya, Tanzania, and Eritrea have been associated with highly prevalent cases of endemic fluorosis [8]. The EARV hosts an estimated 80 million people out of which, 90% of the population have been exposed to a wide range of fluorosis [8, 12]. In Tanzania, fluorosis, particularly crippling and skeletal fluorosis, is a surging disease burden at the community level in several regions like Arusha, Manyara, Singida, Mara, Mwanza, and Shinyanga regions [8, 13]. As a result, sustainable and economical water defluoridation methods are of great essence to prevent vulnerable communities mostly in developing countries from the fluorosis pandemic as part of sustainable development goals (SDGs) for the provision of safe and clean drinking for all.

Substantial studies on water treatment technologies have been advanced in recent decades to combat the health effects prompted by the consumption of water contaminated with fluoride. This includes conventional methods of water treatment like chemical precipitation [14], adsorption [15, 16], ion exchange [17], membrane filtration [18], electrodialysis [19], and reverse osmosis [20]. Adsorption is the most extensively used of these techniques owing to its ease of design and operation, minimal maintenance requirements, reliability, affordability and accessibility of a broad range of adsorbents [21–23]. Other techniques afore mentioned are expensive in terms of operational and maintenance costs, unreliable, energy-demanding, and inefficient in extracting fluoride at low concentrations [24]. In recent times, the research community has been drawn to the use of biosorbents for water treatment owing to their affordability, ease of availability, effectiveness, efficiency, recyclability, and non-toxic nature as compared to synthetic materials which demand high-cost design requirements and potential toxicity [25]. In addition, biosorbents harbor on their surfaces specific functional groups like amino, carbonyl, hydroxyl, thiol, and carboxyl groups which greatly influence the biosorption process [26, 27].

This study aimed to synthesize a novel biosorbent material for drinking water defluoridation by impregnating zirconium ion with macadamia nutshell biochar and to test its fluoride adsorption capacity using batch adsorption experiments. Furthermore, this study sought to understand the contribution of Zr (IV) impregnation of MNB through characterization analyses, effect of varying pyrolysis temperatures on MNB, influence of different optimized parameters, and to analyze the adsorption isotherms and kinetics reaction modelling on the fluoride removal capacity by ZMNB biosorbents.

## 2. Materials And Methods

### 2.1 Materials

High purity chemicals and reagents were procured and double distilled water was used in preparing all aqueous solutions for carrying out experimental analyses. Chemicals included sodium nitrate ( $\text{NaNO}_3$ ), zirconium oxychloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ), sodium chloride ( $\text{NaCl}$ ), sodium fluoride ( $\text{NaF}$ ), sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), glacial acetic acid ( $\text{CH}_2\text{COOH}$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), 1,2-cyclohexanedinitro-

tetraacetic acid (CDTA), sodium bicarbonate ( $\text{NaHCO}_3$ ), sodium hydroxide ( $\text{NaOH}$ ), and hydrochloric acid ( $\text{HCl}$ ). Macadamia nutshell wastes were collected from the Lushoto missionary farm in Sakarani in Tanga region, Tanzania.

## 2.2 Preparation of ZMNB adsorbent

To get rid and other exogenous substances, macadamia nutshells (MNS) were repeatedly washed rigorously using flowing tap water and thereafter rinsed using deionized water and dehydrated at  $110\text{ }^\circ\text{C}$  for 48 h in an oven. The dehydrated MNS was ground up and sieved with screen size of 0.15 mm and then pyrolyzed using a tube furnace (CTF 12/65/550) at four varying temperatures i.e.,  $300\text{ }^\circ\text{C}$ ,  $400\text{ }^\circ\text{C}$ ,  $500\text{ }^\circ\text{C}$  and  $600\text{ }^\circ\text{C}$  for 2 h with fixed ramping temperature of  $10\text{ min}^{-1}$  under a steady flow of nitrogen gas ( $100\text{ cm}^3\text{ min}^{-1}$ ). Elevated pyrolysis temperatures ( $400\text{--}700\text{ }^\circ\text{C}$ ) of biomass instils to its resulting activated carbon high adsorption capacities [28]. Thereafter, 150 mL of 0.1 M  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  with an adjusted pH of between 4.0–5.0 was used to impregnate 10 g of MNB, which was magnetically agitated at 200 rpm for 24 h at  $25 \pm 1\text{ }^\circ\text{C}$ . Centrifugation process ensued and the resulting residue was washed numerous times with deionized water to oust unabsorbed fractions of Zr (IV) ions and finally kept overnight in an oven at  $80\text{ }^\circ\text{C}$ . The dehydrated sorbent material was pulverized and sifted to attain fragment size of  $150\text{ }\mu\text{m}$  then named ZMNB-X, where x refers to the pyrolysis temperature and finally kept in air-tight plastic vessel for further analysis.

## Batch adsorption studies

Equilibrium and kinetic investigations were performed by blending together predetermined quantities (0.2–1 g) of the synthesized the ZMNB biosorbent materials with 100 mL of  $10\text{ mg L}^{-1}$  in 250 mL flask and stirred at 200 rpm for 1 h. The suspended sorbent materials were centrifuged immediately after the sorption duration elapsed and the resulting residual  $\text{F}^{-1}$  ion solution was combined with a total ionic strength adjustment buffer (TISAB II) in a 1:1 ratio and measured in triplicates using Ion-Selective Electrode (ISE). Further investigations were done at optimized conditions with the variation of parameters like temperature, adsorbent's exposure time, interfering ions, pH, adsorbent dose, and initial fluoride concentration to establish the ZMNB's biosorbent optimum water defluoridation efficiency and capacity. Moreover, equilibrium adsorption data were subjected to modelling analyses through the application of the Freundlich, Langmuir, Dubinin-Radushkevich (D-R) and Temkin isotherm models whereas the chemical kinetics were modelled by the Lagergren's pseudo-first-order (PFO), pseudo-second-order (PSO) kinetics, and intra-particle diffusion models.

## 2.4 Adsorbent characterization of ZMNB

Chemically modified and non-chemically modified MNB were characterized to ascertain the nature of their chemical composition, functional groups, surface morphology, elemental composition, and crystallinity. Surface structural plus elemental composition of MNB, ZMNB and FZMNB that were pyrolyzed at varying temperatures were delineated using field emission scanning electron microscope-energy with in-built energy dispersive X-ray (FESEM-EDS), attenuated total reflectance Fourier infrared

spectrometer (ATR-FTIR; Bruker Optic GmbH 2011 model was used to establish the main surface functional groups at wavelengths between  $4000 - 400 \text{ cm}^{-1}$  using spectral resolution of  $2 \text{ cm}^{-1}$ . XRD spectrometer (Bruker BV 2D PHASER Best Benchtop model with Cu K $\alpha$  radiation ( $\lambda = 0.15406$ ) at 50 kV and 30 Ma with reflection geometry at  $2\theta$  was used to analyze the crystallinity or amorphous nature of the sorbent material. Nitrogen adsorption-desorption isotherms were generated with the use of a nitrogen adsorption apparatus (TriStar II 3020 gadget) at 77 K with 0.01-1.0 relative pressure range (P/Po) to measure the adsorbents' pore volume and specific surface area via BET method. Porosity and distribution of pore sizes was estimated by applying the Barnett-Joyner-Halenda (BJH) procedure. The stability of raw the macadamia nutshell powder was established using a thermogravimetric analyzer (PerkinElmer STA 600 simultaneous thermal analyzer) under inert conditions by supplying N $_2$  gas at a  $20 \text{ mL min}^{-1}$  flow speed, 3.2 bar pressure and a heating frequency of  $10 \text{ }^\circ\text{C min}^{-1}$  from 0–900  $^\circ\text{C}$ . Finally, the solid addition approach was utilized to analyze the point of zero charge (pHpzc) for the ZMNB biosorbents as previously reported in other studies [29].

- **Results and discussion**

- **Spectral studies**

Figure 1a illustrates the FT-IR spectra for the functional groups present on the MNB 300, ZMNB 300 and FZMNB 300 biosorbents were analyzed by FTIR spectrometer. The broad peaks on the biosorbents around  $3435 \text{ cm}^{-1}$ ,  $3365 \text{ cm}^{-1}$  and  $3483 \text{ cm}^{-1}$  elucidated the O-H stretch that are characteristic of the hydroxyl functional group [30]. The broad and small peaks at  $2924 \text{ cm}^{-1}$  on MNB 300 and ZMNB 300 indicated the stretching vibrations of  $-\text{CH}_2$  [31]. The peaks placed at  $1510 \text{ cm}^{-1}$  and  $1595 \text{ cm}^{-1}$  elucidated C = C stretching for lignin's aromatic components [32]. The peaks that appeared at  $1696 \text{ cm}^{-1}$  and  $1711 \text{ cm}^{-1}$  constituted C = O stretching from the  $-\text{COOH}$  bond whereas the  $1010 \text{ cm}^{-1}$  and  $674 \text{ cm}^{-1}$  peaks represented Zr-O and Zr-OH respectively. The XRD spectra for the ZMNB 300 and FZMNB 300 biosorbents illustrated in Fig. 1b exhibited peaks near  $2\theta = 21.7045$  and  $41.0671$  indicated the existence of large amounts of amorphous carbon with similar results supported in literature [33]. The amorphous characteristics of the peaks lacked a definite crystallographic pattern as observed in studies by [34, 35] whereas similar non-crystallographic observations were reported using carbonaceous materials [10, 36].

## 3.2 SEM analysis

Figure 2 (a, b, c) exhibited non-modified MNB, Zr-loaded MNB, and fluoride-loaded ZMNB biosorbents structural morphologies that were analyzed using FESEM. The SEM micrograph for the non-modified MNB in Fig. 2a exhibited flaky-like structures accompanied by varying large-sized-pores with particles characteristic of biochar of plant biomass [37]. The SEM image for the Zr-loaded MNB 300 adsorbent in Fig. 2b exhibited spherical agglomerated particles whereas Fig. 2c illustrated an increased agglomeration of particles by Zr-loaded MNB 300 biosorbent after adsorbing fluoride. The increased agglomeration may be owed to the hydrogen bonding between the adsorbed F $^-$  and the adsorbent loaded with Zr (IV) which

showed a similar observation made by [38]. The corresponding EDX spectra with its inset description of their percentage elemental weight composition analyzed are illustrated in Fig. 2. (d, e, and f). Presence of O, Mg, Ca, Si, Fe, S and K with varying percentage weight compositions was evident in the EDX spectra for MNB 300, ZMNB 300 and FZMNB 300. The C peaks were not captured in EDX spectra because the chemically modified biochar was coated with graphite prior to its analysis. The non-modified MNB 300 exhibited a small percentage weight of Zr which its peak concentration may have resulted from the uptake of the geogenic zirconium present in the Earth's crust by the macadamia plant [39]. However, the Zr percentage weight composition increased as a result of impregnation of MNB 300 with Zr (IV) aqueous solution forming ZMNB 300 which further adsorbed the  $F^-$  ions onto its surface yielding F adsorption peaks as evidenced in Fig. 2f. After the  $F^-$  adsorption, the elemental oxygen concentration was reduced whereas the Ca adsorption peaks disappeared may be due to the formation of  $CaF_2$  as illustrated in Fig. 2 (d, e, and f), with a similar case reported by [40]. Macadamia nuts has substantial amount of Fe [41] which was exhibited in all the EDX spectra with decreased percentage weight composition after  $F^-$  adsorption (Fig. 2f) due to the affinity of Fe towards fluoride ions.

### 3.3 Thermo-gravimetric analysis (TGA/DTA)

In order to assess a material's thermal stability, TGA/DTA study is essential. Figure 3. depicted the TGA/DTA thermograms for MNS powder. The dehydration of physically and chemically adsorbed water molecules and volatile compounds is represented by the temperature range of 20 to 210 °C by the TGA curve and the associated endothermic peak for the DTA curve. The weight loss at 210 °C to 380 °C may be attributed to the degradation of hemicellulose, pectin and cellulose as well as the volatilization of volatile substances like  $H_2$ , CO,  $CH_4$ , and  $CO_2$  [42, 43].

### 3.4 Effect of pore size and BET isotherm

Figure 4a-d depicted how  $N_2$  adsorption-desorption isotherms plus pore size distribution affected the performance for the ZMNB 300 and FZMNB 300 biosorbents. The BET isotherm curve for FZMNB 300 depicted a typical monolayer sorption pattern of the fluoride ions onto the ZMNB 300 with similar findings reported by [44]. This was further supported by the Langmuir isotherm modelling results that depicted a monolayer distribution of the fluoride ions onto the biosorbents. Moreover, the isotherms were also characteristic of microporous substances with relatively paltry surfaces with limited adsorption [45]. Table 1. indicated very small pore volume and surface area of the synthesized biosorbents ( $0.003-0.027$  cc  $g^{-1}$ ) and  $1.248-29.239$  m<sup>2</sup>  $g^{-1}$ ) respectively. Additionally, the pore sizes were not significantly varied as their pore diameters ranged from 1.385 to 1.614 nm. A sorbent material with pore diameter < 2 nm is classified to be microporous in nature as categorized by the International Union of Pure and Applied Chemistry (IUPAC) [44]. The non-modified MNB 300 biosorbent possessed small surface area of  $1.248$  m<sup>2</sup>  $g^{-1}$  roughly 8 times smaller than that of ZMNB 300 biosorbent which exhibited a surface area of  $9.907$  m<sup>2</sup>  $g^{-1}$ . Moreover, sorption of fluoride onto the ZMNB 300 surface further increased the surface area to  $29.239$  m<sup>2</sup>  $g^{-1}$  which is around 23 times that of the MNB 300. This may infer that the chemical activation

of MNB with Zr (IV) might have contributed significantly to the increased surface area which further translated into higher F<sup>-</sup> adsorption capacity as shown in Fig. 6.

Table 1  
Morphological features for MNB, ZMNB and FZMNB

Adsorbent	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore size (nm)	Pore volume (cc g <sup>-1</sup> )
MNB 300	1.248	1.385	0.003
ZMNB 300	9.907	1.548	0.010
FZMNB 300	29.239	1.614	0.027
<b>3.5 Batch adsorption studies</b>			

### 3.5.1. Effect of solution pH

The initial pH of a solution considerably affects adsorption processes [46]. An initial fluoride solution with varied pH interval range of 2 (pH 1–11) was used to investigate the impact of solution's pH on F<sup>-</sup> removal efficiency. Figure 5a showed maximum percentage fluoride removal efficiencies of 98.7%, 97.8% and 98.4% at pH 3 by ZMNB 300, ZMNB 400 and ZMNB 500 biosorbents respectively. Similar trends were observed on zirconium impregnated cashew nut shell carbon [47]. Additionally, it was also shown that at PH > 7.0, F<sup>-</sup> adsorption reduced significantly. At pH 11, percentage fluoride removal by ZMNB 300, ZMNB 400 and ZMNB 500 adsorbents were 0.5%, 6.8% and 5% respectively as a result of the extra OH<sup>-</sup> ions battling with F<sup>-</sup> ions for the adsorbents' active spheres thus reducing the F<sup>-</sup> ions' ability to be adsorbed onto ZMNB's biosorbent surface. [48]. Additionally, Fig. 5b illustrated the pH values for the MNB 300 and ZMNB 300 at the point of zero charge (pHpzc), were revealed as 6.8 and 3.2 respectively. This implied that the MNB 300 and ZMNB 300 adsorbents produced more positive charged sites on the adsorbent when protonated in solutions at pH < 6.8 and < 3.2 respectively thus increasing the fluoride removal efficiencies.

### 3.5.2 Influence of adsorbent dosage and pyrolysis temperature

The varying ZMNB 300 dosages (0.2–1.0 g L<sup>-1</sup>) were utilized to acquire the most favorable dose for fluoride removal efficiency at fixed adsorption conditions like neutral pH, 10 mg L<sup>-1</sup> initial fluoride solution, and 200 rpm stirring for 60 min. Figure 6a illustrated that the ZMNB 300 had an excellent percentage fluoride removal efficiency of 99.06% and 99.5% using adsorbent doses of 0.2 g L<sup>-1</sup> and 1.0 g L<sup>-1</sup> correspondingly. However, Fig. 6b exhibited that ZMNB 400, ZMNB 500 and ZMNB 600 attained 63.2%, 48.5% and 36.9% fluoride removal efficiencies respectively using 0.2 g L<sup>-1</sup> dosage. The curves for ZMNB 400 and ZMNB 500 biosorbents flattened with the use of 0.4 g L<sup>-1</sup> dosage while that of ZMNB 600 biosorbent flattened with the use of 0.6 g L<sup>-1</sup> dose. Decomposition of vital functional groups might



have resulted the differences in the adsorption efficiencies of the ZMNB biosorbents as a result of the increased pyrolysis temperatures hence hindering the anchoring of the Zr (IV) ions onto the biosorbents surface. Furthermore, the analysis depicted that the active adsorption sites for fluoride uptake exacerbated with the dosage increment, which caused the percentages of fluoride adsorption to steadily increase, a similar trend reported elsewhere [49]. Research has shown that biochar that has been pyrolyzed at 300 to 400 °C contains O-containing functional groups like phenolic -OH, -COOH, and -OH that exhibit hydrophobicity, hydrophilicity or buffer acid-base ability and may significantly contribute to elevate anion exchange magnitude [50]. In contrast, biochar achieved by biomass pyrolysis at 500 to 1000 °C contain ash content with high thermal stability, but bear less hydrogen and oxygen containing functional groups with declined ion exchange capacity owing to biomass deoxygenation and dehydration [51].

### 3.5.3 Effect of contact time

Experimental verification on the influence of adsorbents' exposure period was done to ascertain the removal efficiency of the ZMNB 300, ZMNB 400 and ZMNB 500 biosorbents. The impact of contact periods of 5, 10, 15, 20, 30, 40, 50 and 60 min were investigated using 100 mL of 10 mg L<sup>-1</sup> F<sup>-</sup> ion solution with neutral pH, 0.2 g biosorbent dose with 200 rpm stirring for 1 h at 25 ± 2 °C. From Fig. 7a, all the three biosorbents reached adsorption equilibrium concentration after 20 min. ZMNB 300 and ZMNB 400 biosorbents performed well within 1 min of fluoride adsorption with a percentage removal of 74.5% and 71.7% respectively as compared to 59.4% for ZMNB 500. In addition, the ZMNB 300 and ZMNB 400 biosorbents exhibited a rapid increase in their initial sorption capacity inside 10 min of the adsorption process. This may be substantiated by the biosorbents' greater surface area and more adsorptive zones on the biosorbents in the early phases of the adsorption process [40]. After the 10 min-mark, the removal efficiency gradually increased up to 20 min beyond which the curve flattened signifying that the adsorption equilibrium concentration had been established. At the 60 min-mark, the ZMNB 300, ZMNB 400 and ZMNB 500 biosorbents achieved a percentage removal efficiency of 98.9%, 98.4% and 96.8% respectively. The findings showed that as the adsorbent dosages were increased, the amount (%) of fluoride ions that were removed increased. Similar findings were reported using chemically activated cotton nutshells carbon for drinking water defluoridation [26].

Figure 7. Influence of a) adsorbent's contact time and b) initial fluoride concentration on the adsorbents' defluoridation efficiencies

### 3.5.4 Influence of initial fluoride ion concentration

To assess the impact of initial fluoride ion concentration, varying volumes (5 to 30 mg L<sup>-1</sup>) were used to ascertain the fluoride removal efficiencies on the ZMNB biosorbents. A measured volume of 100 ml of fluoride ion solution, 0.2 g L<sup>-1</sup> adsorbent dose, temperature (25 ± 1 °C), neutral pH, and exposure period of 60 min with agitation at 200 rpm were utilized as fixed experimental conditions. Figure 7b illustrated that the ZMNB 300 and ZMNB 400 biosorbents had a higher fluoride removal efficiency between 5 mg L<sup>-1</sup>

$1 - 20 \text{ mg L}^{-1}$  whereas that of ZMNB 500 performed well up to  $15 \text{ mg L}^{-1}$  however, all of them registered low adsorption capacities above  $25 \text{ mg L}^{-1}$   $\text{F}^-$  ion solution. Decline in removal efficiency of fluoride with enhanced initial  $\text{F}^-$  ion concentration may be ascribed to great access to abundant active adsorptive sites on the biosorbent by solutions with low initial fluoride ion concentration as compared to the ones with high fluoride concentrations. A similar trend was observed using rice husk coated with iron oxyhydroxide to remove fluoride as reported by [35].

### 3.5.5 Effect of interfering ions

Natural waters are prone to have a variety of co-existing negatively charged ions that might hinder with the adsorption process of  $\text{F}^-$  ions. Fluoride ions compete with co-existing ions like  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  during adsorption process. Fig. depicted that all the ZMNB biosorbents were interfered with by the stated co-existing anions in the following order:  $\text{CO}_3^{2-} > \text{NO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ . However, fluoride adsorption efficiency was greatly inhibited by the  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  whereby a similar trend was reported by [26, 30]. The hydrolysis of these anions in aqueous solution exacerbates the concentration of  $\text{OH}^-$  ions causing the solution's pH to raise. Thus, the biosorbents' adsorption capability is decreased when  $\text{OH}^-$  ions rival with  $\text{F}^-$  ions for available adsorption sites.

## 3.6 Adsorption isotherm models

Linear versions of the Langmuir, Temkin isotherm Freundlich, and Dubinin-Radushkevich (D-R) isotherms were applied to fit the experiment data. In accordance with Langmuir isotherm, a monolayer surface is formed by an even dispensation of adsorbed particles on the active adsorptive sites of an adsorbent and furthermore, no interaction amongst the adsorbed particles and possess similar adsorption energy for all sites during an adsorption process [52].

The linearized expression for the Langmuir isotherm is provided in Eq. 1:

$$\frac{1}{q_e} = \left( \frac{1}{q_m K_L} \right) \cdot \frac{1}{C_e} + \frac{1}{q_m}$$

1

where  $q_e$  ( $\text{mg g}^{-1}$ ) represents equilibrium adsorption capacity,  $q_m$  ( $\text{mg g}^{-1}$ ) stands for theoretical maximum adsorption capacity of the adsorbent,  $C_e$  represents the equilibrium concentration ( $\text{mg L}^{-1}$ ), and  $K_L$  ( $\text{L mg}^{-1}$ ) is the Langmuir isotherm constant. The values for  $K_L$  and  $q_m$  were computed from the intercept and slope of the graph. The highest Langmuir adsorption capacity was  $6.68 \text{ mg g}^{-1}$  at neutral pH. In comparison to the Temkin, D-R, and Freundlich, the Langmuir isotherm produced the highest  $R^2$  values of 0.903, 0.967, and 1.00 for ZMNB 300, ZMNB 400, and ZMNB 500 correspondingly, as displayed in Fig. 8 (a, b and c), and thus the best fit isotherm as shown in Table 2. This confirmed that the  $\text{F}^-$  ions

were bound by same the energy and formed a monolayer surface [53] on all the afore stated ZMNB biosorbents.

The expression for separation factor ( $R_L$ ) [54] is shown in Eq. 2.

$$R_L = \frac{1}{1 + C_i \times K_L}$$

2

where the dimensionless Langmuir constant,  $R_L$ , denotes the possibility of adsorption possibility to be either linear ( $R_L=1$ ), favourable ( $0 < R_L > 1$ ), unfavorable ( $R_L > 1$ ) or irreversible ( $R_L =0$ ) [55]. The calculated  $R_L$  values for the fluoride adsorption by the ZMNB biosorbents shown in Table 1, fell between 0 and 0.017 ascribing that the adsorption process was strongly favorable [31, 54]. The Freundlich isotherm presupposes a heterogenous adsorbent surface with an exponential distribution of active sites and energy [30]. Figure 8(d, e, and f) displayed the Freundlich isotherms. The Freundlich's isotherm linear form is expressed in Eq. 3.

$$\text{Log}q_e = \text{Log}K_f + \frac{1}{n}\text{Log}C_e$$

3

where  $1/n$  expresses the adsorption of intensity, indicating whether adsorption is favorable ( $0.1 < 1/n < 0.5$ ) or unfavorable ( $1/n > 2$ ) and  $K_f$  is the Freundlich's constant applied for computing the adsorption capacity. Results for  $1/n$  were in the range of -0.211 and 0.172 as presented in Table 2, showing that the adsorption intensity was favorable.

Equation 4 represents the Dubinin-Radushkevich (D-R) isotherm's linearized form.

$$\ln q_e = \ln q_m - k\varepsilon^2$$

4

Where, according to Eq. 5,  $q_e$  ( $\text{mg g}^{-1}$ ) represents the quantity of  $\text{F}^-$  ions adsorbed at equilibrium,  $q_m$  ( $\text{mg g}^{-1}$ ) expresses the maximum adsorption capacity,  $(\text{kJ mol}^{-1})$  is the Polanyi potential, and  $\beta$  ( $\text{mol}^2 \text{kJ}^2$ ) is an adsorption energy constant.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$$

5

where  $R$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) and  $T$  (K) represents the gas constant and absolute temperature respectively.

The mean free energy,  $E$  ( $\text{kJ mol}^{-1}$ ) expression is given in Eq. 6.

$$E = \frac{1}{\sqrt{2\beta}}$$

6

The  $E$  ( $\text{kJ mol}^{-1}$ ) values for the three prepared biosorbents were computed as shown in Table 2 and all of them were greater than  $8 \text{ kJ mol}^{-1}$  signifying that chemisorption process was involved [56]. Table 6 provides a contrast of the maximal  $\text{F}^-$  adsorption capacities of several adsorbents.

Table 2

Computed parameters of the adsorption isotherms for  $\text{F}^-$  removal by ZMNB biosorbents

Adsorption isotherm models	Parameters	Type of biosorbent		
		ZMNB 300	ZMNB 400	ZMNB 500
Langmuir	$q_{\text{max}}$ ( $\text{mg g}^{-1}$ )	6.482	6.679	5.503
	$R_L$	0.017	0.015	0.010
	$K_L$ ( $\text{L mg}^{-1}$ )	5.841	6.622	9.909
	$R^2$	0.903	0.967	1.000
Freundlich	$K_f$	4.214	2.597	3.963
	$1/n$	-0.211	0.166	0.172
	$R^2$	0.639	0.783	0.637
Temkin	$K_T$ ( $\text{L g}^{-1}$ )	219.8	556.5	1375
	$B_T$ ( $\text{J mol}^{-1}$ )	0.821	0.772	0.596
	$R^2$	0.631	0.712	0.698
(D-R)	$q_m$ ( $\text{mg g}^{-1}$ )	6.081	6.201	5.443
	$E$ ( $\text{KJ mol}^{-1}$ )	4481	4682	5108
	$\beta$ ( $\text{mol}^2 \text{kJ}^{-2}$ )	0.000	0.000	0.000
	$R^2$	0.844	0.967	0.898

### 3.7 Adsorption Kinetic studies

Adsorption kinetics indicates the time required for an equilibrium to be attained during an adsorption process [57]. As indicated in Table 3, the Lagergren's PFO, PSO, and intra-particle diffusion models were employed to determine the speed at which the  $F^-$  ions were adsorbed.

Equation 7 expresses the linear form of the pseudo-first-order-kinetics

$$\ln(q_e - q_t) = \ln q_n - K_1 t$$

7

where, the time  $t$  (min) and adsorption capabilities at equilibrium are represented by  $q_t$  ( $\text{mg g}^{-1}$ ) and  $q_e$  ( $\text{mg g}^{-1}$ ) respectively. The slope of the plot  $(q_e - q_t)$  versus  $t$  was used to determine the value of  $K_1$  as depicted in Fig. 9 (a, b and c).

Equation 8 illustrates the PSO kinetics model's linear form.

$$\frac{t}{qt} = \frac{1}{q_e^2 K_2} + \frac{t}{q_e}$$

8

where  $K_2$  ( $\text{g gm}^{-1} \text{min}^{-1}$ ) is the PSO kinetics constant,  $q_t$  ( $\text{mg g}^{-1}$ ) represents biosorbent's  $F^-$  ion removal capacity at time  $t$ , and  $q_e$  is the equilibrium sorption capacity. Computed values of  $K_1$  and  $q_e$  for the intercept and slope respectively originated from the plots of  $t/qt$  against  $t$  are displayed in Fig. (d, e, and f).

Table 3

Computed kinetic adsorption parameters for F<sup>-</sup> adsorption onto ZMNB biosorbents

Order of reaction	Parameters	Type of biosorbent		
		ZMNB 300	ZMNB 400	ZMNB 500
Pseudo-first-order	q <sub>e</sub> Cal (mg g <sup>-1</sup> )	0.075	0.928	1.020
	K <sub>1</sub> (L mg <sup>-1</sup> )	-0.001	-0.007	-0.001
	R <sup>2</sup>	0.606	0.662	0.648
Pseudo-second-order	q <sub>e</sub> Cal (mg g <sup>-1</sup> )	4.887	5.079	4.926
	K <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )	1.462	0.129	0.222
	R <sup>2</sup>	0.999	0.999	0.999
Intra-particle diffusion	C	4.034	3.672	3.381
	K <sub>p</sub>	0.135	0.190	0.228
	R <sup>2</sup>	0.643	0.804	0.747

### 3.8 Thermodynamic studies

Thermodynamics analyses at 303, 313, and 323 K were investigated in order to understand the viability and spontaneity of the adsorption process, as shown in Table 4. The standard enthalpy ( $\Delta H^\circ$ ), standard free energy change ( $\Delta G^\circ$ ), and standard entropy change ( $\Delta S^\circ$ ) which were used to examine the adsorption process, were computed from the Gibbs free energy equation expressed in Eq. 9.

$$\Delta G^\circ = -RT \ln K_L$$

9

According to Gibbs free energy

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

10

where T is the temperature (K),  $\Delta S^\circ$  is the standard entropy change (kJ mol<sup>-1</sup> K<sup>-1</sup>),  $\Delta G^\circ$  is the standard free Gibbs energy change (kJ mol<sup>-1</sup>),  $\Delta H^\circ$  is the standard enthalpy change (kJ mol<sup>-1</sup>),  $K_L$  is the adsorption equilibrium constant, and R is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>).

By replacing Eq. (10) in Eq. (9), Eq. 11 is achieved:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

11

The adsorption process is said to be spontaneous and rapid if the  $\Delta G^\circ$  value is negative, endothermic, irreversible, and chemisorption process if the  $\Delta H^\circ$  value is positive, and an intensified randomness at the liquid/solid interface if the  $\Delta S^\circ$  value is positive [47]. According to the findings in Table 4, it was concluded that the adsorption process was spontaneous, quick, irreversible, endothermic, and a chemisorption process. Moreover, the findings indicated that as the temperatures increased, the fluoride adsorption also increased.

Table 4  
Thermodynamic studies for the ZMNB 300, ZMNB 400, and ZMNB 500 biosorbents

Type of Adsorbent	Temperature (K)	Computed Thermodynamic Parameters		
		$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> k <sup>-1</sup> )
ZMNB 300	303	- 5.593	30.102	118.547
	313	- 7.485		
	323	- 7.933		
ZMNB 400	303	- 6.163	20.873	89.403
	313	- 7.224		
	323	- 7.944		
ZMNB 500	303	- 4.732	25.773	100.738
	313	- 5.799		
	323	- 6.744		

### 3.10 Defluoridation mechanism

The characterization and adsorption isotherm studies revealed that ZMNB adsorbed fluoride through chemical sorption process. The FTIR spectral analysis revealed the existence of -COOH, Zr-O and Zr-OH on the ZMNB through which fluoride adsorption was achieved mainly by ion exchange between the -OH and F<sup>-</sup> ions. Zr (IV) ions yielded by ZrOCl<sub>2</sub> hydrolysis might have interacted electrostatically with the MNB adsorbent surfaces to form a C-O-Zr which in turn adsorbed the fluoride ions as reported in the literature elsewhere [58]. Also, zirconium ion may have interacted with the primary -OH group forming Zr-O bond [59]. In addition, the interaction between the cellulosic -OH groups of MNB and F<sup>-</sup> might have contributed to the establishment of a H bonding (Zr-OH-F).

### 3.10 Field study

To test the applicability of the ZMNB 300 biosorbent for defluoridation capacity, natural water was collected from Mwakenyi stream flowing from the slopes of Mt. Meru in Arusha -Tanzania which contained a measured fluoride contamination level of  $6.06 \text{ mg L}^{-1}$ . Results in Table 5 revealed that  $1 \text{ g L}^{-1}$  of ZMNB 300 adsorbed fluoride ions to  $0.92 \text{ mg L}^{-1}$  implying its potential applicability as a cheap alternative for water defluoridation.

Table 5  
Field trial results of ZMNB 300

Water quality parameters	Before defluoridation	After defluoridation
$\text{F}^- (\text{mg L}^{-1})$	6.06	0.92
pH	8.7	6.8
$\text{EC} (\text{ms cm}^{-1})$	479.8	274.4
DO	6.43	4.96
Temperature	25.7	26.1
$\text{TDS} (\text{mg L}^{-1})$	224	196
<b>3.11 Reusability and desorption potential</b>		

The economic viability of any adsorbent is of critical importance concerning its re-generatability and reusability after multiple cycles of its application. To ascertain the desorption and reusability capacity of the adsorbent, the exhausted ZMNB 300 biosorbent was repeatedly studied using fluoride ion solution with  $10 \text{ mg L}^{-1}$  as its initial concentration and regenerated using 0 to 10% NaOH and HCl solution. It was revealed that NaOH regenerated better than HCl. Additionally, ZMNB 300 biosorbent was better regenerated using 2% of the NaOH solution with 94.8%, 76% 51%, and 27% for the first, second, third and fourth regeneration cycles respectively.



Table 6  
Summary of biosorbents for fluoride sorption and their removal efficiency

Biosorbent type	Adsorption capacity (mg g <sup>-1</sup> )	Maximum Removal Capacity (%)	Working Temperature (°C)	Working pH	References
Zr-loaded macadamia nutshell biochar	6.48	99.05	25	7	Present study
Zr-loaded grape pomace	7.54	96	25	3	[60]
Citrus limetta (sweet lime) residue	12.6	80–86	25	4	[61]
Calcium-rich crabs-based adsorbent	13.6	92	25	3	[62]
Triethylamine modified maize tassels	0.19	86	25	4	[63]
Zr-modified tea powder waste	12.43	90	25	3–10	[64]
Zr-impregnated cashew nutshell carbon	1.83	81.7	30	7	[47]

## 4. Conclusion

Zirconium ion-impregnated macadamia nutshell biochar that were carbonized at 300, 400, 500 and 600 °C were studied to determine their fluoride removal efficiency from aqueous solution using batch mode experimental studies. The consequences of numerous optimized parameters viz. initial fluoride concentration, pH, exposure time, temperature, and adsorbent dosage were investigated. ZMNB 300 biosorbent exhibited a maximum percentage fluoride adsorption efficiency of 99.05% with a 1.0 g L<sup>-1</sup> adsorbent dose at pH 7 for a contact duration of 1 h at temperature of (25 ± 2 °C). In comparison to the Freundlich, Temkin, and Dubinin-Radushkevich isotherm models, the adsorption isotherms for fluoride adsorption onto the ZMNB 300, ZMNB 400 and ZMNB 500 biosorbents were very well correlated to the Langmuir isotherm. When compared to pseudo-first order and intra-particle diffusion kinetic models, the findings of the adsorption kinetic modeling investigations evinced that the pseudo-second-order kinetics produced the best correlation of the experimental results. The ZMNB biosorbents characterization by XRD, FTIR, SEM-EDX pointed to the anchoring of the fluoride ions on the ZMNB 300 biosorbent surface whereas the BET surface adsorption analysis disclosed that the surface area increased upon Zr (IV) impregnation of MNB. The effect of pyrolysis temperature showed that temperature between 300–400 °C were effective for biochar preparation for adsorption experiments as

compared to 500–1000 °C. Therefore, this may be concluded that the Zr (IV) treated macadamia nutshell biochar might be a prospect low-cost material for fluoride removal in contaminated water due to its sorption capacities at wide pH range and its reusability and desorption capability.

## Declarations

## Declarations

### Ethical Approval

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## Declarations

### Competing interest

The authors affirm that they have no known competing financial interest or interpersonal conflicts that would have appeared to have an influence on the research findings presented in this study.

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## Author contributions

Andrew Kipruto Yegon; conceptualization, methodology, experiments, data curation, data analysis, writing of the original draft, Stanslous George Mtavangu; methodology and review and editing, Mwemezi Jehovan Rwiza; supervision, methodology, review and editing and Machunda Lazaro Machunda; writing-review and editing, resources and fund sourcing.

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## References

1. Dey, S., Giri, B.: Fluoride fact on human health and health problems: a review. *Med. Clin. Rev.* **2**(1), 11 (2016). DOI: <https://doi.org/10.21767/2471-299X.1000011>
2. Sani, T., et al.: Defluoridation performance of nano-hydroxyapatite/stilbite composite compared with bone char. *Sep. Purif. Technol.* **157**, 241–248 (2016)
3. Akuno, M., et al.: Factors influencing the relationship between fluoride in drinking water and dental fluorosis: a ten-year systematic review and meta-analysis. *J. Water Health.* **17**(6), 845–862 (2019)
4. WHO: Guidelines for drinking-water quality, vol. 1. World health organization (2004)
5. Lennon, M., et al.: Rolling Revision of the WHO Guidelines for Drinking-Water Quality. World Health (2004)
6. Nair, V.V., Aravind, A., Varghese, D.K.: Defluoridation of water by composite bed of low-cost bio-adsorbents. *Int. J. Adv. Technol. Eng. Sci.* **4**, 122–131 (2016)
7. Ganvir, V., Das, K.: Removal of fluoride from drinking water using aluminum hydroxide coated rice husk ash. *J. Hazard. Mater.* **185**(2–3), 1287–1294 (2011). DOI: 10.1016/j.jhazmat.2010.10.044
8. Ijumulana, J., et al.: Spatial uncertainties in fluoride levels and health risks in endemic fluorotic regions of northern Tanzania. *Groundw. Sustainable Dev.* **14**, 100618 (2021)
9. Mohanta, A.: Dental Fluorosis- Revisited. *Biomedical J. Sci. Tech. Res.* **2**(1), 2243–2247 (2018). DOI: 10.26717/bjstr.2018.02.000667
10. Patel, S.B., et al.: Development of new zirconium loaded shellac for defluoridation of drinking water: Investigations of kinetics, thermodynamics and mechanistic aspects. *J. Environ. Chem. Eng.* **4**(4), 4263–4274 (2016)
11. Chowdhury, A., et al.: A critical review on geochemical and geological aspects of fluoride belts, fluorosis and natural materials and other sources for alternatives to fluoride exposure. *J. Hydrol.* **574**, 333–359 (2019)
12. Kimambo, V., et al.: Fluoride occurrence in groundwater systems at global scale and status of defluoridation–state of the art. *Groundw. Sustainable Dev.* **9**, 100223 (2019)
13. Mjengera, H., Mkongo, G.: *Appropriate defluoridation technology for use in fluorotic areas in Tanzania*. *Physics and Chemistry of the Earth. Parts A/B/C.* **28**(20–27), 1097–1104 (2003)
14. Huang, H., et al.: Investigation on the simultaneous removal of fluoride, ammonia nitrogen and phosphate from semiconductor wastewater using chemical precipitation. *Chem. Eng. J.* **307**, 696–706 (2017)
15. Ali, I., Gupta, V.K.: Advances in water treatment by adsorption technology. *Nat. Protoc.* **1**(6), 2661–2667 (2007). DOI: 10.1038/nprot.2006.370
16. Meenakshi, S., Sundaram, C.S., Sukumar, R.: Enhanced fluoride sorption by mechanochemically activated kaolinites. *J. Hazard. Mater.* **153**(1–2), 164–172 (2008). DOI: 10.1016/j.jhazmat.2007.08.031

17. Paudyal, H., et al.: Removal of fluoride by effectively using spent cation exchange resin. *J. Mater. Cycles Waste Manage.* **20**(2), 975–984 (2018)
18. Zhang, J., et al.: Fluoride removal from aqueous solution by zirconium-chitosan/graphene oxide membrane. *Reactive and Functional Polymers.* **114**, 127–135 (2017)
19. Bhatnagar, A., Kumar, E., Sillanpää, M.: Fluoride removal from water by adsorption—A review. *Chem. Eng. J.* **171**(3), 811–840 (2011). DOI: 10.1016/j.cej.2011.05.028
20. Richards, L.A., Vuachère, M., Schäfer, A.I.: Impact of pH on the removal of fluoride, nitrate and boron by nanofiltration/reverse osmosis. *Desalination.* **261**(3), 331–337 (2010)
21. Borah, R., et al.: Efficacy and field applicability of Burmese grape leaf extract (BGLE) for cadmium removal: An implication of metal removal from natural water. *Ecotoxicol. Environ. Saf.* **147**, 585–593 (2018). DOI: 10.1016/j.ecoenv.2017.09.002
22. Kumar, P., et al.: Batch technique to evaluate the efficiency of different natural adsorbents for defluoridation from groundwater. *Appl. Water Sci.* **7**(5), 2597–2606 (2017)
23. Saikia, et al.: Removal of arsenic and fluoride from aqueous solution by biomass based activated biochar: optimization through response surface methodology. *J. Environ. Chem. Eng.* **5**(6), 5528–5539 (2017)
24. Maheshwari, R.: Fluoride in drinking water and its removal. *J. Hazard. Mater.* **137**(1), 456–463 (2006)
25. Hegde, R.M., et al.: Bio-inspired materials for defluoridation of water: a review. *Chemosphere.* **253**, 126657 (2020)
26. Mariappan, R., Vairamuthu, R., Ganapathy, A.: Use of chemically activated cotton nut shell carbon for the removal of fluoride contaminated drinking water: kinetics evaluation. *Chin. J. Chem. Eng.* **23**(4), 710–721 (2015). DOI: <https://10.1016/j.cjche.2014.05.019>
27. Bashir, M., et al.: Fluoride removal by chemical modification of palm kernel shell-based adsorbent: A novel agricultural waste utilization approach. *Asian J. of Microbial Biotech. Env Sc.* **17**(3), 533–542 (2015)
28. Zhao, B., Nartey, O.D.: *Characterization and evaluation of biochars derived from agricultural waste biomasses from Gansu, China.* in *of the World Congress on Advances in Civil, Environmental, and Materials Research.* (2014)
29. Mourabet, M., et al.: Removal of fluoride from aqueous solution by adsorption on Apatitic tricalcium phosphate using Box–Behnken design and desirability function. *Appl. Surf. Sci.* **258**(10), 4402–4410 (2012)
30. Biswas, A., Prathibha, C.: Fe (III) and Zr (IV) surface functionalized 1-D hydrogen titanate nanotubes for remediating fluoride from water at neutral pH. *J. Water Process Eng.* **37**, 101331 (2020)
31. Wang, J., et al.: A sorbent of carboxymethyl cellulose loaded with zirconium for the removal of fluoride from aqueous solution. *Chem. Eng. J.* **252**, 415–422 (2014)
32. Orton, C.R., et al.: Fourier transform infrared studies of heterogeneity, photodegradation, and lignin/hemicellulose ratios within hardwoods and softwoods. *Appl. Spectrosc.* **58**(11), 1265–1271

(2004)

33. Faisal, A.D., Aljubouri, A.A.: Synthesis and production of carbon nanospheres using noncatalytic CVD method. *Int. J. Adv. Mat. Res.* **2**, 86–91 (2016)
34. Mullick, A., Neogi, S.: Ultrasound assisted synthesis of Mg-Mn-Zr impregnated activated carbon for effective fluoride adsorption from water. *Ultrason. Sonochem.* **50**, 126–137 (2019). DOI: 10.1016/j.ultsonch.2018.09.010
35. Pillai, P., et al.: Synthesis, characterization, and application of iron oxyhydroxide coated with rice husk for fluoride removal from aqueous media. *Environ. Sci. Pollut. Res.* **27**(17), 20606–20620 (2020)
36. Soradech, S., et al.: An approach for the enhancement of the mechanical properties and film coating efficiency of shellac by the formation of composite films based on shellac and gelatin. *J. Food Eng.* **108**(1), 94–102 (2012)
37. Zhao, X., et al.: *Surface characterization of corn stalk superfine powder studied by FTIR and XRD.* *Colloids Surf B Biointerfaces*, **104**: p.207–12 DOI: (2013). 10.1016/j.colsurfb.2012.12.003
38. Mtavangu, S.G., et al.: Cockle (*Anadara granosa*) shells-based hydroxyapatite and its potential for defluoridation of drinking water. *Results in Engineering.* **13**, 100379 (2022)
39. Kumpiene, J., et al.: Spatial variability of topsoil contamination with trace elements in preschools in Vilnius, Lithuania. *J. Geochem. Explor.* **108**(1), 15–20 (2011)
40. Goswami, R., Kumar, M.: Removal of fluoride from aqueous solution using nanoscale rice husk biochar. *Groundw. Sustainable Dev.* **7**, 446–451 (2018). DOI: 10.1016/j.gsd.2017.12.010
41. Xavier, T., et al.: A study of pyrolysis of macadamia nut shell: parametric sensitivity analysis of the IPR model. *Braz. J. Chem. Eng.* **33**, 115–122 (2016)
42. Rangabhashiyam, S., Selvaraju, N.: Efficacy of unmodified and chemically modified *Swietenia mahagoni* shells for the removal of hexavalent chromium from simulated wastewater. *J. Mol. Liq.* **209**, 487–497 (2015)
43. Jha, R., et al.: Fluoride sorption by zirconium (IV) loaded carboxylated orange peel. *Desalination Water Treat.* **53**(8), 2144–2157 (2015)
44. Rwiza, M.J., Kleinke, M., Kim, K.-W.: A study on Pb removal kinetics using modified agricultural wastes from Tanzania. *SN Appl. Sci.* **2**(11), 1–12 (2020)
45. Yan, L., et al.: ZnCl<sub>2</sub> modified biochar derived from aerobic granular sludge for developed microporosity and enhanced adsorption to tetracycline. *Bioresour Technol.* **297**, 122381 (2020). DOI: 10.1016/j.biortech.2019.122381
46. Sundaram, C.S., Viswanathan, N., Meenakshi, S.: *Defluoridation chemistry of synthetic hydroxyapatite at nano scale: equilibrium and kinetic studies.* *Journal of Hazardous Materials*, 2008. **155**(1–2): p.206–215
47. Alagumuthu, G., Rajan, M.: Equilibrium and kinetics of adsorption of fluoride onto zirconium impregnated cashew nut shell carbon. *Chem. Eng. J.* **158**(3), 451–457 (2010)

48. Liu, Y., et al.: Adsorptive removal of fluoride from aqueous solutions using Al-humic acid-La aerogel composites. *Chem. Eng. J.* **306**, 174–185 (2016)
49. Dehghani, M.H., et al.: Adsorptive removal of fluoride from water by activated carbon derived from CaCl<sub>2</sub>-modified *Crocus sativus* leaves: Equilibrium adsorption isotherms, optimization, and influence of anions. *Chem. Eng. Commun.* **205**(7), 955–965 (2018). DOI: <https://doi.org/10.1080/00986445.2018.1423969>
50. Yuan, J.-H., Xu, R.-K., Zhang, H.: The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresour. Technol.* **102**(3), 3488–3497 (2011)
51. Uchimiya, M., et al.: Contaminant immobilization and nutrient release by biochar soil amendment: roles of natural organic matter. *Chemosphere.* **80**(8), 935–940 (2010)
52. Mullick, A., Neogi, S.: Acoustic cavitation induced synthesis of zirconium impregnated activated carbon for effective fluoride scavenging from water by adsorption. *Ultrason. Sonochem.* **45**, 65–77 (2018). DOI: <https://doi.org/10.1016/j.ultsonch.2018.03.002>
53. Lou, Z., et al.: Contribution of tertiary amino groups to Re(VII) biosorption on modified corn stalk: competitiveness and regularity. *Bioresour Technol.* **133**, 546–554 (2013). DOI: [10.1016/j.biortech.2013.01.165](https://doi.org/10.1016/j.biortech.2013.01.165)
54. Ayub, A., et al.: Development of sustainable magnetic chitosan biosorbent beads for kinetic remediation of arsenic contaminated water. *Int. J. Biol. Macromol.* **163**, 603–617 (2020). DOI: [10.1016/j.ijbiomac.2020.06.287](https://doi.org/10.1016/j.ijbiomac.2020.06.287)
55. Weber, T.W., Chakravorti, R.K.: Pore and solid diffusion models for fixed-bed adsorbers. *AIChE J.* **20**(2), 228–238 (1974)
56. Li, X., et al.: Novel magnetic beads based on sodium alginate gel crosslinked by zirconium(IV) and their effective removal for Pb<sup>2+</sup> in aqueous solutions by using a batch and continuous systems. *Bioresour. Technol.* **142**, 611–619 (2013). DOI: [10.1016/j.biortech.2013.05.081](https://doi.org/10.1016/j.biortech.2013.05.081)
57. Tran, H.N., et al.: Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. *Water Res.* **120**, 88–116 (2017)
58. Velazquez-Jimenez, L.H., et al.: Zirconium–carbon hybrid sorbent for removal of fluoride from water: oxalic acid mediated Zr (IV) assembly and adsorption mechanism, vol. 48, pp. 1166–1174. *Environmental science & technology* (2014). 2
59. Muxel, A.A., et al.: Cotton fiber/ZrO<sub>2</sub>, a new material for adsorption of Cr (VI) ions in water. *CLEAN–Soil, Air, Water.* **39**(3), 289–295 (2011)
60. Zhang, Y., Huang, K.: Grape pomace as a biosorbent for fluoride removal from groundwater. *RSC Adv.* **9**(14), 7767–7776 (2019). DOI: [10.1039/c9ra00109c](https://doi.org/10.1039/c9ra00109c)
61. Ibrahim, M., et al.: Adsorptive removal of fluoride from aqueous solution by biogenic iron permeated activated carbon derived from sweet lime waste. *Acta Chim. Slov.* **66**(1), 123–136 (2019)
62. Wagutu, A.W., Machunda, R., Jande, Y.A.C.: Crustacean derived calcium phosphate systems: Application in defluoridation of drinking water in East African rift valley. *J. Hazard. Mater.* **347**, 95–105 (2018). DOI: [10.1016/j.jhazmat.2017.12.049](https://doi.org/10.1016/j.jhazmat.2017.12.049)

63. Mwangi, C.K., et al.: Remediation of fluoride laden water by complexation with triethylamine modified maize tassels. *Environ. Nat. Resour. J.* **6**(1), 44–58 (2016)
64. Cai, H., et al.: Removal of fluoride from drinking water using tea waste loaded with Al/Fe oxides: a novel, safe and efficient biosorbent. *Appl. Surf. Sci.* **328**, 34–44 (2015)

## Unsectioned Paragraphs

Not applicable to this study.