



Review article

Transformative and sustainable insights of agricultural waste-based adsorbents for water defluoridation: Biosorption dynamics, economic viability, and spent adsorbent management

Koyeli Das^{a,b}, Uttara Sukul^{a,b}, Jung-Sheng Chen^c, Raju Kumar Sharma^{b,d}, Pritam Banerjee^{a,b}, Gobinda Dey^{a,b}, Md. Taharia^b, Christian J. Wijaya^{e,f}, Cheng-I Lee^{a,g}, Shan-Li Wang^h, Nguyen Hoang Kim Nuong^b, Chien-Yen Chen^{b,g,*}

^a Department of Biomedical Sciences, Graduate Institute of Molecular Biology, National Chung Cheng University, 168 University Road, Min-Hsiung, Chiayi County, 62102, Taiwan

^b Doctoral Program in Science, Technology, Environment, and Mathematics, Department of Earth and Environmental Sciences, National Chung Cheng University, 168 University Road, Min-Hsiung, Chiayi County, 62102, Taiwan

^c Department of Medical Research, E-Da Hospital, Kaohsiung, 82445, Taiwan

^d Department of Chemistry and Biochemistry, National Chung Cheng University, 168 University Road, Min-Hsiung, Chiayi County, 62102, Taiwan

^e Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya, 60114, Indonesia

^f Collaborative Research Center for Zero Waste and Sustainability, Kalijudan 37, Surabaya, 60114, Indonesia

^g Center for Nano Bio-Detection, Center for Innovative Research on Aging Society, AIM-HI, National Chung Cheng University, 168, University Road, Min-Hsiung, Chiayi County, 62102, Taiwan

^h Department of Agricultural Chemistry, National Taiwan University, Taipei, 106319, Taiwan

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ABSTRACT

With the progression of civilization, the harmony within nature has been disrupted, giving rise to various ecocidal activities that are evident in every spheres of the earth. These activities have had a profound and far-reaching impact on global health. One significant example of this is the presence of fluoride in groundwater exceeding acceptable limits, resulting in the widespread occurrence of “Fluorosis” worldwide. It is imperative to mitigate the concentration of fluoride in drinking water to meet safety standards. While various defluoridation techniques exist, they often have drawbacks. Biosorption, being a simple, affordable and eco-friendly method, has gained preference for defluoridation. However, its limited commercialization underscores the pressing need for further research in this domain. This comprehensive review article offers a thorough examination of the defluoridation potential of agro-based adsorbents, encompassing their specific chemical compositions and preparation methods. The review presents an in-depth discussion of the factors influencing fluoride biosorption and conducts a detailed exploration of adsorption isotherm and adsorption kinetic models to gain a comprehensive understanding of the nature of the adsorption process. Furthermore, it evaluates the commercial viability through an assessment of regeneration potential and a cost analysis of these agro-adsorbents, with the aim of facilitating the scalability of the defluoridation process. The elucidation of the adsorption mechanism and recommendations for overcoming challenges in large-scale implementation offer a comprehensive outlook on this eco-friendly and sustainable approach to fluoride removal. In summary, this

* Corresponding author. Department of Earth and Environmental Sciences, National Chung Cheng University, 168 University Road, Min-Hsiung, Chiayi County 62102, Taiwan.

E-mail addresses: chien-yen.chen@oriel.oxon.org, yen@eq.ccu.edu.tw (C.-Y. Chen).

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review article equips readers with a lucid understanding of agro-adsorbents, elucidates their ideal conditions for improved performance, offers a more profound insight into the fluoride biosorption mechanism, and introduces the concept of effective spent adsorbent management.

1. Introduction

Water, creator as well as the conveyor of existence of life has always been taken into consideration on account its safety and sufficiency [1,2]. With the evolution of human civilization, reliance on this enlivening resource has been amplified by many folds leading to a substantial increase in our ecological footprint and concurrently diminishing the bio-capacity of the ecosystem [3,4]. Even more, this ecological imbalance exerts a monumental impact on the health outcomes of the human population [5]. Furthermore, extensive exploitation of groundwater causes weathering of the rock wall of aquifer eventually alters the composition of groundwater by releasing chemical contaminants [6,7]. Presence of geogenic contaminants [e.g. arsenic [8], fluoride [9], manganese and iron [10] etc.] beyond permissible limit has threatened human survival by generating noxious diseases (e.g. Arsenicosis, Fluorosis, Haemochromatosis etc.) [11]. Among the various inorganic contaminants, fluoride and arsenic are particularly noteworthy due to their pronounced health effects, which can manifest even at low concentrations. Moreover, these two chemicals are included in the evaluation of drinking water safety targets established by sustainable development goals [12–16]. Groundwater pollution with fluoride is receiving attention of today's globe due to the severity of the resultant crippling disease 'Fluorosis' [17].

Fluorine, a naturally occurring element constitutes about 0.32 % of the earth's crust [18] and found in minerals such as fluorite, biotite, cryolite, mica etc. [19–21]. Fluoride can be released into groundwater through weathering of fluorine-containing minerals [22–24] or anthropogenic activities such as use of phosphate-containing agrochemicals, industrial processes etc. [21,25–28]. The recidivism of industrial practices contributing to fluoride contamination in groundwater is a notable concern, particularly when some industries disregard appropriate waste disposal methods [29]. High concentration of fluoride in industrial effluent can leach into groundwater, making it unsuitable for human consumption [30]. The dissolution of fluoride (F^-) in groundwater is facilitated by iso-ionic exchange with hydroxyl ions (OH^-) [31] and can be influenced by factors such as residence time, hydraulic conductivity, well depth and climatic conditions [32,33]. The World Health Organization (WHO) recommends a safe level of fluoride in drinking water to be 1.5 parts per million (ppm) [34], while other organizations such as the Bureau of Indian Standard (BIS), U.S Environment Protection Agency (USEPA) and European Union (EU) have set their acceptable limits at 1 mg/l, 4 mg/l and 1.5 mg/l respectively [35]. The Optimum level of fluoride can strengthen enamel by preventing it from dissolving in acidic conditions [36] and promoting bone formation by facilitating the growth of osteoblasts [37]. However, higher concentration of fluoride can lead to dental and skeletal fluorosis, characterized by various health issues such as joint pain, limited joint motion, structural damage of the teeth and spinal cord compression etc. [17,38,39]. Moreover, high levels of fluoride can interfere with the regulation of osteocalcin [40] and accumulate in the pineal gland, potentially affecting the neurological system [21]. Additionally, a study conducted in Mexico has reported that an excessive level of fluoride can adversely affect pubertal development. Furthermore, there are still places where boys lack proper awareness regarding puberty, underscoring the importance of addressing the potential impacts of fluoride contamination on overall health and development, especially in regions with limited education and awareness [41,42]. Recent research links long-term fluoride-contaminated water consumption to nervous system disruptions and potential anxiety and depression symptoms [43–45]. Additionally, during the Covid-19 pandemic, a significant correlation has emerged between groundwater fluoride content and Covid-19 infection rates, emphasizing the multifaceted impact of fluoride contamination on both physical and mental well-being. This highlights the importance of addressing water fluoridation issues with a holistic health perspective [46]. Several defluoridation technologies have been developed including coagulation and precipitation [47], reverse osmosis [48], ion exchange [49], adsorption [50], electrocoagulation [51] and electrodialysis [52]. Coagulation and precipitation is one of the simplest defluoridation methods whereby, fluoride is settled using chemicals like alum [$Al_2(SO_4)_3$], calcium carbonate ($CaCO_3$), lime [$Ca(OH)_2$], and magnesium hydroxide [$Mg(OH)_2$] [53]. Reverse osmosis and nanofiltration use semipermeable membrane to remove fluoride employing pressure (driving force), however, they differ in their pore size i.e. nanofiltration (1–2 nm) and reverse osmosis (0.1–1 nm) [54]. The reduction of pore size in nanofiltration deliberated less energy-intensive as compared to reverse osmosis [55]. On the other hand, electrocoagulation and electro-sorption are two highly selective technique for removal of fluoride from water [56]. Electrocoagulation uses Al^{3+} to create an insoluble complex of $Al(OH)_3-F$ [57] and electrosorption implement an electrical field to enhance the adsorption rate of fluoride on the material surface [58]. However, these techniques have limitations such as high maintenance cost, operational complexity and the generation of secondary byproducts, which hinder their wide-scale commercial application [59]. Therefore, to address this issue, embracing pro-environmental behavior is crucial [4]. This green approach simultaneously integrates Industry 4.0 principles and supports the attainment of the sustainable goal for universal access to safe and clean water [60–62].

Adsorption is a widely used method for defluoridation and is considered superior on account of its "4E" concepts, i.e. (i) Easy to use (ii) Effective at operation (iii) Economical and (iv) Eco-friendly nature. A variety of adsorbents have been employed for defluoridation including activated alumina [63], calcite [64], ferric hydroxide [65], bauxite [66], activated carbon [67], natural clay [50], zeolite [68], chitin [69], metal oxide nanoparticle [70–72], metal organic framework [73,74] etc. Although these adsorbents possess several positive traits, they also exhibit certain drawbacks, such as expensive synthesis process, lack of selectivity, low adsorption potential, difficulty in regeneration, leaching of toxic chemicals and time-consuming operation [75].

In pursuit of a harmonious balance between economic growth and environmental protection, a novel approach has gained attention: the concept of a sustainable economy, as highlighted by Balsalobre-Lorente et al. [5]. In alignment with this perspective,

research has been directed towards the utilization of waste materials, including agricultural and industrial waste, as potential adsorbents [76–84]. However, the leaching, recovery and processing of industrial waste have constrained its widespread commercial use as an adsorbent, which has led to an increasing emphasis on sustainable research endeavors that focus on the use of agricultural waste instead. Agricultural waste encompasses the residues produced during the cultivation and processing of agricultural goods (e.g. fruits, crops, vegetables, dairy products etc.) [85]. The world generates approximately 998 million tons of such waste annually, and projections indicate that most Asian nations will produce 4.0–5.0kg/capita/month of agricultural waste by 2025 [86,87]. Inadequate management of agricultural waste can result in the emergence of multiple infectious diseases, thereby contributing to the global disease burden [88,89]. Therefore, a sustainable approach is urgently required to manage the substantial volume of waste, and waste valorization can be an effective strategy to accomplish this while also promoting the bio-economy [90]. Utilization of agricultural waste as an adsorbent is a promising approach to waste valorization due to its easy availability, renewability, affordability and environment friendly nature [59,67]. The lignocellulosic compounds found in agricultural waste contain functional groups that enable it to act as a binding agent for fluoride, making it a sustainable and effective adsorbent for defluoridation [21,91,92]. Furthermore, agricultural waste is a source of natural biopolymers, with cellulose being the most abundant and easily modifiable biopolymer [93]. Its chemical composition allows it to effectively remove fluoride from water, making it a promising alternative to synthetic polymer adsorbents, which can be expensive and harmful to the environment [94]. Hence, the utilization of agricultural waste as a natural biopolymer source offers a sustainable approach to defluoridation, concurrently mitigating waste and pollution. Current research efforts are increasingly directed toward the development of nanocomposites mediated by agricultural waste, with the aim of further improving its defluoridation capabilities [95–97]. A comprehensive comparison of various defluoridation techniques can be found in Fig. 2.

While numerous review articles exist on biosorption as a defluoridation method, these publications encompass a broad spectrum of bio-sorbents, such as algae, microbial biomass, plant and animal biomass, and more. Nonetheless, there is a noticeable absence of comprehensive literature that offers a thorough examination of the defluoridation potential and practical viability of agro-based adsorbents for potential commercial applications. This literature review bridges this gap by delivering a comprehensive analysis of various agro-adsorbents developed for defluoridation, encompassing their adsorption capabilities and the mechanisms behind their effectiveness. The primary objective of this review is to inspire additional research efforts aimed at identifying agricultural waste materials with substantial defluoridation potential and investigating methods to enhance their efficacy and commercial feasibility. Developing an agro-based adsorbent with robust defluoridation capabilities would be a valuable tool in addressing the widespread issue of fluorosis. This review also highlights the importance of considering the long-term fate of these agro-based adsorbents to prevent fluoride from reentering the ecosystem. The framework of the study is depicted in Fig. 1.

2. Agricultural waste as an adsorbent

The selection of an adsorbent significantly determines the effectivity of adsorption process since it depends on interaction between adsorbate and adsorbent [98]. The sorption potential of target adsorbent depends upon several factors such as specific surface area, presence of active site on adsorbent surface, solution pH, selectivity for adsorbate, environmental stability, regeneration potential etc. [99–101]. The commercialization of effective adsorbents is often limited by cost [91,102,103]. Therefore, current research is focused on exploring the adsorption potential of agricultural wastes which are readily available and affordable. Due to their distinct chemical composition, agricultural wastes have been used in various defluoridation studies [104]. Agricultural wastes are lignocellulosic compounds mainly composed of three components such as 25.0–44.2 wt% Cellulose, 10.5–40.4 wt% hemicellulose and 21.7–44.0 wt%

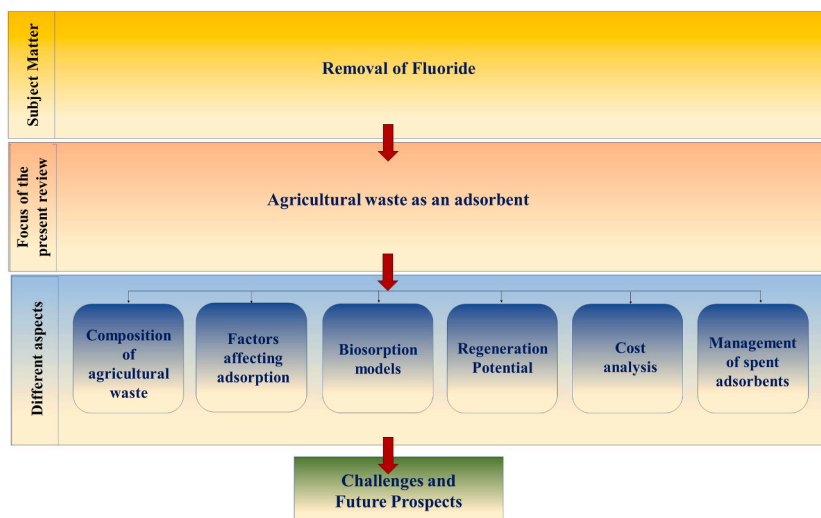


Fig. 1. Theoretical framework.

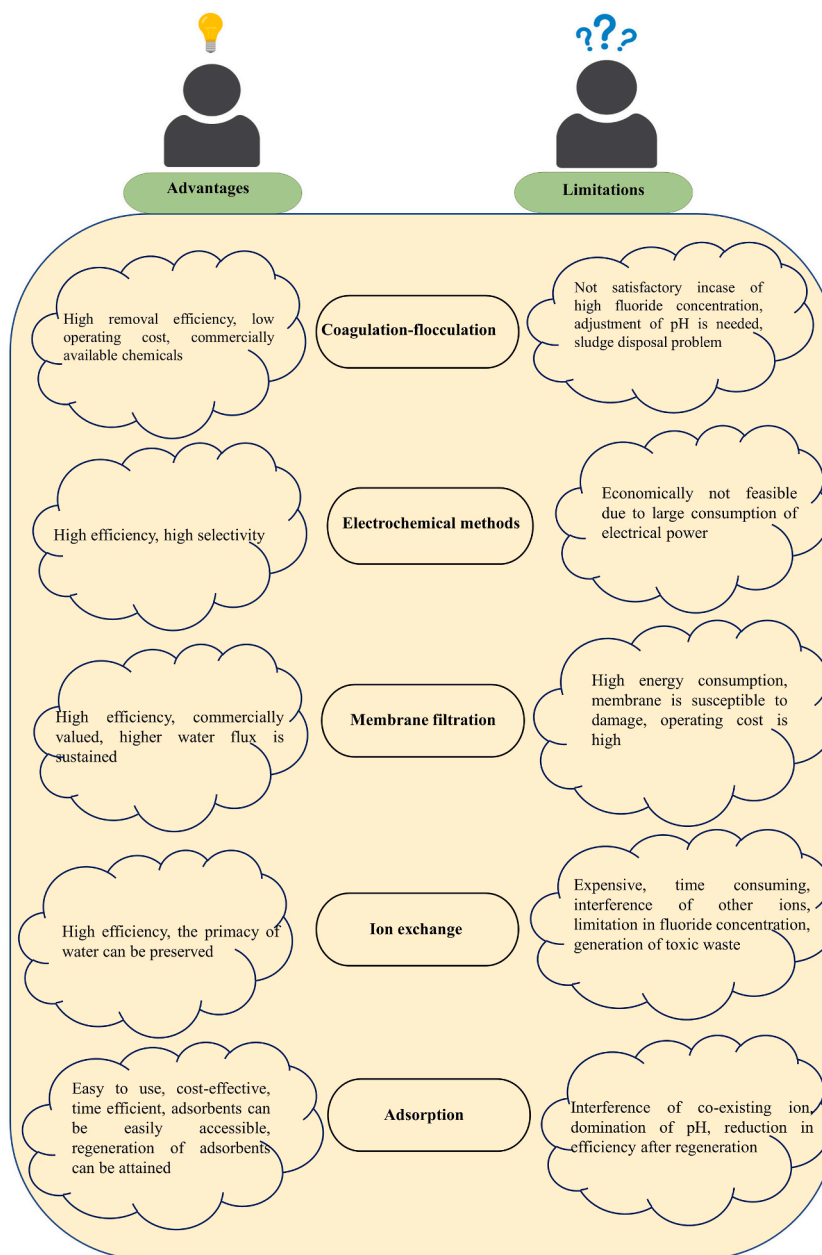


Fig. 2. Comparison among different defluoridation techniques.

lignin with trace amount of proteins, sugars, lipids, starch, water, ash and hydrocarbons [35,105]. Generally, the cellulose content in agricultural waste has been reported higher than hemicellulose and lignin. Pointedly, the cellulose is basically a homopolymer of β -D-glucopyranose and regarded as “holocellulose”, composed of α -cellulose, β -cellulose and γ -cellulose. However, β -cellulose and γ -cellulose are collectively called as hemicellulose [106]. The monosaccharides xylose, arabinose, mannose and glucose make up the heteropolymer known as hemicellulose. In contrast, lignin, a complex heteropolymeric aromatic structure of lignols, provides structural rigidity to plants [87]. These biomolecules consist of several functional groups which act as a binding agent of fluoride. The main functional groups involved in this bio-adsorption are hydroxyl (-OH), carboxyl (-COOH), carbonyl (C=O), sulfhydryl (-SH), etc. [91]. The surface charge of the bio-adsorbent, which regulates the defluoridation process, is dependent on the protonation or deprotonation of its functional groups. At low pH, the surface functional groups become protonated resulting in a positive surface charge that enhances the adsorption of negatively charged fluoride ions. Conversely, at high pH, deprotonation occurs, which impedes the adsorption of fluoride ions [107]. Adsorption potential of various agro-adsorbents varies depending on their chemical composition. The summary of adsorption potential using several agricultural waste-based adsorbents have been represented in Table 1. The

Table 1
Defluoridation potential of agro-based adsorbents.

Adsorbent name	pH	Adsorbent dosage	Initial fluoride concentration	Temperature	Contact time	Adsorption potential	Best kinetic model	Best isotherm model	References	
Tamarind seed	7	2 g/L	40 mg/L	30 °C	50 min	6.09 mg/g	PFO	Langmuir	[164]	
Zr impregnated coconut shell carbon	4	10 g/L	-	Room temperature	6 h	6.41 mg/g	PSO	Langmuir	[169]	
Treated rice straw	2	1.5 g/L	18 mg/L	25 °C	3 h	15.9 mg/g	PSO	Langmuir & Freundlich	[148]	
Zr impregnated coconut fibre carbon	4	20 g/L	-	Room temperature	6 h	40.01 mg/g	PSO	Langmuir	[175]	
Zr impregnated Cashew nut shell	3	15 g/L	10 mg/L	Room temperature	3 h	1.95 mg/g	PSO	Langmuir	[167]	
Zirconium impregnated groundnut shell	3	0.02 g/L	3 mg/L	-	3 h	1.26 mg/g	PSO	Freundlich	[91]	
Aluminum hydroxide coated rice husk	4.5	1 g/L	20 mg/L	27 ± 1 °C	10 min	9.5 mg/g	PSO	Freundlich	[176]	
Egg shell composite	7	1 g/L	5.6 mg/L	29.8 °C	5	24 h	37 mg/g	-	Langmuir	[107]
Tamarind fruit shell	7.05	-	-	25±°C	2	30 min	22.33 mg/g	PSO	Langmuir	[177]
Zr impregnated walnut shell	3	15 g/L	3 mg/L	Room temperature	3 h	3.11 mg/g	PSO	Freundlich	[171]	
Modified Pecan nut shell	-	8 g/L	20 mg/L	30 °C	-	2.51 mg/g	-	Langmuir	[178]	
Eggshell powder	6	24 g/L	5 mg/L	29.85 °C	2 h	1.09 mg/g	PSO	Langmuir	[179]	
Zr loaded dried orange juice residue	4	0.5 g/L	0.5 mmol/L	30 °C	4 h	1.43 mmol/g	-	Langmuir	[170]	
Raw saw dust	6	4 g/L	5 mg/L	28 ± 3 °C	1 h	1.73 mg/g	PSO	Freundlich	[88]	
Wheat straw raw	6	4 g/L	5 mg/L	28 ± 3 °C	1 h	1.93 mg/g	PSO	Freundlich	[88]	
Activated baggase carbon	6	4 g/L	5 mg/L	28 ± 3 °C	1 h	1.15 mg/g	PSO	Freundlich	[88]	
Corn stover biochar	2	5 g/L	10 mg/L	25 °C	-	6.42 mg/g	PFO	Langmuir, Redlich-Peterson, Sips, Koble Carrigan, Toth	[180]	
Magnetic cornstover biochar	2	5 g/L	10 mg/L	25 °C	-	4.11 mg/g	PFO	Langmuir, Redlich-Peterson, Sips, Koble Carrigan, Toth	[180]	
Punica granatum seed	7	0.75 g/L	2 mg/L	25 °C	75 min	1.68 mg/g	PSO	Langmuir	[181]	
Chemically activated cotton nut shell	7	1.75 g/L	10 mg/L	29 ± 2 °C	3 h	1.87 mg/g	PSO	Freundlich	[130]	
Thermally and chemically activated coconut fibre dust	6	0.5 g/L	5 mg/L	29.85 °C	2 h	38.46 mg/g	PSO	Langmuir	[102]	
Mousambi peel	7	-	-	29 ± 1 °C	40 min	1.942 mg/g	PSO	-	[182]	
Treated banana peel	2	1 g/L	10 mg/L	-	13 h	0.395 mg/g	PSO	Langmuir	[183]	
Treated coffe husk	2	18 g/L	10 mg/L	-	3 h	0.4159 mg/g	PSO	Langmuir	[183]	
Treated orange peel	5-7	0.7 g/L	2 mg/L	25 ± 2 °C	50 min	5.605 mg/g	PSO	D-R isotherm model	[83]	
Chemically modified	6-7	0.4 g/L	2.5 mg/L	-	45 min	2.34 mg/g	PSO	Langmuir	[184]	

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Table 1 (continued)

Adsorbent name	pH	Adsorbent dosage	Initial fluoride concentration	Temperature	Contact time	Adsorption potential	Best kinetic model	Best isotherm model	References
Palm kernel shell									
Sugarcane bagasse	5.4	1 g/L	4 mg/L	50 °C	1 h	1.82 mg/g	PSO	Redlich-Peterson	[89]
Pineapple peel	4	0.6 g/L	4 mg/L	80 °C	1 h	90 mg/g	Elovich	Temkin	[185]
Modified Banana peel	6	0.1 g/L	10 mg/L	40 °C	3 h	39.5 mg/g	PSO	Langmuir	[168]
Zirconium modified Tea leaf waste	3–9	3.2 g/L	5–200 mg/L	–	2 h	12.43 mg/g	PSO	Langmuir	[90]
Aluminum modified Pine saw dust	6	0.5 g/L	20 mg/L	25 °C	2 h	3.6 mg/g	PFO	Langmuir-Freundlich	[101]
Treated sugarcane	2	2 g/L	5 mg/L	29.85 °C	100 min	10.99 mg/g	PSO	Langmuir	[156]
Modified Jamun Seed	2.5	0.4 g/L	10 mg/L	25 °C	2 h	3.65 mg/g	PSO	Dubinin-Radushkevich	[98]
Bael shell	6	2 g/L	4 mg/L	50 °C	1 h	1.07 mg/g	PSO	Redlich-Peterson, Toth, Radke-Prausnitz, Langmuir, Freundlich, Temkin	[114]
Banana peel	4	0.15 g/L	10 mg/L	26.85 °C	1 h	1.212 mg/g	PSO	Freundlich	[120]
Chemically modified corn cob	6	4 g/L	23 mg/L	–	300 min	8.3 mg/g	PSO	Langmuir	[186]
<i>Pongamia pinnata</i> seed cake	7	10 g/L	10 mg/L	30 °C	90 min	0.985 ± 0.025 mg/g	Ritchie second order model	Langmuir	[187]
SnO ₂ nano composite modified from saw dust	6	–	10 mg/L	Room temperature	2 h	4.6 mg/g	PFO	Langmuir	[188]
<i>Limonia acidissima</i> shell activated carbon	7.2 ± 0.2	–	–	–	–	2.755 mg/g	PFO	Langmuir, Redlich Peterson	[189]
<i>Cucumis pubescens</i> peel	4	5 g/L	16 mg/L	30 °C	50 min	2.955 mg/g	PSO	Langmuir	[112]
Rice husk biochar	7	1 g/L	3 mg/L	30 ± 1 °C	1 h	21.7 mg/g	PSO	Langmuir & Freun	[75]
Coconut husk activated carbon	5	1.4 g/L	10 mg/L	–	–	6.5 mg/g	–	–	[48]
Zeolite modified from rice husk	5	0.105 g/L	10 mg/L	45 °C	4 h	22.83 mg/g	PSO	Freundlich	[111]
Avocado kernel seeds	7	2 g/L	15–200 mg/L	30 °C	24 h	2.77 mg/g	PSO	Sips	[166]
Al modified Guava seed	6	70 g/L	10 mg/L	25 °C	1 h	0.344 5 mg/g	PFO	Langmuir, Langmuir-Freundlich	[47]
MgO coated Peanut shell biochar	8	–	–	45 °C	400 min	83.05 mg/g	PSO	Langmuir	[190]
Black gram straw biochar	2	2.5 g/L	–	45 °C	24 h	16 mg/g	PSO	Koble-Corrigan, Langmuir, Redlich Peterson and Sips	[191]
Okra stem biochar	2	2.5 g/L	–	35 °C	24 h	20 mg/g	PSO	Koble-Corrigan and Sips	[191]

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Table 1 (continued)

Adsorbent name	pH	Adsorbent dosage	Initial fluoride concentration	Temperature	Contact time	Adsorption potential	Best kinetic model	Best isotherm model	References
Zr modified extruded tea waste	3–10	1.2 g/L	200 mg/L	Room temperature	90 min	20.56 mg/g	PSO	Langmuir	[92]
Avocado seed	6	19 g/L	5.2 mg/L	Room temperature	1 h	1.2 mg/g	PSO	Langmuir	[121]
Modified Oak shell	3	1.5 g/L	20 mg/L	40 °C	25 min	454.54 mg/g	Quasi second order PSO	Freundlich	[155]
Palm shell activated carbon	7	0.2 g/L	–	25 ± 1 °C	–	150 mg/g	PSO	Freundlich	[104]
Rice straw activated carbon	6.1	4 g/L	10 mg/L	26 ± 1 °C	3 h	2.386 mg/g	PSO	Temkin isotherm	[100]
Camellia oleifera seed shell biochar	3–9	1.6 g/L	50 mg/L	–	3 h	11.04 mg/g	PSO	Langmuir	[109]
Peanut hull biochar	7	8 g/L	10 mg/L	25 °C	2 h	3.665 mg/g	PSO	Langmuir	[122]
Chemically treated date stem	5–11	1.5 g/L	10 mg/L	Room temperature	1 h	13.03 mg/g	–	Langmuir, Temkin, Sips, and Redlich-Peterson	[115]
Ce impregnated <i>Luffa cylindrica</i>	7	0.5 g/L	10 mg/L	24.85 °C	1 h	212 mg/g	PSO	Langmuir & Freundlich	[62]
FeCl ₃ activated Citrus limetta peels	6.6	1 g/L	5 mg/L	45 °C	4 h	9.709 mg/g	PSO	Langmuir	[53]
Peanut hull	7	8 g/L	10 mg/L	25 °C	2 h	3.665 mg/g	PFO	Langmuir	[122]
Silica nano adsorbent modified from rice husk	8	4 g/L	10 mg/L	20 °C	1 h	12 mg/g	PSO	Langmuir	[63]
Watermelon rind biochar	1	0.2 g/L	50 mg/L	35 ± 2 °C	3 h	9.5 mg/g	PSO	Freundlich	[65]
HCl modified rice husk	6.5	5 g/L	–	60 °C	50 min	15.2 mg/g	–	–	[123]
Tamarind seed coat	6	0.3 g/L	5 mg/L	Room temperature	1 h	1.79 mg/g	PSO	Langmuir	[192]
Pisum sativum peel	7	4 g/L	10 mg/L	25 °C	300 min	4.71 mg/g	PSO	Freundlich	[163]
Torrefied rice husk biochar	4	4 g/L	5 mg/L	–	2 h	4.45 mg/g	PSO	Langmuir	[99]
Al/La hydroxide loaded Wheat straw biochar	9	1 g/L	6 mg/L	25 °C	7 h	51.28 mg/g	PSO	Langmuir	[193]
Lanthanum doped magnetic teff straw biochar	3.97	3.57 g/L	–	–	56.4 min	98.89 %	–	–	[194]
Sunflower husk	5.5	4 g/L	80 mg/L	Room temperature	150 min	10.9 mg/g	PSO	Freundlich	[113]
Zr loaded Macademia nut shell biochar	7	1 g/L	10 mg/L	25 ± 2 °C	1 h	6.48 mg/g	PSO	Langmuir	[195]
Date stem	–	–	–	–	–	20.05 mg/g	PSO	Langmuir	[127]
Modified Palm shell	7	5 g/L	20 mg/L	–	2 h	0.44 mg/g	PSO	Langmuir	[165]
Magnetic tea waste biochar	3.6	0.5 g/L	50 mg/L	34	24 h	18.78 mg/g	PSO	Freundlich	[160]
Tri metal impregnated	7.0 ± 0.2	1 g/L	6 mg/L	–	2 h	111.11 mg/g	PSO	Langmuir	[118]

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Table 1 (continued)

Adsorbent name	pH	Adsorbent dosage	Initial fluoride concentration	Temperature	Contact time	Adsorption potential	Best kinetic model	Best isotherm model	References
rice straw biochar									
Bajra husk	2	1 g/L	5 mg/L	Room temperature	6 h	1.942 mg/g	–	–	[196]
Chemically treated corncob biochar	4	1 g/L	0.5–10 mg/L	25 °C	250 min	7.24 mg/g	PSO, Elovich kinetic model	Langmuir and Hills	[162]
Chemically treated rice husk biochar	3	50 g/L	40 mg/L	55 °C	2 h	97.57 mg/g	PSO	Langmuir	[174]

adsorption capacity of an adsorbent can be altered by modifying the way of its preparation. Generally, raw agricultural waste-based adsorbents have been reported to have lower adsorption potential as compared to commercial ones [107–109]. Thus, to enhance the adsorption efficiency, several modifications have been incorporated. One of such modification is impregnation of multivalent metal in the adsorbent surface. For example, Ce impregnated *Luffa cylindrica* showed a higher adsorption efficiency of 212 mg/g compared to raw *Luffa cylindrica*, which had an efficiency of 52.63 mg/g [76]. Similarly, Zirconium impregnated groundnut shell carbon exhibited almost 84 % removal of fluoride, whereas raw groundnut shell carbon achieved only 63.67 % of removal [110]. Another modification involves reducing the particle size of metal impregnated adsorbents, as it can increase their surface area and improve adsorption efficiency. For instance, Zirconium (Zr) modified ultrafine tea powder showed a higher percentage (93.6 %) of fluoride removal than Zr modified ground tea powder (55.7 %) due to its larger surface area [109]. Further improvements in adsorption efficiency were reported by Mei et al. [111] who utilized extrusion technology to enhance particle surface area. For instance, Zr-Tea waste exhibited a removal percentage of 61 %, whereas, extruded Zr-Tea was reported to have an efficiency of 97 %. Moreover, these agricultural wastes have been used as precursors for biochar production, which has been extensively studied for defluoridation purposes [112]. Another approach is the utilization of these agricultural wastes as precursors for the green synthesis of nanoparticles. Studies have reported significant defluoridation potential of Cerium oxide nanoparticles synthesized from *Litchi chinensis* seed extract [113]. Similar findings have been reported by Ayinde et al. [114], where nano Ag–MgO–HaP synthesized from *Citrus paradise* peels exhibited defluoridation capabilities. Fig. 3 illustrates the application of agricultural waste as an adsorbent for the aqueous removal of fluoride. Although commercial adsorbents such as activated carbon, zeolite, activated alumina etc. outperform bio-adsorbents in terms of higher adsorption capacity, larger surface area and greater porosity, they also have certain limitations, such as being expensive, increasing sludge volume, generating carbon fines, leaching of toxic chemicals and requiring frequent filter changes [115,116]. Therefore, identification of an agro-based adsorbent with the potential to perform well under optimal environmental conditions is the necessity to address this crisis.

3. Factors affecting bio-sorption of fluoride

Adsorption potential of the target adsorbent relies on several factors, such as; pH, adsorbent dose, initial concentration of pollutant,

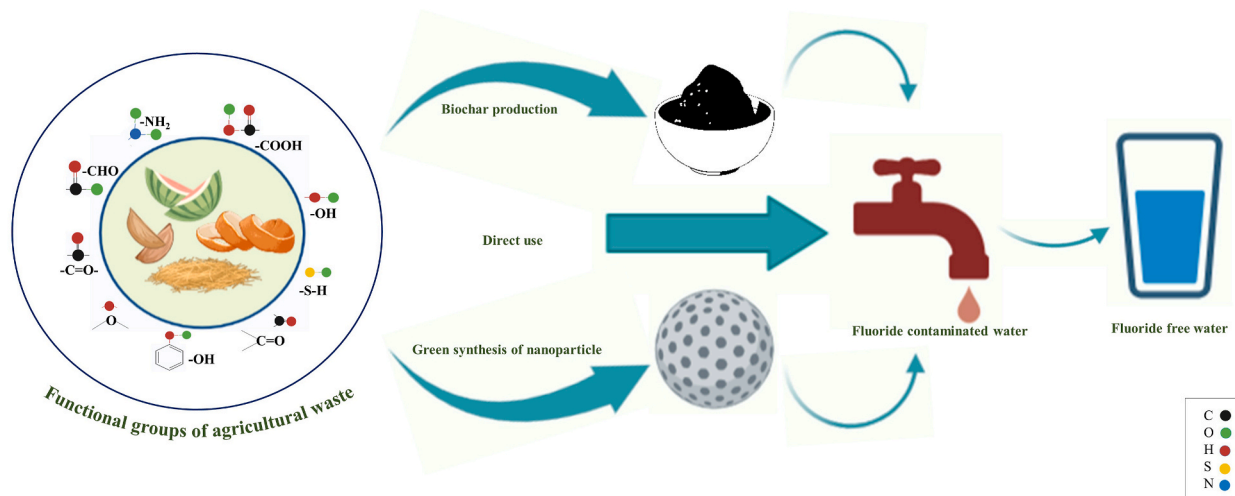
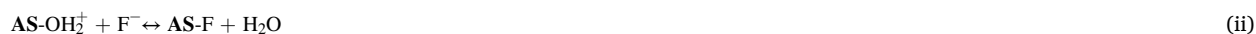


Fig. 3. Different approaches of using agro-waste for water defluoridation.

temperature, effects of co-existing ions. Each of the factors have been discussed in detail in the following section. Furthermore, [Table 1](#) exhibits the defluoridation potential of various agro-based adsorbents, accompanied by the parameters that influencing adsorption.

3.1. pH

The efficiency of adsorption is greatly influenced by the pH level of the aqueous solution. The nature of the interaction between fluoride and the adsorbent surface is determined by the pH level, which affects the affinity of fluoride towards the adsorbent surface. Research has indicated that agro-adsorbents demonstrate their optimal adsorption potential typically within the pH range of 4–7, as demonstrated in [Table 1](#). Although, some has been reported to exhibit their maximum adsorption potential at very low pH (>4) [[79](#), [117](#)]. The surface charge of the adsorbent can explain the differences in its optimum pH for fluoride adsorption. The pH at which the adsorbent has zero net charge, known as the zero-point charge pH (pH_{zpc}), is essential in determining its surface charge and thus its fluoride adsorption capability. For example, Zr modified rice husk biochar with a pH_{zpc} (5–6) has been reported to exhibit optimum adsorption potential at pH 4 [[118](#)]. Alumina impregnated activated carbon with pH_{zpc} 8.6 has exhibited maximum adsorption potential at pH 6.1 [[119](#)]. According to Alagumuthu and Rajan [[110](#)], the Zr-modified groundnut shell exhibited the highest level of fluoride adsorption at pH 3, consistent with the pH (pzc) value of 4.6. At pH below pH_{zpc} the adsorbent surface is positively charged thus the negatively charged ion fluoride gets attached with the adsorbent surface whereas, pH above pH_{zpc} the rate of adsorption gets decreased due to its negative surface charge at that pH [[67](#),[120](#),[121](#)]. Fluoride adsorption has been found to decrease at very low pH due to its existence in the form of weakly ionized Hydrofluoric acid (HF) [[102](#)]. Conversely, at high pH (above 7–8) defluoridation efficiency has also been observed to decrease on account of strong repulsion between negatively charged fluoride and hydroxyl (OH⁻) ions [[122](#)]. The possible reason for the enhancement of fluoride adsorption at lower pH levels could be explained by the following reactions [[118](#),[123](#),[124](#)].



Where, **AS** = Adsorbent surface and **F⁻** = Fluoride.

At lower pH, due to surface protonation, the positive charge on the surface is increased. This heightened positive charge facilitates the adsorption of fluoride through both hydrogen bonding and electrostatic attraction. Agro-adsorbents, capable to perform in neutral pH range could be the ideal choice for field application eliminating the need for any further pH adjustment. Although commercial adsorbents such as activated alumina, bauxite and ferric hydroxide exhibit maximum adsorption capacity in the neutral pH range, their adsorption efficiency is comparable to that of adsorbents derived from agricultural waste, including treated eggshells, coconut fiber, *Luffa cylindrica* etc. [[65](#),[66](#),[76](#),[125](#),[126](#)].

3.2. Adsorbent dose

Adsorbent dose has a significant influence on fluoride removal efficiency. For a fixed fluoride concentration, an increase in the adsorbent dose results in higher removal efficiency. This is because the increased dosage leads to an expansion of the surface area, creating more active binding sites for fluoride adsorption [[127](#)]. However, after an optimum dose, the percentage of fluoride removal remains constant. This could be attributed to the lower fluoride concentration present in the solution [[76](#)]. Saini et al. [[119](#)] has reported sharp increase in fluoride removal efficiency from 40 % to 94.93 % with increase in adsorbent dose from 0.5 g/l to 4 g/l. Nevertheless, there has not been reported any significant change in adsorption efficiency after the dosage of 10 g/l. Mei et al. [[128](#)] observed that the adsorption capacity has increased with increasing dosage of ZrO₂ impregnated biochar and reached equilibrium at dosage of 1.6 g/l with an adsorption efficiency of 5.6 mg/g. After adsorbent dosage 1.6 g/l, no such significant enhancement in adsorption capacity has been reported owing to lower fluoride concentration present in the solution. Furthermore, adsorption capacity per unit weight of adsorbent has found to decrease with increase in adsorbent dosage. The reason for this can be attributed to the stronger intermolecular attraction among the adsorbent molecules, which results in their clustering and the consequent overlapping of the active binding sites [[129–131](#)]. Scheverin et al. [[95](#)] has reported a similar trend, where the highest adsorption (88.91 %) was observed at an adsorbent dose of 4 g/l, and any further increase in the adsorbent dose led to a decrease in the adsorption capacity. Singh et al. [[132](#)] has also reported that the highest percentage of fluoride removal, which was 53 %, occurred at an adsorbent dose of 2 g/l. However, increasing the adsorbent dose beyond this point resulted in a decrease in adsorption capacity. Bakhta et al. [[133](#)] reported similar findings, where an increase in AC-Al dosage from 0.2 to 1.5 g/L resulted in a significant increase in fluoride removal percentage from 29 % to 90 %. This can be attributed to the greater surface area of the adsorbent at higher dosages, which facilitates the creation of more active binding sites for fluoride adsorption. However, it was observed that further increase in the adsorbent dose (beyond 1.5 g/L) did not result in significant improvements in fluoride removal due to a reduction in surface area caused by the overlapping of binding sites at higher doses. Although there is a positive correlation between the adsorbent dose and the efficiency of fluoride removal, it is important to note that there exists an optimal dose of adsorbent required for achieving maximum fluoride removal efficiency. Exceeding this optimum dose can negatively impact the interaction between the adsorbent molecule and fluoride, ultimately leading to a disruption of the adsorption process [[134](#)].

3.3. Initial concentration of fluoride

The efficacy of adsorbents for removing fluoride is significantly affected by the initial concentration of fluoride in the solution. As the concentration of fluoride increases, the capacity of the adsorbent to remove fluoride also increases. However, this increase is only observed up to a certain concentration, after which the adsorption capacity reaches equilibrium [109]. This is because at lower concentrations of fluoride, there are more active sites available for the adsorption process, which facilitates the rate of fluoride adsorption. On the other hand, at higher concentrations, the active sites on the adsorbent surface become saturated, and the adsorption capacity reaches equilibrium [128]. In addition, a higher concentration gradient between the solid and aqueous phase interface increases the driving force, which helps to overcome the mass transfer resistance of fluoride, leading to a higher uptake of fluoride until saturation is reached [59,135]. Several studies have reported similar trends in the relationship between fluoride concentration and adsorption capacity. For instance, Zhou et al. [136] found that the adsorption capacity of an adsorbent increased from 5.75 mg/g to 107.87 mg/g with increasing fluoride concentration ranging from 6 mg/L to 160 mg/L. The adsorption capacity of Tea-Al-Fe was also observed to increase from 4.56 mg/g to 17.06 mg/g with increasing fluoride concentration ranging from 10 mg/L to 200 mg/L [137]. Similarly, Mondal [138] reported that fluoride removal increased with increasing fluoride concentration ranging from 2.0 to 20.0 mg/L. This could be due to the higher interaction between fluoride and the bio-sorbent surface at higher concentrations. At lower concentrations of fluoride, the number of available binding sites is higher than the number of adsorbate molecules, and the adsorption process becomes independent of adsorbate concentration. However, at higher adsorbate concentrations, the adsorption process gradually becomes dependent on adsorbate concentration due to the limited availability of active binding sites [139]. The percentage of fluoride removal can be calculated using equation.

$$\%R = \frac{C_0 - C_e}{C_e} \times 100 \quad (\text{iv})$$

Where, %R = Percent removal of fluoride.

C_0 = Initial concentration of fluoride (mg/L)

C_e = Final concentration of fluoride (mg/L)

3.4. Temperature

Temperature has an influential effect towards adsorbents efficiency. The impact of temperature on adsorbent effectiveness varies depending on the properties of the adsorbent. While some adsorbents perform well at lower temperatures, others require higher temperature for optimal performance. Majority of studies have reported defluoridation as an exothermic process, where with increasing temperature, the percentage of removal has found to decrease. For instance, Kumar reported reduction in fluoride removal with increasing temperature ranging from 25 °C to 45 °C. The reason for this could be ascribed to the rise in Brownian motion and the rupture of intermolecular bonds between PHP biochar and fluoride at elevated temperatures. Similarly, Mondal [138] noted a decrease in fluoride removal with rising temperatures between 300 and 333K. This can be attributed to the weakening of the attractive forces between the adsorbent surface and fluoride atoms. However, studies have also been reported with endothermic nature of adsorption where, with increasing temperature fluoride removal has found to increase. For example, Siddique et al. [67] found that the removal of fluoride increased from 73.1 % to 91.3 % with increasing temperature from 25 °C to 45 °C for AC-CLP₅₀₀. The reason for this that higher temperatures (i) can lead to swelling in the internal structure of AC-CLPs and (ii) can increase the mobility of fluoride ions, allowing for deeper penetration towards the adsorbent surface. Vijila et al. [140] also reported a similar trend, showing that an increase in temperature (from 293K to 333K) resulted in a higher percentage of fluoride removal, with a maximum removal rate of around 83 %. Apparently, this endothermic nature implies that this process of adsorption is governed by diffusion process and with rising temperature, the thickness of the boundary layer reduces, causing an increase in the diffusion rate of adsorbate molecules [108]. Furthermore, some investigations have noted a combination of the two effects, with an initial increase in adsorption as temperature is raised, followed by a diminishing trend in further enhancement [141]. Numerous variables, such as the type of adsorbent, the selected temperature range, and the experimental condition can affect the impact of temperature on adsorption [142]. For instance, high temperature was preferred for defluoridation using treated *Nostoc* sp. (algal biomass) as it promotes the growth of algae and speeds up the defluoridation process [122]. However, special care must be taken when attempting defluoridation in the field, as a change in temperature can affect the adsorbent's efficiency, which is not ideal for commercial application. In general, physisorption is more advantageous at lower temperatures, whereas chemisorption is more advantageous at higher temperatures. However, beyond optimum temperature, the freshly formed bond may rupture, resulting in desorption.

3.5. Effects of co-existing ions

To accurately determine the effectiveness of an adsorbent for removing fluoride from groundwater, it is important to consider the impact of other ions present. Co-existing ions can interfere with the defluoridation process by competing for the active binding sites on the surface of the adsorbent. Groundwater typically contains several ions, including nitrate (NO₃⁻), sulfate (SO₄²⁻), phosphate (PO₄³⁻), chloride (Cl⁻), carbonate (CO₃²⁻), bicarbonate (HCO₃⁻), among others. Multiple studies have investigated the effect of co-existing ions and found that increasing concentrations of other ions can significantly reduce fluoride adsorption [79,143,144]. Scheverin et al.

[95] conducted batch experiments to determine the impact of co-existing ions and reported that the reduction in fluoride adsorption followed the order of $\text{Cl}^- < \text{SO}_4^{2-} < \text{HCO}_3^- \approx \text{PO}_4^{3-}$ [145]. also found that Cl^- does not interfere with fluoride adsorption as much as sulfate, which, being a divalent ion, increases the coulombic repulsive force and reduces the probability of fluoride adsorption on the adsorbent surface. The significant reduction due to PO_4^{3-} can be explained by the fact that both phosphate and fluoride are inner-sphere complex-forming ions that compete for the same binding site on the adsorbent surface. Manna et al. [146] studied the effects of other ions and found that bicarbonate (HCO_3^-) and sulfate (SO_4^{2-}) had a significant impact on the removal process. An increase in bicarbonate concentration raises the concentration of OH^- ions, causing competition for the active binding sites between fluoride and hydroxyl ions, ultimately leading to a reduction in adsorption. Cai et al. [109] determined the adsorption capacity of UTP-Zr in the presence of various co-existing ions and reported a reduction in defluoridation in the following order: $\text{NO}_3^-/\text{Cl}^- < \text{SO}_4^{2-} < \text{HCO}_3^-$. Mariappan et al. [147] found that fluoride adsorption decreased by almost 25 % with increasing concentrations of HCO_3^- from 10 to 50 mg/L. However, Cl^- and SO_4^{2-} were found to have less impact on fluoride adsorption. The preferential selection of phosphate and sulfate over fluoride can be attributed to the fact that both ions have surface charges higher than fluoride. The increased surface charge density of these two ions eventually interferes with fluoride adsorption [148]. Overall, the impact of co-existing ions on fluoride adsorption depends on their concentration and charge, as well as the adsorbent properties.

4. Adsorption isotherm

In-depth examination of the adsorption process at the solid-liquid interface can be accomplished through several mathematical models. The equilibrium interaction between the adsorbate and adsorbent can be represented graphically using an adsorption isotherm [149]. Through this analysis, the distribution of solute molecules in the adsorption system can be examined and the related parameters can be optimized accordingly [150]. The equilibrium models for adsorption provide accurate predictions of the efficiency of the target adsorbent, which is critical for determining its commercial viability [151]. Furthermore, these models also offer insight into the surface properties and affinities of the employed adsorbent towards solute molecule [152,153]. Several models have already been developed to study adsorption isotherms, including Langmuir, Freundlich, Redlich–Peterson, Dubinin–Radushkevich, Sips, Temkin, Brunauer–Emmett–Teller, Toth, Koble–Corrigan, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm etc. [35]. Table 1 demonstrates that Langmuir and Freundlich isotherm models have exhibited consistent effectiveness in fitting adsorption data and are widely recognized as the most reliable models. However, the Sips, Dubinin–Radushkevich (D-R), Temkin and Redlich–Peterson (R–P) isotherm models are rarely found to fit with the adsorption data. Generally, the popularity of an isotherm model depends on its ability to be applied universally and its simplicity in terms of mathematics. However, the accuracy of an isotherm model is influenced by the availability of independent factors in the model [154]. The Langmuir isotherm model is widely used due to its clarity and strong theoretical basis. Originally developed for gas molecule adsorption, further it has been modified to study adsorption in solution system [155]. This model assumes that adsorption takes place at a fixed number of localized, identical and equivalent sites. It represents monolayer adsorption on a homogenous surface with no interaction or steric hindrance between adjacent adsorbed molecules [156]. Another assumption of this model is that each adsorption site exhibits equal affinity for the adsorbate molecule and transmigration of adsorbate in the surface plane is restricted [157]. The Langmuir isotherm model provides information about the efficiency of the target adsorbents and can also determine the nature of adsorption using the separation factor (R_L) [158]. $R_L < 1$ indicates favorable adsorption, $R_L > 1$ indicates unfavorable adsorption, $R_L = 1$ indicates linear adsorption, and $R_L = 0$ indicates irreversible adsorption. The Freundlich isotherm is another popular model that assumes random distribution of adsorption heat and affinity on the adsorbent surface, where each adsorption site has a different bond energy. Furthermore, the adsorption energy decreases rapidly throughout the entire adsorption process [159,160]. Dubinin–Radushkevich model describes nature of adsorption depending upon the free energy (E) required for 1 mol of adsorbate to get attached on solid surface of the adsorbent. Adsorption with E value between 8 and 16 will be termed as chemisorption whereas physisorption will be regarded having E value < 8 [161]. The Temkin isotherm depicts about heat of adsorption as well as illustrate the relationship between adsorbate and adsorbent [162]. The Hill isotherm suggests that adsorption is a cooperative phenomenon as binding sites can influence each other's ligand binding ability [163]. The Redlich–Peterson isotherm combines the characteristics of the Langmuir and Freundlich isotherms to generate a comprehensive isotherm equation [164]. There are studies that have reported adsorption data that can be fit with more than one isotherm model [76,91,165].

5. Adsorption kinetics

Kinetic study is conducted to investigate the mechanism of an adsorption process. It depicts the rate of solute uptake at the solid-liquid interface, which serves as a secondary indicator of efficacy of the chosen adsorbent. Therefore, while developing a water treatment facility, it is crucial to evaluate the relationship between sorbate and sorbent molecules [166]. Solute uptake is typically achieved through a combination of diffusion and chemical reactions. The entire process can be further subdivided into following steps: (a) the adsorbate ion moves from the bulk solution to the adsorbent surface (bulk diffusion); (b) Diffusion of the adsorbate molecule towards the external surface of the adsorbent (external film diffusion); (c) Transfer of adsorbate molecule into the internal pores of the adsorbent (internal pore diffusion); and (d) the solute molecule is adsorbed onto the active binding sites of the adsorbent surface [167]. There are numerous mathematical models available for evaluating adsorption kinetics data, including the pseudo first-order model, pseudo second-order model, Pore diffusion model, Weber, and Morris intra-particle diffusion model, etc. By employing these models, it is possible to determine the rate-controlling step of the entire adsorption process [67]. Depending on the rate-controlling step, the mechanism of the adsorption can be specified. For instance, according to the pseudo first-order model, the adsorption nature may be physisorption. Therefore, in such a case, the rate-controlling step is diffusion which is independent of the concentration of both

reactants [35]. In the physisorption process, the rate of adsorption is inversely proportional to the particle size, distribution coefficient and film thickness. However, in the case of chemisorption indicated by the pseudo second-order model, the rate-controlling step is a chemical reaction. In such instances, the reaction rate is not dependent on particle diameter but instead relies on the ionic concentration of the solution and temperature [166]. The use of the pseudo first-order model has been successful in fitting data for fluoride adsorption using aluminum-modified Pine sawdust [120]. On the contrary, the pseudo second-order model has been found to support data for fluoride adsorption using materials such as rice husk, sawdust, coconut husk etc. [59,91,107]. Another model that can be utilized to identify the rate-controlling step of the adsorption process is the intra-particle diffusion model. However, this model is not commonly used due to its complex mathematical formulation [168]. On the other hand, the pore diffusion model suggests that the solute molecule travels from the surface of particles to the interior sites of a particle via pore diffusion [169]. For, defluoridation using agricultural waste as an adsorbent, the kinetics data have generally been found to fit well with the pseudo second-order model, followed by the pseudo first-order model.

6. Thermodynamics study

Thermodynamic parameters play a crucial role in determining the type of adsorption and provide valuable insights into the adsorption process. By conducting adsorption tests at different temperatures, the values of enthalpy change (ΔH°), entropy change (ΔS°), and Gibbs free energy change (ΔG°) can be calculated [77]. A positive value of ΔH° indicates an endothermic nature of adsorption, while a negative value suggests an exothermic nature [79,102]. An increase in temperature leads to an increase in

Table 2
Fluoride removal mechanism of different agro-based adsorbents.

Adsorbent name	Probable mechanism	References
Tamarind seed	Electrostatic bonding, hydrogen bonding	[164]
Zr impregnated coconut shell carbon	Van der Waals interaction, ion exchange	[169]
Treated rice straw	Ion exchange	[148]
Zirconium impregnated coconut fibre carbon	Van der Waals interaction, ion exchange	[175]
Zirconium impregnated cashew nut shell carbon	Ion exchange	[167]
Modified groundnut shell carbon	electrostatic attraction, ion exchange	[91]
Tamarind fruit shell carbon	Complexation with Calcium	[177]
Modified Walnut shell carbon	Electrostatic attraction, Ion exchange	[171]
Modified nut shell	Ion exchange	[178]
Zirconium loaded orange peel	Ligand exchange	[83]
Orange juice residue	Ligand exchange	[170]
Modified Banana peel	Electrostatic attraction, Ion exchange	[168]
Modified cottonnut shell carbon	Ion exchange	[147]
Modified Palm kernel shell	Electrostatic attraction, chemisorption	[184]
Pineapple peel and Orange peel	Electrostatic attraction	[185]
Modified ultrafine tea powder	Ion exchange, electrostatic attraction	[90]
Aluminum modified Pine saw dust	Electrostatic interaction, ionic bonding, ion exchange	[101]
Natural Banana peel	Electrostatic attraction, Ion exchange	[120]
Modified Jamun seed	Electrostatic interaction	[98]
Bael shell activated carbon	Electrostatic attraction	[114]
Coconut husk activated carbon	Ion exchange	[48]
Avocado kernel seed carbon	Electrostatic attraction, Ligand exchange	[166]
Aluminum modified guava seed	Ligand exchange	[47]
SnO ₂ nano composite modified from saw dust	Ion exchange	[188]
MgO coated Peanut shell biochar	Electrostatic attraction, inner sphere complexation	[190]
Black gram straw biochar	Electrostatic attraction, ligand exchange, Hydrogen bonding	[191]
Zirconium modified tea waste	Ion exchange, electrostatic interaction	[92]
Camellia oleifera seed shell	Ion exchange	[109]
Palm shell activated carbon	Electrostatic attraction, hydrogen bonding, ion reaction	[165]
Palm shell activated carbon	Electrostatic attraction, Ion exchange	[104]
Rice straw activated carbon	Electrostatic interaction	[100]
Rice husk derived silica nano adsorbent	Electrostatic attraction, Ion exchange	[63]
Modified <i>Luffa cylindrica</i>	Ion exchange, electrostatic attraction, Ion-pair formation, Hydrogen bonding	[62]
Camellia oleifera seed shell biochar	Hydrogen bonding, ion exchange	[109]
Torrefied rice husk biochar	Electrostatic attraction, Ion exchange	[99]
Al/La hydroxide loaded Wheat straw biochar	Electrostatic attraction, Ion exchange	[193]
Rice husk	Electrostatic interaction, ion exchange	[123]
Pisum sativum peel	Ion exchange, complexation, electrostatic interaction	[163]
Magnetic tea waste biochar	Ion exchange, electrostatic force, surface complexation, hydrogen bonding	[160]
Tri-metal-impregnated rice straw biochar	Electrostatic attraction, ion exchange	[118]
Zr loaded Macademia nut shell biochar	Hydrogen bonding, electrostatic attraction, ion exchange	[195]
Watermelon rind biochar	Metal fluoride precipitation, electrostatic attraction	[65]
Date stem activated carbon	Ion exchange, complexation, electrostatic interaction	[127]
Chemically treated corn cob biochar	Electrostatic attraction, ion exchange, Ligand exchange	[162]
Chemically treated rice husk biochar	Surface complexation, ion exchange, Electrostatic attraction	[174]

adsorption in endothermic reactions due to factors such as pore size enlargement, surface activation, an increase in the kinetic energy of fluoride ions and reduction in the thickness of the boundary layer [170]. In contrast, exothermic reactions lead to a reduction in adsorption with an increase in temperature due to the weakening of the attractive force between fluoride and the adsorbent molecule [171]. The nature of adsorption process can be identified based on the change in enthalpy (ΔH°). In physisorption, ΔH° mostly ranges within 2.1–20.9 KJ/mol⁻¹, whereas in chemisorption, it ranges between 80 and 200 KJ/mol⁻¹ [67]. Positive value of enthalpy (ΔH°) has been reported by Takmil et al. [172] which indicates endothermic nature of adsorption process. However exothermic nature of adsorption has been reported by Kazi et al. [131] with negative (–42.2 kJ/mol) change value in enthalpy. The degree of randomness in the adsorption process determined by the change in entropy (ΔS°) [173,174]. An increase in entropy (positive ΔS°) indicates greater disorder at the solid-liquid interface, resulting from changes in the hydration of adsorbed fluoride ions [110]. Conversely, a negative ΔS° value indicates a decrease in the degree of randomness at the solid-solution interface, which can have a significant impact on fluoride adsorption [123,175]. Araga et al. [117] investigated the thermodynamic parameters and found a negative value (–42.98 kJ mol⁻¹ K⁻¹) of entropy which implies that due to decrease in randomness the adsorbate molecules tend to escape from the solid phase to liquid phase eventually, causes reduction in adsorption. Furthermore, positive entropy value was observed by Saini et al. [119], which indicates the adsorbent's activeness towards adsorption due to significant change occurred in the internal structure during adsorption. Gibbs free energy change (ΔG°) determines the spontaneity of the adsorption process. A positive value of ΔG° indicates non-spontaneous adsorption, while a negative value indicates spontaneous adsorption [102]. Negative ΔG° values indicates a strong affinity of fluoride ions towards the adsorbent molecule. The range of ΔG° values within 0 to –20 kJ/mol indicates physisorption whereas values within the range of –80 to –400 KJ/mol⁻¹ suggests chemisorption [142,176]. Mei et al. [128] reported a negative value of ΔG° and found a spontaneous adsorption process. Moreover, non-spontaneous nature of adsorption has also been reported by Patil et al. [177] while performing defluoridation employing Pineapple peel as an adsorbent. Overall, thermodynamic parameters are vital in understanding the nature of the adsorption process and can be used to optimize the conditions for effective adsorption.

7. Mechanism of fluoride removal

The biosorption of fluoride from water involves various physical and chemical interactions between the adsorbate and adsorbent. The specific properties of the adsorbent such as surface area, porosity and functional groups play a crucial role in determining the pathway of the biosorption process. However, studies have reported that the removal of fluoride from water involves multiple mechanisms. Therefore, understanding the actual process of fluoride removal is important to optimize the efficiency of the adsorbent.

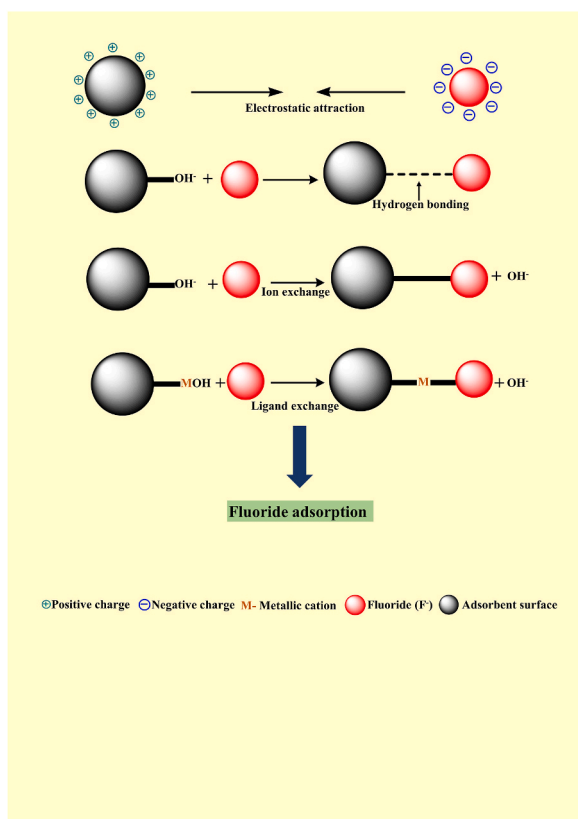


Fig. 4. Probable mechanism of fluoride bio-sorption employing agro-based adsorbents.

Table 2 summarizes the mechanisms involved in the removal of fluoride using various agro-adsorbents. In most cases, multiple mechanisms have been identified through analysis of data obtained from instruments such as Fourier-transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDS), x-ray photoelectron spectroscopy (XPS), and zeta potential analyzer. The primary pathways of adsorption include electrostatic attraction, hydrogen bonding, ion exchange and ligand exchange, which are illustrated in Fig. 4.

7.1. Electrostatic attraction

The process of fluoride adsorption involves the attraction between molecules of opposite charge. Specifically, the positively charged adsorbent surface and the negatively charged fluoride ion experience an electrostatic force of attraction. The surface charge of the adsorbent is closely related to the pH of the solution, and can be determined by measuring its point of zero charge (ZPC). When the pH is lower than the ZPC value, the adsorbent surface carries a positive charge, enabling the adsorption of negatively charged fluoride. Ashraf et al. [178] found that the optimum pH for fluoride adsorption was 3.6, which was lower than the observed pH_{zpc} (5.6) of magnetic tea waste biochar. This is because at a lower pH than the pH_{zpc} , the surface carries a positive charge, attracting the negatively charged fluoride ion. Similarly, Yadav and Jagadevan [118] reported an optimum pH of 4 for fluoride adsorption, which was lower than the pH_{zpc} value of BCF-700. The predominance of electrostatic attraction has also been observed in defluoridation studies using watermelon rind biochar and rice husk as adsorbents, as reported by Refs. [79,140].

7.2. Hydrogen bonding

Fluoride can be adsorbed on the surface of an adsorbent through hydrogen bonding, which occurs between the electropositive hydrogen atom in the adsorbate and the electronegative fluoride atom. This results in physisorption, which is faster to reach equilibrium compared to chemisorption where electron exchange occurs [179]. Hettithanthri et al. [180] observed effective adsorption of fluoride on LDH-CCBC500 at a $pH < pH_{zpc}$, attributing it to protonation of hydroxide groups (OH^{2+}), which attracts and adsorbs fluoride on the adsorbent surface through hydrogen bonding. This is supported by the displacement and low intensity of OH^- ions, indicating the presence of strong hydrogen bonding. Sahu et al. [181] also reported similar findings for fluoride adsorption using iron-infused *Pisum sativum* peel as an adsorbent, while hydrogen bonding has been attributed to fluoride adsorption by Tamarind seed and Palm shell activated carbon as well [182,183].

7.3. Ion exchange

Ion exchange, involves the replacement of one ion with a counter ion of the same size and charge. This process is rapid and reversible, and is not specific to fluoride as the selection of ions by an ion exchange resin depends on the size, valency, and concentration of the ions in the solution. The preferential selection trend followed by ion exchange resins is typically as follows: Citrate > Sulfate > Oxalate > Iodide > Nitrate > Chromate > Bromide > Thiocyanate > Chloride > Acetate > Fluoride [49]. However, agro-adsorbents contain a large amount of OH^- in their structure, which allows for fluoride to attach easily to the adsorbent surface through the exchange of OH^- . Although this pathway is imprecise, it plays a crucial role in conducting biosorption of fluoride from water. For instance, Choong et al. [123] investigated the fluoride adsorption capacity of $MgSO_3$ impregnated Palm shell activated carbon and reported both C-OH/C-OOH as ion exchange sites for fluoride adsorption. Similarly, Mei et al. [128] observed the same mechanism for fluoride adsorption in Zirconium impregnated biochar and reported the plausible reason as an ion exchange between Zr-OH and F^- .

7.4. Ligand exchange

The prime mechanism by which fluoride is adsorbed onto the adsorbent surface is ligand exchange, which is specific and irreversible in nature. Ligand exchange involves the exchange of a ligand, resulting in fluoride being adsorbed onto the adsorbent surface through the formation of a covalent bond [142]. Ligand exchange precedes chemisorption, where electron exchange and the formation of an inner sphere complex occur. This mechanism provides high adsorption capacity owing to its strong selectivity for anions [53]. Apparently, while dealing with metal impregnated agro-sorbents, a layer of hydroxyl ions forms on the adsorbent surface due to hydration reactions. However, due to the high affinity of metal ions for fluoride ions, these metal ions are attached to the adsorbent surface through ligand exchange, and the OH^- ions are released into the aqueous solution. The plausible reason of fluoride adsorption by Avocado kernel seed was investigated by Salomón-Negrete et al. [184] and reported ligand exchange as the responsible mechanism with -SiOH functionalities. Similarly, Zhou et al. [136] identified ligand exchange as the key mechanism for fluoride adsorption by La/Fe/Al-RSBC.

8. Regeneration study

The reusability of an adsorbent is evaluated through regeneration studies, which determines its economic effectiveness. Many researchers have investigated the regeneration potential of agricultural waste-based adsorbents and found that they can be effectively regenerated using acid or alkali reagents such as NaOH or HCl [102,144,185]. NaOH is preferred because it is effective in replacing fluoride with hydroxyl ions due to their almost similar size [185]. Various reagents such as water, NaOH, HCl, and Na_2SO_4 have been

used for desorption, with NaOH found to be the most effective, achieving up to 98 % desorption [144]. The concentration of NaOH used for desorption affects the percentage of fluoride desorbed, with higher concentrations resulting in higher desorption rates. For example, 91 % fluoride was desorbed with 0.1 M NaOH, while only 4 % was desorbed with 0.001 M NaOH [102]. Similar findings were reported by Alagumuthu and Rajan [185], where 92.6 % of fluoride was desorbed at 2.5 % NaOH concentration. Bhaumik and Mondal [186] observed that fluoride ion leaching started at pH 8, with maximum desorption recorded at pH 12. The adsorbent's regeneration potential varies widely depending on its composition. Some adsorbents have shown the same adsorption potential over several regeneration cycles, while others have shown no regeneration potential at all. For example, Zirconium impregnated coconut shell carbon retained almost similar adsorption potential after performing four regeneration cycles, while adsorbents such as sugarcane bagasse and bael shell activated carbon, were reported with no regeneration potential at all [108,132,187]. According to Jha et al. [102] and Paudyal et al. [188], Zr loaded orange peel showed over 80 % fluoride adsorption after eight regeneration cycles, while dried orange juice residue demonstrated above 96 % fluoride adsorption after four cycles of adsorption-desorption. Date stem biochar and Walnut shell demonstrated a very low regeneration capacity, with fluoride adsorption potential of only 20 % and 28 % respectively, after three regeneration cycles [144,189]. Basically, the gradual reduction in adsorption capacity of a regenerated adsorbent can be ascribed to inactive nature of the substituted hydroxide group [76].

9. Cost analysis

Efficiency and cost effectiveness are critical factors that need to be considered for successfully commercializing any product. The cost of a product is usually determined by calculating the expenses incurred at various stages of its production. While many adsorbents made from agricultural waste are freely available in nature, they cannot be used directly for defluoridation purposes and need to be processed to serve as effective adsorbents. Therefore, the cost of producing an adsorbent is determined by the phases involved in the preparation process, which include the collection of raw materials, size reduction, cleaning, drying, and the consumption of chemicals and electricity. According to Mukherjee et al. [130], the cost of producing zeolite NaA from rice husk as a template was found to be 26.092 USD for 94g. This production cost lower than that of commercially available zeolite, which costs 97.03 USD for 100g making the zeolite produced from rice husk more economical. Nehra et al. [76] reported that the net production cost of Lc-Ce (Ce impregnated *Luffa cylindrica*) was USD 35.5/Kg, which was comparatively cheaper than other adsorbents studied. Furthermore, Ibrahim et al. [190] reported the cost-effectiveness of modified Sweet Lime waste ACP-250 and ACP-500. The adsorbent made from beal shell (BAC) and *Parthenium hysterophorus* (PHAC) was also found to be cost-efficient, with estimated costs of 1.22 USD/Kg and 1.0615 USD/kg, respectively, which is significantly lower than commercially available activated charcoal, which costs around 15.56 USD/Kg [191]. Iron modified rice husk biochar was found to be approximately 24.35 % cheaper than commercially activated carbon, with a production cost of 11.78 USD/kg [118]. Magnetic tea biochar was reported as an effective bio-sorbent for defluoridation with an estimated production cost 71.9 USD/Kg [178]. Similarly, chemically modified rice husk biochar was investigated and found to have a comparable production cost of (0.062 USD/g) [192]. The reusability of an adsorbent significantly impacts its cost. If an adsorbent can be recycled multiple times, it would be more cost-effective. Agricultural waste-based adsorbents have the potential to replace expensive chemicals used for defluoridation, while also reducing the burden of agricultural waste production by adding value to these waste materials.

10. Management of spent adsorbent

The environmental suitability of a product is determined by evaluating its entire lifecycle. In the case of agro-adsorbents, which are based on sustainable principles, questions arise regarding their ultimate fate after the adsorption process. To date, most research has focused on using adsorption as a novel approach for defluoridating water. However, this has led to an increased generation of spent adsorbents. Consequently, there is a growing need to address the proper management of these spent adsorbents, as inadequate management could result in the re-release of contaminants into the environment, leading to secondary environmental pollution [193]. Various disposal methods are available for spent adsorbents, but the choice of the most suitable method depends on various associated factors. These spent adsorbents can either be integrated into other materials or simply disposed of in landfills. To assess their suitability for landfill disposal, it's essential to conduct toxicity tests. The two most commonly used methods for leaching tests are the Toxicity Characteristics Leaching Procedure (TCLP) and the California Waste Extraction Test (CalWET) as described by Obe et al. [194]. However, before opting for landfill disposal, several other factors should be evaluated, such as the chemical composition, the presence of fluoride content in the spent adsorbent, and the physicochemical properties of the landfill area's soil, including pH, natural organic matter, and the presence of microbial communities. These factors can significantly influence the chemical state of the contaminants and may impact the leaching process, as highlighted by Yadav et al. [195]. Studies have shown the potential for reusing spent adsorbents from defluoridation in various applications. For instance, Rathore and Mondal [196] utilized spent adsorbents as additives in brick formation, and toxicity tests confirmed their safety for use. Similarly, Da et al. [197] incorporated fluoride-containing sludge as an additive in cement clinker, yielding positive results in terms of clinker properties. Kiziniiev et al. [198] also used spent adsorbents as fillers for building materials, and Damian et al. [199] reported the use of bone char, used for fluoride removal, as a soil amendment agent. Although some studies have addressed the management of spent adsorbents used for defluoridation, there is a lack of clarity regarding post-management strategies for agro-adsorbents employed for the same purpose. Therefore, in addition to identifying the ideal agro-adsorbent for defluoridation, extensive research is needed to explore proper disposal methods, aiming for holistic sustainability.

11. Conclusion and future prospects

This review addresses widespread fluoride contamination in water and evaluates conventional removal methods, highlighting their advantages and limitations. Among these methods, biosorption stands out as a simple, cost-effective, and eco-friendly approach. Choosing the right bio-adsorbent is crucial for maximizing adsorption efficiency, and agricultural waste materials have proven effective due to their versatile properties. Optimal adsorption conditions, including pH, initial fluoride concentration, adsorbent dosage, temperature, and contact time, significantly influence the adsorption process, and this review thoroughly discusses these parameters. Field experiments using real water samples with co-existing ions have been conducted to accurately assess agro-adsorbent efficiency. To gain a clear understanding of the adsorption process, biosorption models like Langmuir and Freundlich isotherm models, as well as adsorption kinetics, have been analyzed. Cost considerations, including raw material processing costs, are vital for practical application, particularly in developing countries. Additionally, the regenerative capacity of the adsorbent is essential for economic viability, ensuring both efficiency and cost-effectiveness.

Furthermore, managing spent adsorbents after defluoridation is crucial to prevent fluoride reintroduction into the ecosystem. This study promotes sustainability through efficient natural resource utilization while maintaining environmental balance. Discovering an agricultural waste with strong defluoridation potential offers an affordable and eco-friendly water treatment solution. It enhances our understanding of biosorption processes, encouraging the development of more targeted adsorbents for fluoride removal. The research underscores the importance of adopting green adsorbents to prevent secondary environmental pollution. This approach empowers local communities with user-friendly systems, benefiting both human health and the environment. Despite challenges in creating adsorbents from agricultural waste, this review identifies areas for future research and improvement in this field.

- I. Despite the availability of several adsorbents prepared from agricultural waste, the primary hindrance to their successful utilization is their efficiency. Consequently, the adsorbents should undergo surface modification through appropriate functionalization to augment their adsorption efficiency.
- II. Although agricultural waste-based adsorbents have been modified in various ways, the modification process should be both simple and economical to produce an end product that is universally acceptable.
- III. In spite of numerous adsorption studies that have employed agro-adsorbents, there is insufficient documentation regarding the precise mechanism involved. Thus, future research should focus on exploring the optimal mechanism involved in the process to further facilitate the modification pathway.
- IV. The majority of defluoridation studies utilizing agro-adsorbents have been carried out on a laboratory scale. Hence, future studies should emphasize column-based investigations to determine their practical feasibility towards large-scale commercial applications.
- V. Fluoride is present in relatively higher concentrations in industrial water and is often associated with other co-existing ions, which can interfere with the defluoridation process. Therefore, an agro-adsorbent that can effectively operate in high concentrations of fluoride and is less impacted by co-existing ions would be the optimal choice for industrial applications.
- VI. While a significant amount of research is currently underway to decontaminate water from fluoride, the generation of spent adsorbents is also at its peak. Therefore, alongside the pursuit of developing the perfect adsorbent, it is equally essential for research efforts to be directed towards finding appropriate disposal methods for these spent adsorbents. Although there have been reports on post-management strategies for spent adsorbents used in defluoridation, a notable gap exists in the literature, especially concerning agro-adsorbents. This research gap presents an avenue for future studies, encouraging researchers to explore effective disposal strategies for agro-adsorbents.

Overall, it is imperative that future research places a primary focus on investigating agro-based adsorbents endowed with the following characteristics, in conjunction with the development of suitable disposal strategies: (1) Exceptional removal efficiency (2) Versatility in functioning across a broad pH range (3) Proficiency in effective operation under elevated pollutant concentrations (4) Rapid adsorption kinetics (5) Exceptional regeneration and reusability potential etc.

Data availability statement

No data was used for the research described in the article.

Additional information

No additional information is available for this paper.

CRediT authorship contribution statement

Koyeli Das: Writing – original draft, Investigation, Visualization, Preparation of manuscript. **Uttara Sukul:** Conceptualization, Visualization. **Jung-Sheng Chen:** Formal analysis and Resources. **Raju Kumar Sharma:** Visualization and Revision of manuscript. **Pritam Banerjee:** Visualization and Revision of manuscript. **Gobinda Dey:** Visualization and Revision of manuscript. **Md. Taharia:** Visualization and Revision of manuscript. **Christian J. Wijaya:** Visualization and Revision of manuscript. **Cheng-I Lee:** Visualization and Revision of manuscript. **Shan-Li Wang:** Visualization and Revision of manuscript. **Nguyen Hoang Kim Nuong:** Visualization.

Chien-Yen Chen: Conceptualization, Visualization, Methodology background.

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.

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