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Adsorption of Fluorides in Drinking Water by Palm Residues

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Abstract: Fluorides represent a significant problem in low- and middle-income countries (LMICs). In fact, this ion is essential for human health but, if taken in excess, it can cause dental and skeletal fluorosis. In LMICs, the pollution of groundwater from fluorides is of natural origin. Therefore, if providing alternative sources for drinking water (DW) supply is not possible, the use of specific processes for the removal of fluorides becomes essential. The adsorption on alternative materials, such as agro-food residues, can be a valid treatment for the removal of fluorides in the LMIC considering: (i) their optimal removal yields, (ii) the high availability, and (iii) the low cost. In recent years, the interest on the use of palm residues (PRs) becomes significant. Optimal pH, temperature, adsorbent dosage, and possible combination with metals to increase adsorption performances were deeply investigated. The activated PRs also present two other advantages: (i) very high surface area, and (ii) very low reduction in uptake capacity when regenerated. However, all tests were conducted with synthetic waters in laboratory-scale reactors while application on real-scale are absent. This makes other studies on this type of alternative adsorbent material still necessary.

Keywords: dental fluorosis; fluoride health effects; low-cost defluorination; adsorption; alternative adsorbent; low-cost adsorbent; agro-food residues; coconut

1. Introduction

Fluorine is used in industrial processes for the manufacturing or production of steel, aluminum, iron, glass, plastic and in refrigerants such as freon [1–6]. Another common use of fluorine is for the production of phosphate fertilizers for agricultural use [1,7–9]. For this reason, in the case of biosolids reuse as soil conditioners, some countries adopted threshold limits to reduce the dispersion of fluorides in the environment [10].

In water, fluorine is present mainly in the form of fluoride ion due to its high solubility [11]. Given the wide origin of pollutants in wastewater [12–15], the presence of fluorides in surface water bodies can be primarily ascribed to industrial origin. However, in some surface water and in groundwater, the main source of pollution of fluorides is related to natural origin [16]. This aspect varies according to the environmental conditions and the characteristics of the subsoil [17]. In fact,

the significant presence of fluorine compounds in igneous, granite and sedimentary rocks, determines a greater enrichment of the water due to leaching phenomena [16,18–20].

Fluoride ion is essential for human health, especially for the preservation of teeth and bones. However, if taken in excessive doses, it can cause dental and skeletal fluorosis issues [21]. The World Health Organization (WHO) classified fluorides in water as an inorganic chemical pollutant of natural origin which, over certain concentrations, is capable of determining a harmful effect on human health [22].

In drinking water (DW), the fluorine optimal concentration is between 0.5 mg L^{-1} and 1.5 mg L^{-1} [23,24], which is the value that WHO recommends not to exceed based on a daily water consumption rate of 2 L day^{-1} [22,25]. In fact, fluoride concentration higher than 1.5 mg L^{-1} causes problems such as: (i) loss of functionality of the teeth, which become fragile and take on a dark color and (ii) malformation of the skeleton [23,26,27]. Concentrations between 1.5 mg L^{-1} and 4 mg L^{-1} generally determine dental fluorosis, with staining of the teeth [25,26], while higher concentrations (4–10 mg L^{-1}) can also cause skeletal fluorosis with deformations of the bones [23,25,28]. Fluorine concentrations above 10 mg L^{-1} can cause damage to the central nervous system following bone malformations of the spine that damage the spinal cord [23,25].

The intake of fluorine may be due to dermal contact and ingestion due to the presence in food and beverages (e.g., vegetables and tea) [6,29–31]. However, the presence in DW is the most important exposure pathway of fluoride [32]. This aspect is particularly dangerous especially in low- and middle-income countries (LMICs) where alternative supply points could not be easy to find.

According to recent studies, more than 200 million people worldwide consume more than the recommended amount of fluoride [17,33]. For instance, high fluoride concentrations can be found in DW, particularly in India, China, Central Africa and South America [22], where LMICs are located. Only in India, more than 62 million people suffer from dental, skeletal and non-skeletal fluorosis [20,34,35]. Since the presence of fluorine in groundwater is due to a natural phenomenon, the absence of alternatives for drawing DW represents a significant problem [17]. In these cases, it is necessary to use removal treatments, which are effective and appropriate to the context in which they are to be applied.

Conventional treatments for fluoride removal used in high-income countries (HICs) include: (i) chemical precipitation [36], (ii) electrochemical processes [37], (iii) adsorption on activated carbon [38,39] and (iv) membrane processes [11]. However, these processes are difficult to apply in LMICs, due to the high costs, the complexity of the systems and the need for skilled labour.

Instead, LMICs require fluoride removal treatments that can combine: (i) high fluoride removal efficiency, (ii) low construction and operating costs, (iii) simplicity of installation and (iv) low management requirements. In the recent years, adsorption on alternative materials' agro-food residues, such as palm residues (PRs), attracted the attention of the research [40–42].

In this paper, a brief bibliographic analysis of the state of the art of the research in this field is reported. Moreover, recent studies on the application of PRs for fluoride adsorption are reviewed and future outlooks in this field are discussed.

2. Bibliometric Analysis

The literature search was performed in the Scopus® database by entering "fluoride drinking water", "fluorosis drinking water" and "fluoride developing countries" as keywords. The bibliometric research focuses on papers and books published from 1991 to 2019. Figure 1 shows the trend of the number of publications. As it can be observed, since 2012–2013, there was an increasing interest in the scientific community for the study of aspects related to the presence of fluorides in DW: (i) effects on health, (ii) treatment processes and (iii) situation in the LMICs. In fact, the number of publications significantly increased.
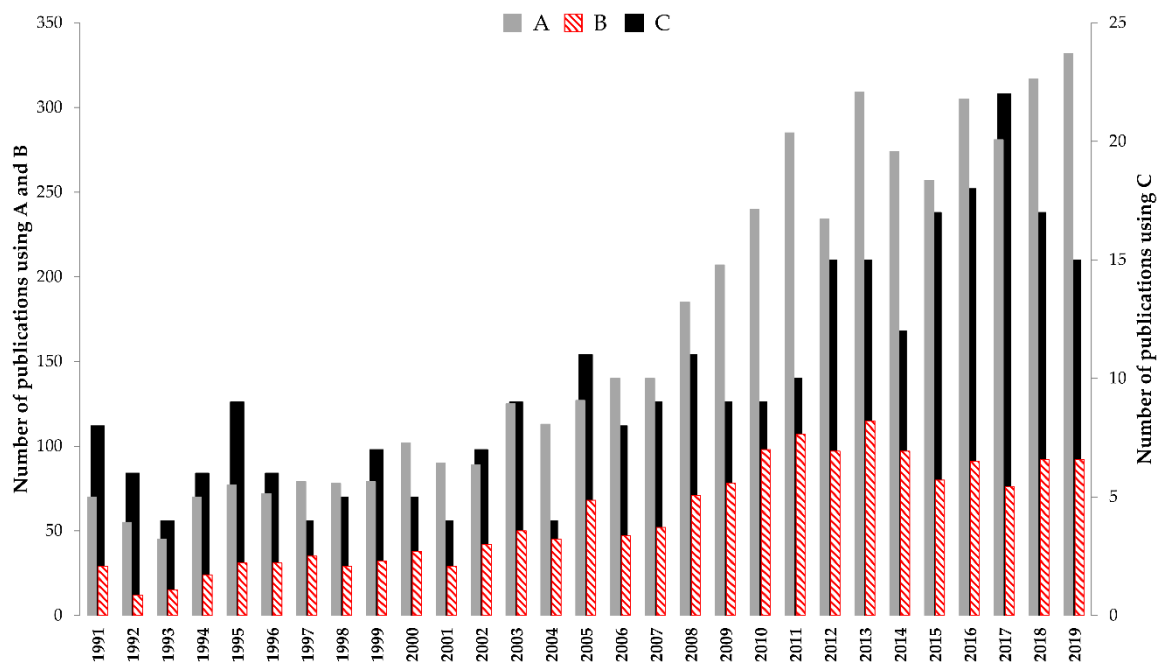
Figure 1. Number of publications per year from 1991 to 2019 searching on Scopus®: (A) "fluoride drinking water", (B) "fluorosis drinking water" and (C) "fluoride developing countries".

Using "fluoride alternative adsorption", "fluoride developing countries adsorption" and "fluoride low-cost adsorption" as keywords (for considering more specifically the trend in the number of publications concerning the study of adsorption processes on alternative materials), it can be noted that the interest of research has definitely grown in the last five years; however, the number of studies still remains quite limited (Figure 2).
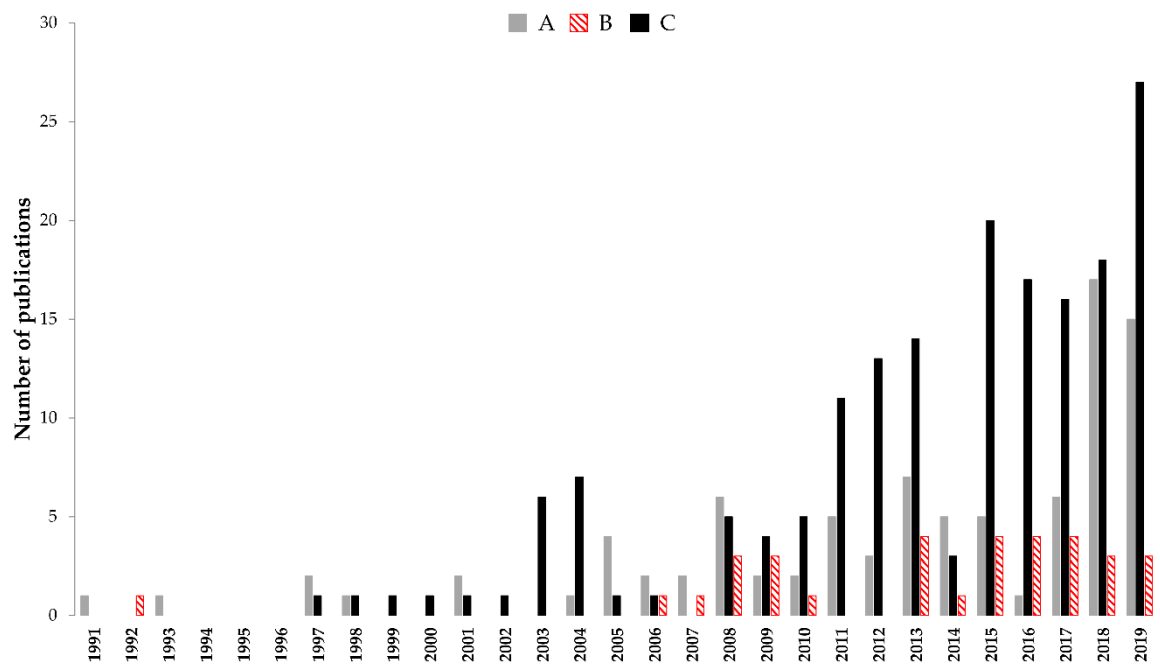

Figure 2. Number of publications per year from 1991 to 2019 searching on Scopus®: (A) "fluoride alternative adsorption", (B) "fluoride developing countries adsorption" and (C) "fluoride low-cost adsorption".

After the analysis of alternative low-cost materials, a screening of the literature was performed selecting only papers and books concerning the use of PRs for fluoride adsorption. As Figure 3 shows, research in this field is very recent and the number of publications on Scopus® is very limited. However, it can be clearly highlighted that the interest in this issue is still growing: over 50% of the literature production has been published in the last 10 years.
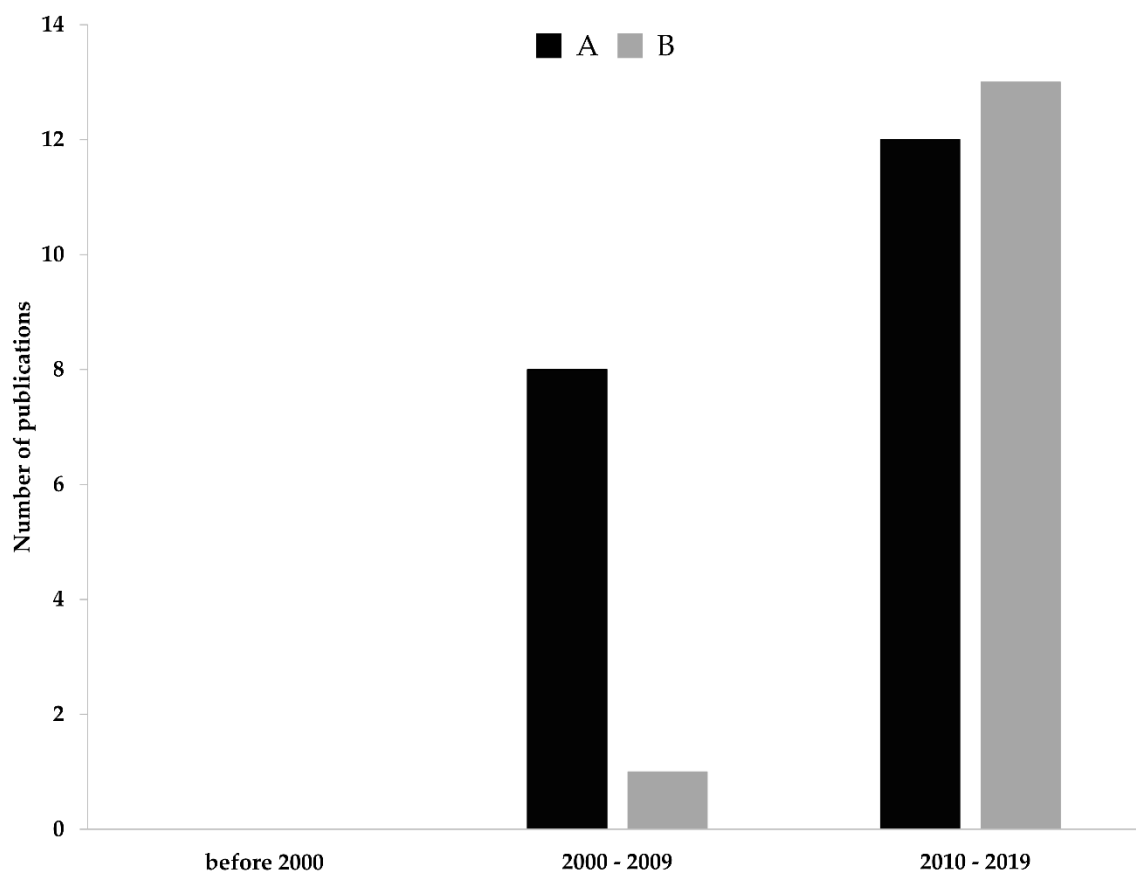

Figure 3. Number of publications up to 2019 searching on Scopus®: (A) "fluoride coconut adsorption", (B) "fluoride palm adsorption".

3. Adsorption on Palm Residues

3.1. Why Use Palm Residues?

Adsorption is a fairly simple process to manage and its implementation does not present any system complications [43–46]. The only requirement is the periodic replacement of the adsorbent material and its possible regeneration [47]. In LMICs, adsorption is well suited to be used, even with small domestic-scale systems, thus by-passing the problem due to the absence of large centralized systems [48].

However, the adsorption on conventional materials is suitable for HICs but is not economically sustainable in LMICs. For this reason, in recent years, the researchers tried to select alternative adsorbent materials that effectively removed fluorides present in DW [49,50], such as rare earth oxides, clay soils rich in iron, titanium and aluminum oxides, and bone char [46,51–55]. Several studies have also focused on the reuse of residues obtained from palm trees [41,56,57].

Palm alternative materials include both the residues directly obtained from the plant (e.g., midribs) and those related to its fruits (e.g., palm kernel shell and coconut). The main advantage of these residues is given by the high availability in most LMICs. For example, considering Indonesia, Philippines and India together, the total production of coconuts exceeds 450,000,000 tons [40,58]. Considering that

more than 65% of coconut is composed of waste materials (husk and shell) [40], the abundance of this agro-food residue is incredibly significant.

Furthermore, the reuse of waste materials complies with the concept of circular economy (CE) which aims to close the product life cycles and eliminate waste with obvious benefits for the environment and the economy [59–61]. Many international organizations, such as the European Commission, have recently issued directives in order to promote the reuse and the recycling of waste [62]. Moreover, adopting a model of sustainable economy can help to achieve sustainable development also in LMICs. Schroeder et al. (2019) [60] found a strong correlation between CE and Sustainable Development Goals (SDGs). Indeed, CE practices and related business models can stimulate the achievement of different SDG objectives such as SDG 6 "Clean Water and Sanitation" and SDG 8 "Decent Work and Economic Growth" [60].

3.2. Performances on Fluorides

In recent years, the researchers tested many different residues from palm trees. Table 1 shows several examples of applications depending on the adsorbent material used, the operating conditions and the surface area and adsorption capacity of the materials. Most studies focused on two materials specifically: palm kernel shell and coconut residues. In all cases, synthetic waters with a concentration of influential fluorides between 1 mg L^{-1} and 20 mg L^{-1} were used, in order to recreate the real conditions of DW. The chemical used to prepare the synthetic solutions was sodium fluoride. The adsorption capacities were different according to the residual used and the operating conditions (Table 1). The pH of the sample solution is an important parameter influencing the adsorption process [63,64]. In the acidic pH solution, the total charge on the adsorbent may be positive and as a result, the attraction of negatively charged fluoride ions with the positive adsorbent surface easily develops [57,65–67]. Bashir et al. [57] employed a pH range of 3 to 9 to study the effect of pH on the removal of fluoride. A 9% reduction in fluoride removal was observed as the pH increased from 5 to 8. Choong et al. [68] observed that the adsorption capacity of fluoride decreased from 287.5 to 262.9 mg g^{-1} as the pH increased from 4 to 7. Generally, the optimal pH for the adsorption of fluorides on PRs has been in a range between 3 and 6 (Table 1).

Temperature also exerts an important effect on the adsorption process; as in literature, the adsorption process is described as exothermic [69–72]. Generally, an increase in temperature causes a decrease in the adsorption capacity of fluoride on the adsorbent surface, as shown in the thermodynamic study of the adsorption of fluoride onto palm kernel shells and coconut fibers conducted by Choong et al. [66], Bhaumik and Mondal [67], and Mondal et al. [73].

Adsorbent dosage seems to have a great influence on adsorption process. Bashir et al. [57] also analyzed the effect of dosage on fluoride adsorption. This study was conducted with chemically modified palm kernel shells at pH values of 6 and 7 with a contact time of 120 min. The results revealed that increases in the doses of the adsorbent up to 0.4 g resulted in the corresponding increase in fluoride removal. The removal rate decreased slightly as the adsorbent dose was continually increased beyond 0.4 g [57]. Similar results were obtained by Bhaumik and Mondal [67]. Increasing the adsorbent dosage, the fluoride uptake increased, and the highest fluoride adsorptions were 80.5–91.5% for different coconut fiber dusts tested, with initial fluoride concentration of 10 mg L^{-1} and 0.5 g L^{-1} adsorbent dosage. Thereafter, the adsorption of fluoride started to decline with an increase in the concentration of adsorbent and then remained constant [67]. This aspect could be due to the balance between adsorbate and adsorbent which render the adsorbent incapable of further adsorption [74]. No significant increase in adsorption was observed with higher dosages from 0.5 g L^{-1} onwards [67]. George and Tembhurkar [75], tested coconut root adsorbent and observed a rapid increase in fluoride adsorption efficiency up to 8 g L^{-1} of adsorbent, the dosage corresponding to the maximum removal of fluoride. The possible reason for the increase in the adsorption of fluorides with higher doses of the adsorbent could be the presence of more active sites for the increase in surface area on adsorbent [76,77].

　　　Higher concentrations of fluorides in influential DW stimulated a higher adsorption capacity of the process, as seen in Table 1. In some cases, to increase adsorption capacity, the residues have been modified with chemicals. For instance, Choong et al. [68] compared the performances of palm shell activated carbon powder (PSAC) and magnesium silicate modified PSAC (MPSAC). The study of the adsorption capacity showed that PSAC and MPSAC overperformed some other reported fluorides' adsorbents, obtaining values of 116 mg g^{-1} and 150 mg g^{-1}, respectively [68]. Radhika [78] studied the efficiency of the adsorption of fluoride ion by activated alumina finely grinded with coconut shell powder, and highlighted that this solution was effective for removing fluoride with an initial concentration of 2–20 mg L^{-1}.

　　　The activated carbon produced from PRs generally presented two other main advantages: (i) very high surface area and (ii) very low reduction in uptake capacity when regenerated. The literature reports that activated PRs have higher specific surface areas (BET surfaces) than alternative adsorbents, such as wheat straw (6.5 m^2 g^{-1}) [79], tamarind seed (0.99 m^2 g^{-1}) [80], pine wood char (2.73 m^2 g^{-1}) [81], powdered biochar of *Conocarpus erectus* tree (9.88 m^2 g^{-1}) [82], and cuttlefish bone (0.07 m^2 g^{-1}) [83]. For instance, Talat et al. [84] tested coconut husk activated carbon with a surface area equal to 1448 m^2 g^{-1} and highlighted that the exhausted adsorbent can be efficiently regenerated with a basic solution of NaOH. Moreover, the regenerated adsorbent showed remarkable uptake capacity with only a low reduction in adsorption performance up to the three cycles [84].

Table 1. Several examples of PRs applications for the adsorption of fluorides from DW. T = temperature; n.p. = not provided; 1: residual concentration = 0.8 mg F$^-$ L^{-1}.

Type of PRs	Surface Area (m^2 g^{-1})	Fluoride in (mg F$^-$ L^{-1})	Operative Conditions	Adsorption Capacity (mg F$^-$ g$_{PR}$$^{-1}$)	References
Palm kernel shell	1099.8	5–125	pH = 7; T = 25 °C; dosage = 0.2 g L^{-1}	116	Choong et al. [66]
	772.1	5–125	+ magnesium silicate; pH = 7; T = 25 °C; dosage = 0.2 g L^{-1}	150	Choong et al. [66]
	422.5	100	+ La/Mg/Si-loaded; pH = 7; T = 25 °C; dosage = 0.2 g L^{-1}	285.7	Choong et al. [68]
	21.75	2–12	pH = 3; T = 25 °C; bed height = 2–10 cm	5.6–27.9	Abu Bakar et al. [56]
	1.717	10–50	pH = 3; contact time = 4 h	1.7	Abu Bakar et al. [63]
	n.p.	2.5–15	pH = 6; contact time = 45 min	2.35	Bashir et al. [57]
Palm midribs	255.1	2–10	pH = 1–3.4; T = 30–60 °C; dosage = 0.1–1 g L^{-1} contact time = 15–300 min	n.p.	Ajisha et al. [42]
Coconut husk	358	4.4	pH = 2–10; T = 30–50 °C; dosage = 10 g L^{-1}; contact time = 3 h	1.3	Araga et al. [41]
	1448	10	pH = 5; dosage = 1.4 g L^{-1}	6.5	Talat et al. [84]

Table 1. *Cont.*

Type of PRs	Surface Area ($m^2\,g^{-1}$)	Fluoride in ($mg\ F^-\ L^{-1}$)	Operative Conditions	Adsorption Capacity ($mg\ F^-\ g_{PR}^{-1}$)	References
Coconut shell	n.p.	2–20	+ alumina; T = 20 min; dosage = 20 g L^{-1}	n.p.[1]	Radhika et al. [78]
	2.82	10	+ zirconium; pH = 2–10; T = 25 °C; dosage = 10 g L^{-1}	6.4–9.1	Sathish et al. [85]
Coconut fiber	163.2	20	+ zirconium; pH = 4; T = 25 °C; Dosage = 20 g L^{-1}; contact time = 6 h	1.95	Sathish et al. [86]
	26.3	6	+ aluminium; pH = 5; T = 40 °C; dosage = 0.5 g L^{-1}	3.2	Mondal et al. [73]
	285.6 –824.5	1.5–15	pH = 7.6–7.8; T = 30–60 °C; dosage = 0.05–2 g L^{-1}; contact time = 20–240 min	12.7–38.5	Bhaumik et al. [67]
Coconut root	312.84	2–25	pH = 7; T = 50 °C; dosage = 8 g L^{-1}; contact time = 90 min	2.037	George et al. [75]

3.3. Future Outlooks

From the researches carried out and reported in the scientific literature, the PRs proved to be suitable for effectively removing fluorides present in DW while maintaining their adsorbent capacity even after repeated regenerations. At present, it should be noted that all researches were conducted on laboratory scale systems, and applications on the real scale are absent. Furthermore, all the tests were carried out with synthetic solutions and not using real DWs. This situation is certainly attributable to the still limited literature on the subject, that makes other studies on this type of alternative adsorbent material still necessary.

In the next years, based on the current information and the recent trend of publications, it is reasonable to expect that the attention on the development of low-cost alternative adsorbent materials will tend to grow further. The authors suggest investigating the application of these agro-food residues because in LMICs, it can be a very promising technology for the removal of fluorides and, consequently, for an improvement in the quality of life of the resident population. While in HICs, it is possible to apply more advanced treatments (and materials) for the removal of fluorides from DW, in LMICs, reuse of recycled materials can be an opportunity because: (i) palm residue are produced in large quantity, (ii) adopting a CE model enhances the promotion of SDGs for a sustainable future, and (iii) they can substitute conventional adsorbents which are very expensive. Despite the PRs presenting significant advantages (e.g., high removal efficiencies), they should be carefully studied because several aspects, such as the best metals to eventually couple them to enhance adsorption process, need to be better clarified.

4. Conclusions

Fluoride represents a very important problem in LMICs. In recent years, the interest on the use of PRs becomes significant and represent a valid treatment for the removal of fluorides in the DW considering: (i) its optimal removal yields, (ii) the high availability and (iii) the low cost. The adsorption capacities were different according to the residual used and the operating conditions. In the scientific literature, in some cases, the residues have been modified with chemicals (e.g., alumina, magnesium silicate and zirconium) in order to increase adsorption capacity. Generally, the optimal pH for the

adsorption of fluorides on PRs was in a range between 3 and 6. The alternative adsorbent produced from PRs generally presented two other main advantages: (i) very high specific surface and (ii) very low reduction in uptake capacity when regenerated. Despite these very interesting results, the alternative PRs adsorbent for fluoride removal will still have to be carefully studied in order to be able to compare the results of a significant number of tests on pilot scale plants, and better clarify some issues such as which are the best metals to eventually couple them to significantly increase their adsorption performance.

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