

Review

Rice Industry By-Products as Adsorbent Materials for Removing Fluoride and Arsenic from Drinking Water—A Review

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Abstract: In drinking water, high concentrations of fluoride and arsenic can have adverse effects on human health. Waste deriving from the rice industry (rice husk, rice straw, rice bran) can be promising adsorbent materials, because they are (i) produced in large quantities in many parts of the world, (ii) recoverable in a circular economy perspective, (iii) at low cost if compared to expensive conventional activated carbon, and (iv) easily manageable even in developing countries. For the removal of fluoride, rice husk and rice straw allowed to obtain adsorption capacities in the range of 7.9–15.2 mg/g. Using rice husk for arsenic adsorption, excellent results were achieved with adsorption capacities above 19 mg/g. The best results both for fluorides and arsenic (>50 mg/g) were found with metal- or chemical-modified rice straw and rice husk. Identifying the next steps of future research to ensure the upscaling of biochar from recovered by-products, it is fundamental to perform: (i) tests on real waters for multicomponent adsorption; (ii) experiments with pilot plants in continuous operation; (iii) cost analysis/real applicability of modification treatments such as metal coupling or chemical synthesis; (iv) more studies on the biochar stability and on its regeneration or recovery after use.

Keywords: low-cost defluorination; groundwater adsorption; geogenic pollutants; rice waste; rice husk; rice straw



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1. Introduction

With the rapid economic development and industrialization, the usage of chemicals has been excessively increased. This leads to environmental pollutions, through the discharge of huge amounts of toxic compounds into the environment. The increasing global population has led to an increase in different human activities, generating a large amount of wastes and a high burden for human wellbeing, together with the natural ecosystem [1]. However, not all the pollutants are linked to anthropogenic activities; some pollutants may be of geogenic origin. Geochemical risk is the result of excesses of chemical elements naturally present in geological materials (rocks, soils, water) from which it is possible to draw substances essential to the livelihood of humans, animals, and plants. Among these, in addition to the main constituents of organic matter, there are some microelements such as iron, zinc, copper, fluorine, selenium, iodine, and chromium [2].

Fluoride ion concentrations of approximately 1 mg/L is a vital component for human health, especially in promoting the development of strong bones and reducing dental caries. However, high concentrations can cause discoloration of teeth, even serious bone fragility and deformation (dental and skeletal fluorosis) [3–5]. It is estimated that in more

than 25 countries, around 200 million people are exposed to drinking water with fluoride concentrations above the World Health Organization (WHO) guideline value of 1500 µg/L. This situation is experienced in India, China, Korea, Thailand, Sri Lanka, Indonesia, Yemen, Pakistan, Iraq, Turkey, Syria, Jordan, Palestine, Bangladesh, Iran, Saudi Arabia, and in Mexico and Argentina [6–10]. A recent study used an algorithm to model more than 12,000 groundwater fluoride concentration data from across India. The results predicted that the total number of people at risk of fluorosis from fluoride in groundwater is around 120 million, or 9% of the population [8].

Moreover, not all chemical elements perform essential functions; on the contrary, some of them (including arsenic, cadmium, lead, mercury) do not seem to provide any beneficial contribution, or can lead even to serious and irreversible damage [2]. Arsenic, in particular, is a ubiquitous toxic element that can cause different cancerous diseases, skin pigmentation problems and cardiovascular disorders [5,11,12]. More than 300 million people in 105 countries have sources of drinking water with arsenic concentrations above the WHO limit of 10 µg/L available. The highest exposures were found in India (West Bengal), Bangladesh, Nepal, Pakistan, China, Taiwan (China), Japan, Cambodia, Vietnam, Australia, Hungary, and Romania, and in the arid and semi-arid areas of fourteen Latin American countries [3,5,12,13]. For the first time in Taiwan (China), As(V) and As(III) species have been studied in Taiwanese spring waters, which have contaminated drinking and irrigation water resources. The highest concentration of As(III), more than 1400 mg/L, was found in the geothermal springs of Beitou [14].

These pollutants, due to their natural presence in the environment, can accumulate in an uncontrolled way in groundwater. However, there are also some human activities, such as mining and the use of phosphate pesticides, which can contribute to the contamination of ground and surface waters by arsenic and fluorine respectively [6,7,13].

Therefore, it is significantly important to either decrease or remove some amount of these toxic compounds from drinking water. Conventional treatment techniques such as chemical precipitation, biological treatments, oxidation, and reduction using chemicals, electro dialysis, ion exchangers, reverse osmosis, ultra-filtration, membrane separation, and adsorption processes have been studied and are currently utilized for the treatment of different environmental pollutants [15–18].

However, many treatment methods—except the adsorption process—are characterized by many economic problems such as installation, operation, and management cost. Moreover, the generation of secondary sludge represents another environmental pollutant problem and needs careful attention in the sludge disposal process [19].

The adsorption techniques have been considered as the most appropriate technology in the decrease and removing of the toxic compounds due to their economic benefit, high effectiveness, simple operation and process control, technological flexibility, lower and affordable energy requirements, and environmental friendliness [20–24].

The adsorbents are porous materials with high specific surface area, which may result in excellent adsorption capacity. The adsorption capacity strongly depends on a series of variables: dosage of the adsorbent, concentration of pollutants in the contaminated water, temperature, contact time and, above all, pH. The efficiency of the adsorption process is also determined by the porosity of the adsorbent, the surface area, the polarity, and the functional groups on the adsorbent surfaces [25].

It is possible to identify two sorption mechanisms: (i) the physisorption, in which the pollutants are adsorbed on the surfaces of the adsorbents by weak van der Waals forces or electrostatic forces, and (ii) chemisorption, in which the pollutants can be immobilized on the active matrix thanks to the presence of functional groups on its surfaces, creating chemical bonds [25]. Regarding adsorption of rice waste-based materials, the interaction mechanisms with As and fluorides are mainly explained by comparing the FTIR spectra before and after adsorption, by porosimetric measurements and surface observation by SEM on the same samples. Moreover, artificial neural network modeling is frequently used as a theoretical tool [26]. In particular, concerning As adsorption, interesting results were

obtained at pH between 6 and 9, and the adsorption efficiency of the rice husk biochar as prepared was a little bit lower or similar to the performance obtained for functionalized biochar (surface modifications, for example, by treatments with FeCl_3 salt), even if the specific surface area was much higher ($25.161 \text{ m}^2 \text{ g}^{-1}$ vs. $1.890 \text{ m}^2 \text{ g}^{-1}$) [27]. This points out to the fact that chemical interactions among functional groups present on the adsorbent surface and detected by FTIR (O- and N-containing groups) and the As containing species and polarity indices $[(\text{O} + \text{N})/\text{C}]$ of the same external groups are more important than porosity in determining adsorption. Really, the formation of complexes between As(III) and As(V) and the detected functional groups is evident by the shift or the disappearance of some IR bands of the biochar after contaminants' adsorption. The functionalization with Fe(III) leads again to adsorption by chemical interactions, with formation of composites like Biochars- $\text{FeH}_2\text{AsO}_3^{3-}$, Biochars- FeHAsO_3^{2-} or Biochars- $\text{FeOH}_2\text{-H}_2\text{AsO}_3$ for As(III), and Biochars- FeH_2AsO_4 , Biochars- FeHAsO_4^{2-} or Biochars- $\text{FeOH}_2\text{-H}_2\text{AsO}_4$ for As(V). Concerning fluoride adsorption, its removal efficiency by rice husk biochar seems to be maximum at acidic pH (values = 4 being the best option); physisorption is the most important mechanism [28], with the adsorption efficiency increasing by increasing the surface area and the pores' number and volumes in the matrix. After surface functionalization with metals (Zn, Fe), adsorption of fluorides is favored also by an electrostatic force of attraction between positively-charged surface of biochar and negatively-charged F^- , leading to the obtainment of $\text{-OH}_2\text{-F}$ pendant groups on the biochar structure [26].

Currently, there is an uptrend on using biochar derived from different materials and various waste streams as an adsorbent in different adsorption processes [29–33]. Biochar is considered as a high potential engineered adsorbent for many types of environmental remediation applications [34]. Biochar derived from different waste streams like agricultural industries presents numerous advantages, such as cost-effectiveness, providing of continued feedstock, the possibility of circulating resources in the economy, and sustainable valorization options for waste [29]. Many literature works have reported that biochar derived from agricultural by-products can be effectively utilized as an adsorbent in different environmental applications, such as for water treatment, as a soil amendment in agriculture, for abating greenhouse gas in soil, and as a stabilizer in the anaerobic digestion process [35–37].

Rice is one of the major consumable foods in more than half of the world. Rice is an annual plant crop and is mostly cultivated in areas with high rainfall. Many Asian countries have an agrarian economy and produce a significant amount of agricultural waste related to the rice industry. In general, agricultural wastes are considered as biomass residues that can be divided into two categories, namely crop residues and agro-industrial residues. Currently, many farmers and other stakeholders who engage with the rice industry are practicing open field burning or open dumping processes to clean their land for the next cultivation instead of extracting their full value [38]. This leads to huge environmental pollution and adverse health effects on humans as well as on animals. Thus, it is possible to minimize these negative effects by considering the valorization process for this potential feedstock by using it as a valuable material or source to the national economy.

Considering the waste quantities and other physical and chemical properties, rice industry by-products have a high potential of generating energy, extracting nutrition elements, minerals, and biochemicals through different valorization processes. However, their potential is still underexplored due to issues related to their supply chain, appropriate technologies for pre-treatment and cost-effective methods, and feasible business models to facilitate valorization of the rice industry by-products in many developed and developing countries. Therefore, the aim of this review paper is twofold:

- i. Reviewing the literature concerning the potential use of rice industry by-products (rice straws, rice husk, and rice husk ash) for the removal of fluoride and arsenic in drinking water.
- ii. Assessing main strengths and limitations in a large-scale implementation of rice industry by-products as an adsorption material in the water treatment sector.

2. Structure and Bibliometric Analysis

The review is focused on the removal of fluoride and arsenic from the water through an adsorption treatment based on the use of rice cultivation waste. First, the precious by-products generated during rice processing are analyzed, underlining the importance of their sustainable recovery. The chemical and physical properties of rice husk, rice husk ash, and rice straw are then described, focusing on their adsorption capacity. Subsequently, the characteristics of fluoride and arsenic are briefly shown, considering in particular (i) the effects on human health, and (ii) the main causes of water pollution; at this point, the importance of removing these pollutants from groundwater has emerged even more to ensure water safe consumption. The scientific literature was then analyzed to collect studies and experiences on the use of rice by-products as adsorbent materials for the removal first of fluoride and then of arsenic from water. Finally, in the paragraph “Final remarks and future outlooks”, the authors described the main pros and cons observed in the discussion of this issue, suggesting some possible prospects for future research.

For a brief bibliometric analysis, the authors took inspiration from the studies carried out by Ashraf et al. [39] and Ebrahimi et al. [40]. The search for documents of the scientific literature was carried out thanks to Scopus[®] (Elsevier, Amsterdam, The Netherlands) database exploiting different keywords. In all the searches carried out, in the “Document type” field, articles, conference papers, conference reviews, and chapter books have been taken into consideration; in the “Language” field, however, only English was chosen.

First, focusing in general on the adsorption treatment of fluorine and arsenic into drinking water, the following keywords have been entered: “fluoride AND adsorption AND drinking water”, “arsenic AND adsorption AND drinking water”. In this case, the bibliometric research focuses on documents published from 2000 to 2022. Figure 1 shows the trend in the number of publications.

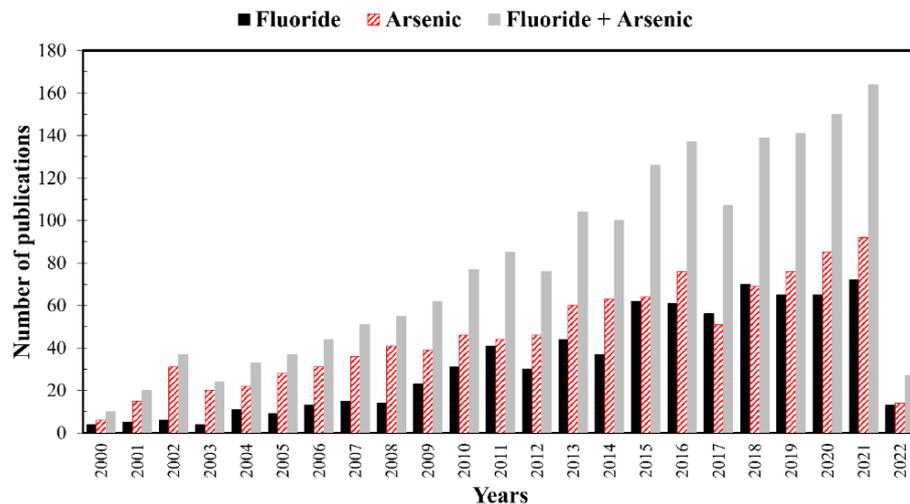


Figure 1. Number of publications per year from 2000 to 2022 searching on Scopus[®]: “fluoride AND adsorption AND drinking water”, “arsenic AND adsorption AND drinking water”. “Fluorine + arsenic” is the sum of the papers relating to fluoride and the papers relating to arsenic.

As it can be observed, there has been a constant growth of interest from the scientific community on the study of this topic from 2000 to today. However, it is to be noted that in the early 2000s, there were more publications regarding arsenic while in recent years, the focus on fluorine has increased, approaching the numbers relating to arsenic.

Subsequently, the keywords “fluoride AND adsorption AND waste AND drinking water”, “arsenic AND adsorption AND waste AND drinking water”, and then “fluoride AND rice AND adsorption AND drinking water”, “arsenic AND rice adsorption AND drinking water” were used, with the aim of (i) considering more specifically the use of recycled adsorbent materials in drinking water sector, and (ii) focusing on low-cost by-

products deriving from the rice industry. Figure 2 compares the three bibliographic searches carried out, both the latter two described (“By-product adsorption” and “Rice by-product adsorption” in Figure 2), and the first concerning, in general, the adsorption treatment for the removal of fluoride and arsenic from drinking water (“Adsorption” in Figure 2), evaluating the results of both fluorine and arsenic all together.

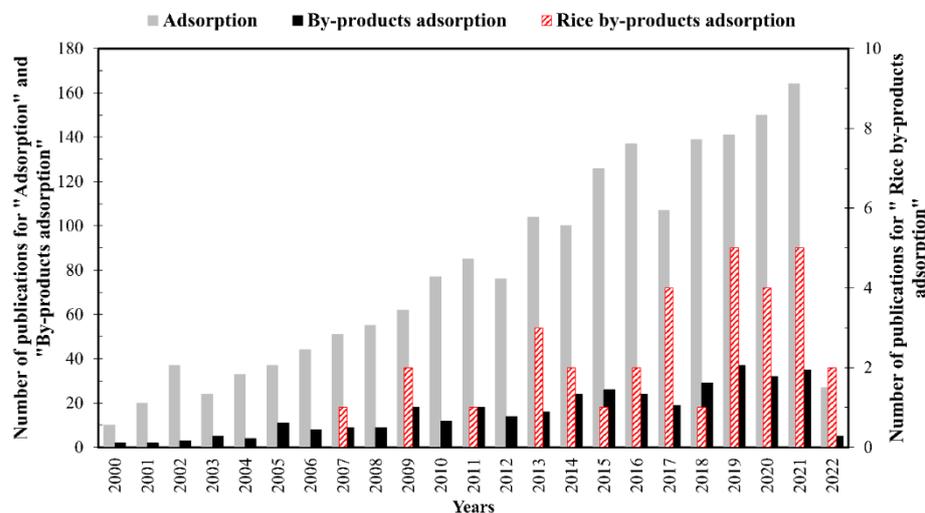


Figure 2. Number of publications per year from 2000 to 2022 searching on Scopus[®], for both arsenic and fluoride: (i) Adsorption (keywords: “adsorption AND drinking water”); (ii) By-products adsorption (keywords: “adsorption AND waste AND drinking water”); (iii) Rice by-products adsorption (keywords: “rice AND adsorption AND drinking water”).

It can be observed that over the years, the increase in studies on alternative adsorption materials has occurred in synergy with adsorption in general; in fact, publications on the use of by-products have always consistently represented around 20% of the total over the years. The documents from the year 2000 to today were considered, but as it can be seen from Figure 2, the first publications on the use of rice husk and rice straw as adsorbent materials appeared only in 2007. Without considering the incomplete year 2022, the documents present in the scientific literature concerning waste from the rice industry represented only 2% of “Adsorption” and 9% of “By-products adsorption” as an average value since 2007. A growth trend of “Rice by-products adsorption” is however visible from year 2017, indicating a growing interest from the scientific community.

3. Rice Industry By-Products

3.1. Rice Industry Value Chain

Agricultural food processing consists of a variety of value chains and generates a significant amount of different types of agricultural waste through their value chain from the way of farm to fork process. According to the previous literature regarding by-products, the usable product ratios of rice straw, rice husk, and rice bran are 0.4–1.4 kg/kg [41], 0.28 kg/kg [41], and 0.1 kg/kg [42] respectively. Rice straw mainly consists of full part of the rice plant, therefore, producing 1 kg of rice may require more rice plants.

A large quantity of valuable wastes is produced during their harvesting and processing stage and hence, those wastes should be studied and analyzed in order to extract their valuable parts in a sustainable way. Waste production throughout the rice industry is represented in Figure 3. Paddy straws are produced in large quantities during the paddy harvesting process. These straws are commonly found in fields and are often used as fodder for animals and as bedding for livestock. The remaining part is burned by the farmers when ready for the next cultivation. Additionally, rice husks frequently ended up as a burning material and were discarded in landfills. The destruction of this valuable biomass without proper use will cause irreversible damage to the environment and other

living beings on the planet. Bran is also another by-product of the rice processing value chain (Figure 3). After harvesting and processing in mills, residues of rice have a higher potential to convert into another raw material in other products [43]. Non-harvest rice, half fill grains, dead grains, damaged paddy seeds during the harvesting process, and rotten rice in domestic consumption were not considered for this study.

Conceptual model on the rice waste generated all along the food chain

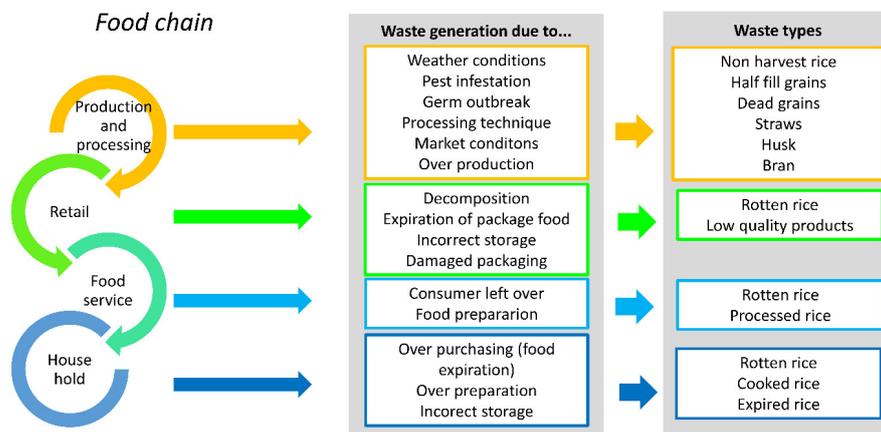


Figure 3. Conceptual model on the rice waste generated all along the food chain adopted from [42,43].

3.2. Properties of Rice Husk and Rice Husk Ash

Rice husk is generated as a by-product of the rice milling process and it is the outer cover of the rice grain. It is also known as hull and chaff [44]. This is the most common agricultural by-product in agrarian countries. In general, rice husk is utilized as source biomass fuel in rice mills, silica-rich cementitious material, and poultry farming [43,45,46]. In addition, a minor amount is used as fertilizer and building material [47]. Due to its low economic value, the availability in huge quantities, higher chemical stability, mechanical strength, and insolubility in water, rice husk is considered as a sustainable absorbent material [48–51]. However, higher quantities of rice husks are frequently terminated in landfills or open burning, creating huge environmental pollution.

The composition and quantity of rice husk depends on several environmental factors such as area, soil type and characteristics of soil, water availability, harvesting and processing technology, and behavior of the market [52–54]. However, Carbon and Silica are considered as the major components of rice husk for the adsorption process [55]: this is confirmed also by the Energy Dispersive X-Ray Analysis (EDX) performed by the authors and reported in Table 1, where it is evident that Si is the 3rd element after C and O in wt %. Table 2 represents the organic chemical constituents of rice husk, while the chemical analysis of the rice husk ash obtained after pyrolysis of the husk is represented in Table 3.

Table 1. Elemental composition of Carnaroli rice husk as determined by Energy dispersive spectroscopy (EDX; X-max 50 mm² probe by Oxford Instrument (Abingdon, UK) connected to an EVO MA10 scanning electron microscope by Carl Zeiss (Oberkochen, Germany) performed on a sample after drying at 45 °C for 6 h in an oven (own source).

Elemental Composition (Average wt %)	
Carbon	28.22
Oxygen	53.53
Silicon	17.00
Potassium	0.60
Magnesium	0.05
Calcium	0.45
Sulphur	0.11
Chlorine	0.03

Table 2. Chemical constituents of rice husk (the composition of the mineral ash obtained after pyrolysis is reported in Table 3) (modified from [37,56,57]).

Chemical Component	Composition (mg/g)			
	[56]	[56]	[57]	[37]
Cellulose	334.7	292	344	322.4
Hemicellulose	210.3	201	293	213.4
Lignin	267	307	192	214.4
Extractives				18.2
Water				81.1
Mineral ash				150.5

Table 3. Chemical composition of rice husk ash (modified from [37,54,58–61]).

Component	Composition (mg/g)					
	[58]	[59]	[54]	[60]	[61]	[37]
SiO ₂	924	946.4	884.7	810.9	920	945
Al ₂ O ₃	3			0.5	2.9	
Fe ₂ O ₃	4	2.3	4	1.4	1	<5
CaO	7	18.9	18	10.7	12.8	2.5
MgO	3	9.6	7.1	7.5	3.7	2.3
Na ₂ O	0.7	3.9	2.6		0.5	7.8
K ₂ O	25.4	5.8	25	13.9	21.9	11.8
SO ₃				14.5	9.4	6
loss on ignition, LOI	23.1			87.3	34.3	
Zn (ppm)		18.2	32.28			
Mn (ppm)		52.24	56.44			
Cu (ppm)		32.17	16.98			
Cd (ppm)		0.48	0.49			

Adsorption on Rice Husk

Understanding the chemical structure and functional groups present in rice husk is highly important for the adsorption process. Fourier transform infrared (FTIR) spectroscopy and Attenuated Total Reflection (ATR) are commonly used to determine the structure of the backbone carbon chain and whether the backbone consists of linear or branched chains. It also provides information on the characteristics of the functional groups that are bonded with the backbone carbon chain, which aid in the adsorption process for the removal of different pollutants from drinking water. To get a better understanding of the functional groups present in the rice husk surface, the ATR-FTIR spectrum of a real sample is shown in Figure 4. The absorption band at 3293 cm⁻¹ indicates the stretching vibration of free and hydrogen-bonded hydroxyl groups. The small two peaks at 2918 cm⁻¹ and 2850 cm⁻¹ are a signature of the C–H groups of long-chain aliphatic components (alkanes and alkenes structures). Some very weak signals at 2000–2500 cm⁻¹ can be attributable to C≡C or C≡N bonds or accumulated –C=C=C– and –N=C=O bonds. The band at 1654 cm⁻¹ is attributable to C=O presence. Finally, the peaks at 1027 cm⁻¹ can be due to C–O and C–H bonds' vibrations and the bands at 787 cm⁻¹ and around 500 cm⁻¹ to Si–O bonds deformations respectively [62]. The right and left shoulders of the peak centered at 1027 cm⁻¹ can be due to the valence vibrations of C–O–Si or Si–CH₃ bonds [63]. Concerning the composition of husk, the presence of cellulose, hemicellulose, lignin, and silica components is evident, since the bands at 780 and 2920 cm⁻¹, 1030 cm⁻¹ and 3340 cm⁻¹, and at wavenumbers lower than 1200 cm⁻¹ were attributed in literature to C–H deformation vibration and stretching in cellulose, C–O stretching vibration in cellulose/hemicellulose and aryl–OH group in lignin, and free and hydrogen-bonded OH stretching [64–68]. The existence of different types of polar groups on the rice husk surface gives an appreciable amount of cation exchange capacity, outlining the possible effectiveness in physisorption mode [69].

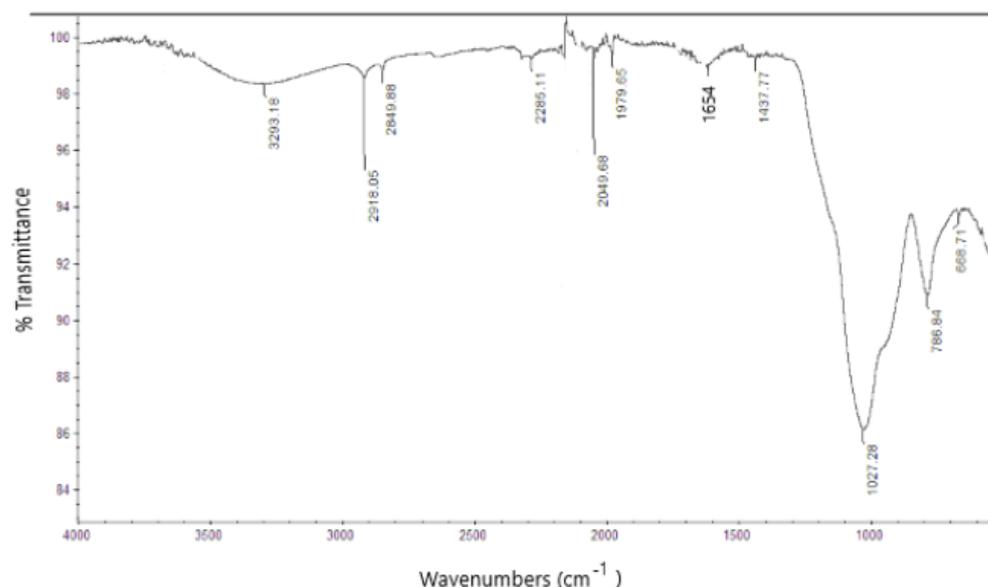


Figure 4. ATR-FTIR spectra of rice husk (own source) acquired at room temperature by a Nicolet FTIR iS10 spectrometer (Nicolet, Madison, WI, USA) equipped with Smart iTR with diamond plate on organic Carnaroli rice husk. Husk was dried at 45 °C, milled and sieved with a 1000 μm mesh sieve before analysis. Thirty-two scans in the 4000–600 cm^{-1} range at 4 cm^{-1} resolution were coadded. The peaks are indexed by the tool “Find Peaks” in the Omnic Spectra software Nicolet, Madison, WI, USA.

According to the works of literature, rice husk adsorbent has been used in different ways for the removal of various types of pollutants such as inorganic anions, heavy metals, phenol, and other organic compounds, pesticides, and dyes from the water and wastewater. Many investigations have been conducted through different treatment methods, such as untreated rice husk as adsorbents, chemical and biological modification of husk, biochar, activated carbons, and ashes. The use of these different treatments for rice husks shows that many works have reported acceptable results from their research with adsorption capacity more than 10 mg/g. However, comparison among different treatment methods is relatively difficult due to different experimental conditions.

3.3. Properties of Rice Straws

Rice straw is the vegetative part of the rice plant (*Oryza sativa* L.) and it is generated after cut at grain harvest. It consists of the stem of the paddy plant, leaves, and spikelet. Typically, rice straw is used for animal feed, composting process, cattle house bedding, the paper industry, to make handmade items, as an energy source in some industries, and covering material for agricultural fields [70]. In addition, the remaining part of the rice straw is burned in the paddy fields before the next ploughing process to prepare the field.

The chemical composition of any biomass is highly dependent on variety, cultivated area, seasons, nitrogen fertilization, plant maturity, plant health, and many other environmental and human factors [71,72]. Variation of chemical and physical factors affect the yield and the quality of the end product. Rice straws consist of cellulose, hemicellulose, lignin, and a considerable amount of other components that are represented in Table 4 [73]. Table 5 lists the elemental composition of dried rice straw as determined by EDX [74]: it is well evident that the amount of Si is strongly lower than for rice husk. Van Soest [75] has revealed that rice plant leaves consist of more silica than their stem. Due to the higher amount of oxalate (1–2% dry matter) in rice straw, the Ca concentration is decreased and therefore, it is necessary to make Ca supplementation when it is used as animal feed [43].

Table 4. Major components of rice straw (mg/g) (modified from [73]).

	Cellulose	Hemicellulose	Lignin	Ash
Rice Straw	320–386	197–357	135–223	100–170

Table 5. Elemental composition and chemical analysis of rice straw (modified from [74]).

Elemental Composition (mg/g)					
Carbon	Oxygen	Silicon	Potassium	Chlorine	Calcium
470.84	467.9	15.4	33.1	9.9	2.9

Adsorption on Rice Straw

Rice straw is rich in cellulose, hemicellulose, silica, and lignin, which provide binding sites for various contaminants like heavy metals and dyes, in water and wastewater [76,77]. Therefore, straw has a large potential for use as a low-cost adsorbent material in water treatment. Gebrewold et al. [78] have emphasized that the surface of this type of biomass adsorbent is activated at lower pH values for removal of heavy metals. Furthermore, Cr adsorption process is more favorable in strong acid conditions [76]. In Figure 5, the ATR-FTIR spectrum of rice straw is reported. In this case, the same peaks outlined for pure husk are evident. In particular, the broad band centered at 3287 cm^{-1} is associated with O-H stretching (in cellulose or hemicelluloses), the bands at around 2900 cm^{-1} are attributing to C-H stretching, the peaks around 2000 cm^{-1} are due to the vibrations of the carbon skeleton bonds (see the table in [79]). Moreover, the OH bending vibration is well evident in the peak at 1606 cm^{-1} and the presence of CH_3 and methoxy ($-\text{OCH}_3$) groups present in lignin is confirmed by the signals between 1320 and 1500 cm^{-1} [68,80]. The bands between 1650 to 1515 cm^{-1} can be assigned to aromatic skeleton stretching and to the presence of $\text{C}=\text{O}$ bonds. Finally, the peaks at 1032 cm^{-1} can be due to C-O and C-H bonds' vibrations and the bands at 782 cm^{-1} to Si-O bonds deformations, respectively.

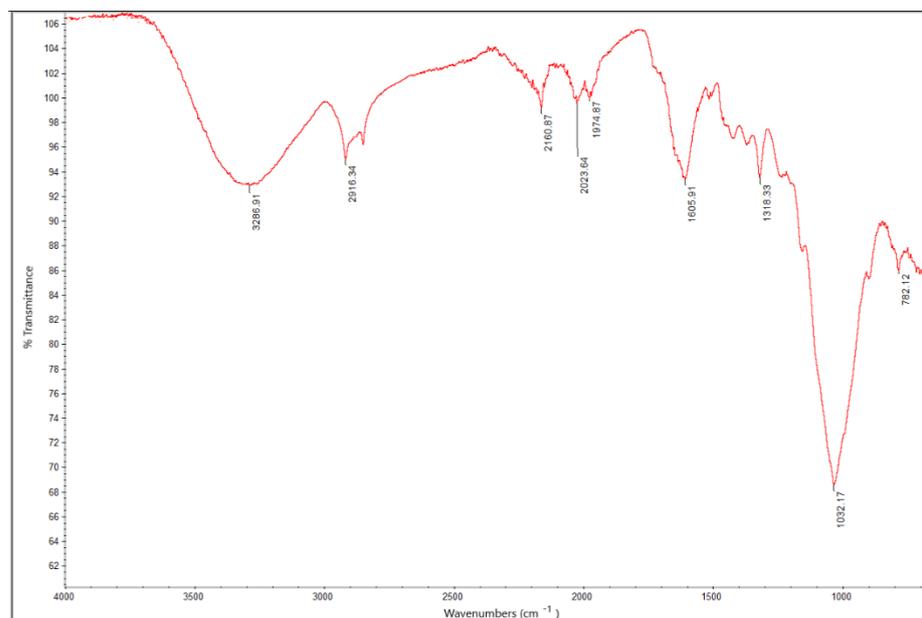


Figure 5. FTIR spectra of rice straw (own source) acquired at room temperature by a Nicolet FTIR iS10 spectrometer (Nicolet, Madison, WI, USA) equipped with Smart iTR with diamond plate on Luna CL rice straw. Just collected straw was washed with distilled water, dried at $45\text{ }^{\circ}\text{C}$, milled, and sieved with a $1000\text{ }\mu\text{m}$ mesh sieve before analysis. Thirty-two scans in the $4000\text{--}600\text{ cm}^{-1}$ range at 4 cm^{-1} resolution were coadded. The peaks are indexed by the tool “Find Peaks” in the Omnic Spectra software.

Through the metallic modifications, some more hydroxyl groups can be produced on the rice straw biochar that means more active sites for adsorption [81]. Moreover, Cao et al. [82] demonstrated that the adsorption capacity is increased by increasing the number of quaternary ammonium groups. Additionally, the adsorption capacity of the rice straw is decreased by the existence of competitive cation in the solution and chelators [77].

3.4. Properties of Rice Bran/Rice Polish

Rice bran is one of the most significant wastes generated during the rice processing value chain. Due to its high nutritional value, it is mainly used as an animal feed and is considered as a good fiber source for pet food. Additionally, because of its availability, its price is considerably economical for farmers. Up to 40% of rice bran is added into the dietary plans of cows, dogs, pigs, and poultry due to its higher amount of fat and fiber [83,84]. Furthermore, rice bran contains 14–18% oil, and therefore, it is a valuable feed for all types of livestock. According to Patsios et al. [43], defatted rice bran can be used at higher levels of the valorization process than ordinary rice bran. The physical and chemical characteristics of rice bran depend on several factors related to the grain itself and to the milling process. The main factors related to rice grain are rice variety, environmental conditions, size and shape of the grains, distribution, chemical constituents, thickness of outer layers, and resistance to breakage [85]. Additionally, type of milling machine and conditions of processing are the key factors related to the milling process. Resurrection et al. [86] have emphasized that different layers of rice kernel at various depths show different chemical compositions. Table 6 represents the proximate analysis of rice bran while Table 7 lists the elemental composition of dried rice bran obtained by the authors by EDX: P and K are more abundant with respect to the other wastes, testifying the nutritional importance of the bran, containing vitamins and proteins.

Table 6. Major components of rice bran (mg/g) (modified from [87]).

Proximate Analysis	
Moisture	83
Volatile matter	431.2
Fixed carbon	301.4
Ash (oxides of Ca, Mn, Si, Fe, Mg, etc.)	184.4

Table 7. Elemental composition of Carnaroli rice bran as determined by Energy dispersive spectroscopy (EDX; X-max 50 mm² probe by Oxford Instrument connected to an EVO MA10 scanning electron microscope by Zeiss) performed on a sample after drying at 45 °C for 6 h in an oven (own source).

Elemental Composition (wt %)							
Carbon	Oxygen	Silicon	Potassium	Magnesium	Phosphorus	Sulphur	Chlorine
45.41	47.84	1.57	1.97	0.80	2.15	0.21	0.05

Adsorption on Rice Bran

Rice bran, due to its granular structure, chemical stability, insolubility in water, and local availability, can be used as an adsorbent material. Its surface contains several active sites [88] for pollutants' removal, whose efficiency depends also on the chemical nature of the solution and the presence of other ions than the one/ones to be trapped. The amount of negatively-charged groups on the rice bran matrix increases at lower pH values (around 4.0–6.0). This effect favors the electrostatic interaction between the surface itself and cations leading to metal ions' binding. Moreover, the adsorption efficiency of rice bran is attributed to some functional groups on the surface such as hydroxyl groups and carbonyl groups [89], whose presence can be confirmed by the ATR-FTIR spectrum reported in Figure 6, which shows similar peaks than rice straw. In particular, the -O-H and -C-H

signals are well evident at 3284 cm^{-1} and between 2850 cm^{-1} and 2920 cm^{-1} . The peaks at 1709 cm^{-1} and 1653 cm^{-1} can be due, respectively, to C=N and C=O bonds, being bran is very rich in proteins and vitamins; proteins' presence can be correlated also in the region of $1400\text{--}1200\text{ cm}^{-1}$, suggesting the N-H stretch first overtone [90]. Finally, the very intense peak at 990 cm^{-1} can be due to C-O and C—H bonds' vibrations.

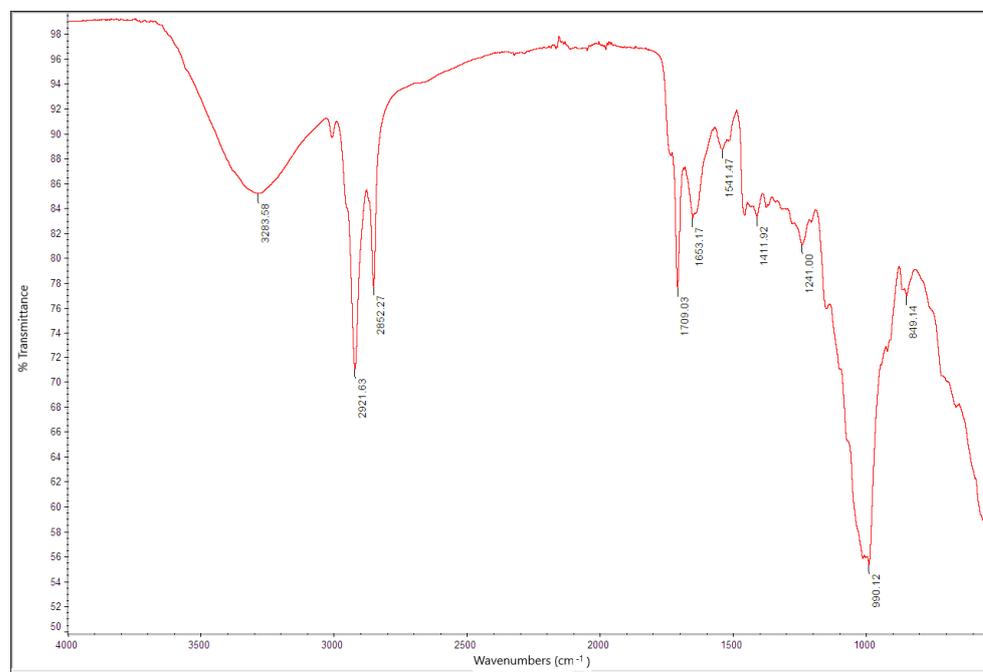


Figure 6. FTIR spectra of rice bran (own source) acquired at room temperature by a Nicolet FTIR iS10 spectrometer (Nicolet, Madison, WI, USA) equipped with Smart iTR with diamond plate on Carnaroli rice bran. The waste was dried at $45\text{ }^{\circ}\text{C}$ before analysis. Thirty-two scans in the $4000\text{--}600\text{ cm}^{-1}$ range at 4 cm^{-1} resolution were coadded. The peaks are indexed by the tool “Find Peaks” in the Omnic Spectra software.

4. Fluoride Removal

Fluorine accounts for around 0.08% mass of the earth's crust and is broadly distributed in numerous geological environments. Since fluorine has strong electronegativity, fluorine naturally exists as different forms of compounds such as sellaite, cryolite, fluorite, fluorapatite, etc. [91,92]. Fluorine is considered as an essential trace element for the human body: the proper amount of fluorine can support maintaining healthy bones and teeth, but an extreme amount of fluorine leads to loss of the toughness of bones and teeth, and makes them brittle [93]. Fluoride can enter the human body in different ways such as drinking water, foods and beverages, drugs, dermal contact, and air inhalation. However, drinking water is the main source of fluoride to enter the human body [94], therefore, the concentration of fluoride in this solvent has become a significant parameter for determining water quality. The value of the fluoride concentration determines whether the anion causes beneficial effects or harmful impacts on the human body. Hence, the concentration of fluoride in drinking water is set as 1.5 mg/L by the World Health Organization (WHO) [95].

The dissolution of fluoride compounds causes the rise of fluoride concentration in groundwater. Literature reports [91–93] have highlighted that there are two main reasons for this phenomenon (Figure 7):

- i. Environmental Factors: weathering, dissolution of fluoride-containing minerals by rainwater, and continuous evaporation of groundwater can affect a gradual increase of fluoride concentration.
- ii. Anthropogenic activities: mining, various industries like glass and coke production, semiconductors, metal smelting, electroplating, photovoltaic activities, etc., release

high fluoride concentrated wastewater which is mixed with surface water resulting in fluoride entering groundwater.



Figure 7. Source of fluoride entering to groundwater (adopted from [91–93]).

4.1. Rice Husk and Rice Husk Ash as Adsorbents for the Removal of Fluoride

There are several sections in literature investigating the efficiency of fluoride removal from water by the different forms of rice husk (Table 8). Tanvir Arfin [96] studied the efficiency of fluoride removal by using different adsorbent materials such as rice husk, eggshell, activated carbon, and rice husk ash, showing that the efficiency of fluoride removal was 40% by rice husk while the efficiencies for the other matrices were 61.8, 53.4, and 42.5% respectively.

A wide range of treatment methods have been proposed and investigated in literature to improve the adsorption efficiency [97,98]. Deshmukh et al. [99] prepared rice husk by chemical impregnation with nitric acid, followed by physical activation to investigate the removal of fluoride in aqueous solution. They reported that the maximum fluoride removal was 75% at pH = 2, with the fluoride uptaking capacity decreasing by increasing pH in the range 2–10. This finding was confirmed by Ahmaruzzaman and Gupta [37]. Therefore, authors emphasized that it is preferable to carry out the fluoride adsorption process at lower pH values. Moreover, fluoride adsorption increases with time, reaching equilibrium within 1–1.5 h. Some authors [37,100] investigated the removal of fluoride by modifying rice husk ash by coating with aluminum hydroxide. The study showed promising results of fluoride removal capacity, and the adsorption was determined to be 910 mg/g. Other authors investigated the fluoride removal capacity by using silica nano adsorbent modified by rice husk [101]. The results illustrated that the fluoride adsorption capacity is 12 mg/g. The summary in Table 8 and Figure 8 represents a comparison of fluoride removal capacities according to different treatment methods of rice husk. By way of comparison with rice husk, according to the experiments of Tembhurkar and Dongre [102], commercially available powdered activated carbon (2.0 g/100 mL) allowed a 94% removal of fluorides under optimal conditions (contact time: 120 min, pH: 2). As reported by Tomar and Kumar [103], some coal-based adsorbents (lignite, fine coke, and bituminous coal) showed an adsorption

capacity in the range of 6.9–7.4 mg/g for the removal of fluoride. A pH between 6 and 12 was more favorable in the case of lignite, while fine coke and bituminous coal showed a greater efficiency at acid pH.

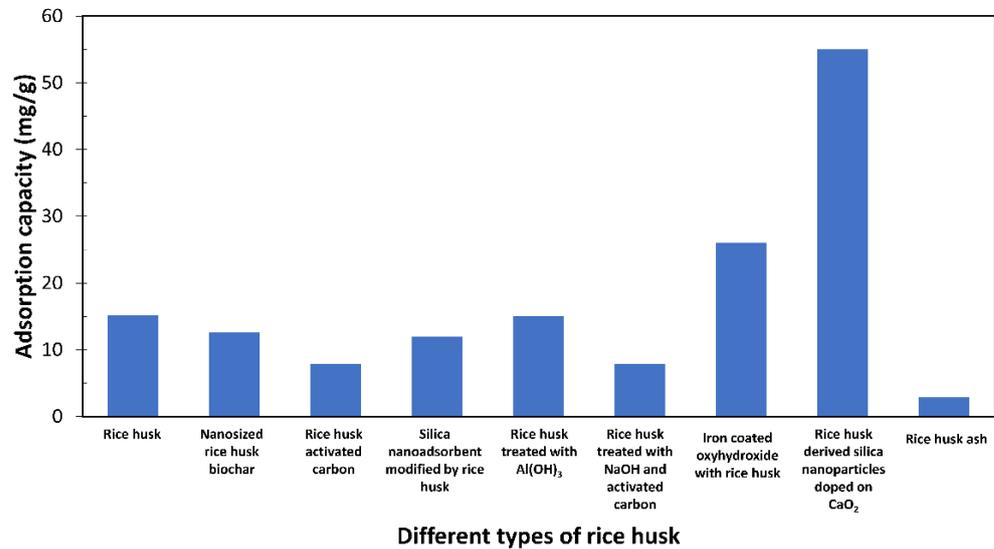


Figure 8. Adsorption capacities by different types of rice husk [78,100,101,104,106–109].

Table 8. Adsorption capacities of fluoride on different types of rice husk and rice husk ash.

Type of Adsorbent	Type of Water	Experimental Conditions	Adsorption Capacity (mg/g)	References
Rice husk	Synthetic	Time = 50 min Adsorbent = 0.5 mg/100 mL pH = 6.5 Initial concentration = 5 mg/L Stirring rate = 150 rpm Temperature = 298 K	15.2	[104]
Rice husk	Synthetic	Time = 180 min Adsorbent = 6 g/L pH = 2 Initial concentration = 5 mg/L Stirring rate = 60 rpm Temperature = 302 K	(Maximum removal: 83%)	[105]
Nanosized rice husk biochar	Synthetic	Time = 60 min Adsorbent = 1 g/L pH = 7 Initial concentration = 5 mg/L Temperature = 298 K	12.6	[106]
Rice husk activated carbon	Synthetic	Time = 3 h Adsorbent = 5 g/L pH = 4 Initial concentration = 23 mg/L Stirring rate = 60 rpm Temperature = 298 K	7.9	[78]
Silica nano adsorbent modified by rice husk	Synthetic	Time = 60 min Adsorbent = 4 g pH = 8 Initial concentration = 10 mg/L	12	[101]
Rice husk treated with Al(OH) ₃	Synthetic	Time = 60 min pH = 5 Initial concentration = 5 mg/L Temperature = 300 K	15.1	[100]
Rice husk treated with NaOH and activated carbon	Synthetic	pH = 4	7.9	[78]

Table 8. Cont.

Type of Adsorbent	Type of Water	Experimental Conditions	Adsorption Capacity (mg/g)	References
Iron oxyhydroxide coated with rice husk	Synthetic	Time = 45 min Adsorbent = 0.8 g/L pH = 4 Initial concentration = 10 mg/L Stirring rate = 400 rpm Temperature = 303 K	26	[107]
Rice husk-derived silica nanoparticles doped on calcium peroxide	Synthetic	Time = 65 min Adsorbent = 1.1 g/L pH = 6.5 Initial concentration = 10 mg/L	55	[108]
Rice husk ash	Synthetic	pH = 8	2.9	[109]

4.2. Rice Straw as Adsorbent for Removal of Fluoride

Rice straw can be utilized as an adsorbent material by subjecting it to different physical and chemical pre-treatments. Daifullah et al. [110] have investigated the potential of activated rice straw for the fluoride removal process from water. The authors of the same study concluded that activated rice straw can produce low-density, highly porous materials. Strong oxidants such as hydrogen peroxide, nitric acid, and potassium permanganate were used for treating the activated rice straw carbon. The results showed significant improvement and higher efficiency values compared to similar activated carbon not treated with strong oxidants. Potassium permanganate showed the highest effect, while nitric acid and hydrogen peroxide had comparably less effect.

Zhou et al. [81] realized a comparison in fluoride adsorption capacity between rice straw biochar and La/Fe/Al oxides loaded rice straw biochar. The La-Fe-Al composite was synthesized into the rice straw biochar by the co-precipitation method. Then, the modified rice straw biochar was grinded and sieved under 100 mesh. The comparison is shown in Table 9. Additionally, authors have highlighted that the presence of other anions such as Cl^- , SO_4^{2-} , NO_3^- , and HCO_3^- , and the pH value of the solution can have little effect on the removal of fluoride by La/Fe/Al rice straw biochar. Therefore, pH from 3 to 11 was suggested as the optimum range.

Table 9. Adsorption capacities of fluoride by different types of rice straw (adopted from [81,110,111]).

Type of Adsorbent	Type of Water	Experimental Conditions	Adsorption Capacity (mg/g)	References
Rice straw biochar	Aqueous solution	pH = 3 Temperature = 298 K Initial concentration = 60–160 mg/L Surface area = 2.59 m ² /g Adsorbent = 1 g	10.9	[81]
Activated carbon-derived Mn treated rice straw-activated carbon	Aqueous solution	pH = 2.0 Temperature = 298 K Initial concentration = 20.0 mg/L Surface area = 123 m ² /g	15.9	[110]
Alumina impregnated onto the activated carbon derived from rice straw	Aqueous solution	pH = 6.1 Initial concentration = 50.0 mg/L Surface area = 151 m ² /g Adsorbent = 4 g	10	[111]
La/Fe/Al oxides loaded rice straw biochar	Aqueous solution	pH = 3–11 Temperature = 298 K Initial concentration = 60–160 mg/L Surface area = 95.36 m ² /g Adsorbent = 1 g	111.1	[81]

Saini et al. [111] have studied the use of alumina impregnate activated rice straw biochar as an adsorbent material in the fluoride removal process. Cleaned rice straw was washed with NaOH and subjected to carbonization under inert atmosphere. Subsequently, it was treated with alum ($\text{Al}_2\text{SO}_4 \cdot 16\text{H}_2\text{O}$) and NaHCO_3 , and the suspension was filtered and carbonized under N_2 atmosphere. A more detailed summary of literature data is reported in Table 9. It can be emphasized that the alumina impregnated activated rice straw biochar can reduce the fluoride concentration to less than 0.4 ppm when starting from a concentration of 10 ppm. Hence, this activated rice straw biochar can be successfully used as an ideal sustainable adsorbent.

5. Removal of Arsenic

The rapid increase of arsenic concentration has been discovered in drinking water sources all around the world and it threatens more than 200 million people in both developed and developing countries [112]. Arsenic has the ability to form compounds in both inorganic and organic phases, therefore, it is distributed in a wide range of environmental sectors [112–114]. In both groundwater and surface waters, arsenic can occur in the form of two inorganic species, arsenate (As(V)) and arsenite (As(III)). The latter is more mobile, toxic, and difficult to remove with the conventionally applied physicochemical treatments than As(V) [27,115].

Arsenic is grossly available in the human body, earth's crust, and seawater with the sequential proportion of 12th, 14th, and 20th, respectively, of all the existing elements [113]. Arsenic is mixed with the natural water system through several leaching processes such as mining waste, weathering of lithosphere deposits, and leaching from geochemically and biologically generated sources. Shih [116] has reported that the range of arsenic concentration is 3–10 mg/kg and 0.5–2.4 mg/kg in sediment and rocks, respectively, which is reportedly less than soils. Naturally, arsenic consists of more than 300 different mineral forms. Figure 9 represents the arsenic cycle and leaching process.

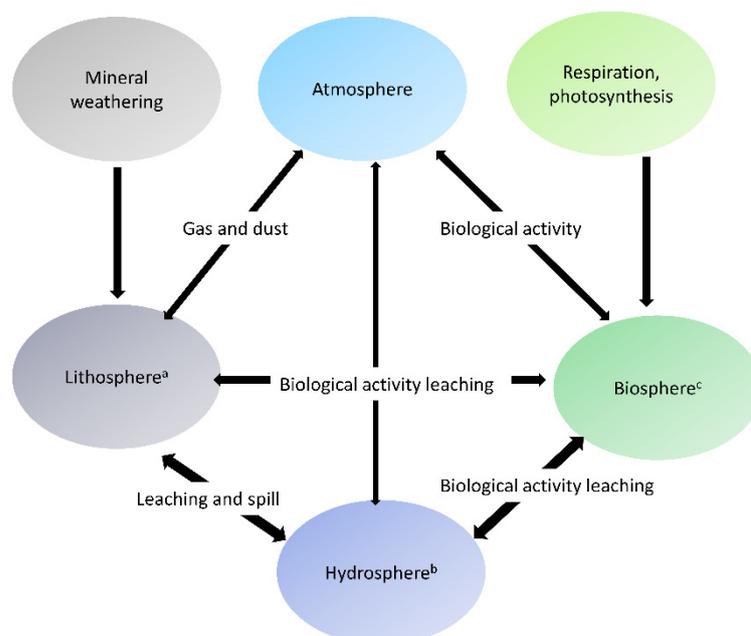


Figure 9. Arsenic cycle and leaching process (adapted from [116,117]). (a) Earth, crust, minerals, soil, sediments, agricultural waste, and industrial waste; (b) Surface water and groundwater; (c) Plants, animals, humans, and microorganisms.

Arsenic is one of the major environmental pollutants and excessive exposure to arsenic can have serious consequences to the human body, especially threatening carcinogenic effects. Therefore, WHO and the United States Environmental Protection Agency (USEPA)

have classified arsenic as a Class A carcinogenic pollutant. Furthermore, the WHO and USEPA have defined the limitation of arsenic concentration in safe drinking water and discharge wastewater as 10 µg/L and 0.2 mg/L, respectively [118,119].

5.1. Rice Husk as Adsorbent for Removal of Arsenic

Many literature papers have shown that rice husk, rice straw, and rice bran (polished rice) can be used as adsorbent material in the arsenic removal process. Babazad et al. [120] have investigated the efficiency of removal of arsenic from aqueous solution by porous carbon material obtained from the rice husk. The study was carried out in different conditions of pH, adsorbent amount, contact time, and initially adsorbed concentration. According to the adsorption analysis results, the removal of arsenic increased up to 85% under the optimum conditions of pH 6 (as reported in Table 10). Asif et al. [121] also investigated the potential of raw rice husk as an adsorbent for the removal of As(V) from drinking water. They have studied the impact of different operating parameters and their effect on removal efficiency in fixed bed columns. Authors have revealed that the maximum removal of As(V) is up to 90.7% under the optimal conditions of pH 8 (Table 10).

To compare, commercial granular activated carbon currently used at drinking water treatment plants allowed As(V) removals between 7 and 61% in batch experiments (carbon dose: 5 g/L, pH: 4, contact time: 24 h). While various types of powdered activated carbon showed a range of 5–84% (carbon dose: 1 g/L, pH: 4, contact time: 24 h) [122]. The removal of As(III), in a solution with an initial concentration of 10 mg/L and 2 g/L of activated carbon, reached the maximum value of 32.8% in batch experiments carried out at approximately pH 7.0 and at a temperature of 30 °C [123]. Another experiment with 24 h of contact time reported an arsenic loading with coal-based carbon (surface area: 1125 m²/g, 5.5% ash content) of 4.09 mg/g of carbon [124].

Rice husk can be subjected to different physical and chemical treatments (as shown in Table 11). Mondai et al. [125] investigated the arsenic removal ability of activated carbons produced from calcium chloride (CaCl₂) impregnated rice husks. The highest arsenic uptake (18.2 µg/g) was obtained using activated rice husk carbon at initial concentration of 1000 ppb (Table 10).

Amin et al. [115] investigated the possibility of using rice husk as an adsorption material without any pre-treatment in the removal of arsenic from aqueous media. Various adsorption and desorption conditions were considered, and the authors highlighted that the adsorption column method shows the complete removal of As(III) and As(V) (Table 10).

Iron oxide nanoparticles have a higher capability of removing heavy metals from aqueous solution due to their magnetic property, size, and high surface area [126]. Based on these promising capabilities, Pillai et al. [126] investigated the efficiency of arsenic removal by modification of iron oxide nanoparticles with rice husk (Table 11). The study showed promising results of removal of arsenic (up to 95%) under the optimal conditions. Bui et al. [127] have investigated the removal of As(III) and As(V) from water by iron–manganese oxide incorporated active rice husk silica (FMRS). They compared the arsenic removal capacity of both original rice husk ash and FMRS, which is 0.4 mg/g and 11.9 mg/g, respectively. Under the same experimental conditions, the adsorption capacity of FMRS for As(III) and As(V) was found to be 19.1 and 20.3 mg/g at pH 7, respectively.

Table 10. Adsorption capacities of arsenic by rice husk.

Type of Adsorbent	Type of Water	Type of Arsenic	Experimental Conditions	Maximum Removal (%)	Adsorption Capacity	References
Rice husk biochar	Aqueous solution	As(V)	Temperature = 298 K Reaction time = 24 h Initial concentration = 90 µg/L Surface area = 155 m ² /g Adsorbent = 8 g	25	0.00259 mg/g	[128]

Table 10. Cont.

Type of Adsorbent	Type of Water	Type of Arsenic	Experimental Conditions	Maximum Removal (%)	Adsorption Capacity	References
Rice husk biochar	Aqueous solution	As(V)	Temperature = 298 K pH = 9.5 Initial concentration = 0–200 mg/L Surface area = 23.2 m ² /g Adsorbent = 2 g	-	0.35 mg/g	[129]
Rice husk biochar	Aqueous solution	As(III)	Temperature = 298 K pH = 8 Initial concentration = 3–300 mg/L Surface area = 25.1 m ² /g Adsorbent = 5 g/L	-	19.3 mg/g	[27]
Rice husk biochar	Aqueous solution	As(V)	Temperature = 298 K pH = 6 Initial concentration = 3–300 mg/L Surface area = 25.1 m ² /g Adsorbent = 5 g/L	-	7.1 mg/g	[27]
Macromolecule carbonized rice husks	Aqueous solution	As(V)	pH = 6 Time = 65 min Initial concentration = 100 µg/L Adsorbent = 0.2 mg	85	-	[120]
Rice husk (column bed method)	Contaminated groundwater	As(III)—60–90%	pH = 7.8 Temperature = 298 K Initial concentration = 270 µg/L Particle size = 780 µm Adsorbent = 12 g Flow rate = 0.8 mL/min	96	-	[115]
Rice husk (column bed method)	Contaminated groundwater	As(III)—60–90%	pH = 7.6 Temperature = 298 K Initial concentration = 596 µg/L Particle size = 780 µm Adsorbent = 12 g Flow rate = 0.8 mL/min	96	-	[115]
Rice husk (column bed method)	Aqueous solution	As(V)	pH = 8 Temperature = 298 K Initial concentration = 15 µg/L Particle size = 710 µm Adsorbent = 42.5 g Flow rate = 7 mL/min Column diameter = 5 cm Bed height = 28 cm	90.7	-	[121]

Table 11. Adsorption capacities of arsenic by synthesized rice husk.

Type of Adsorbent	Type of Water	Type of Arsenic	Experimental Conditions	Maximum Removal (%)	Adsorption Capacity	References
Rice husk–Fe biochar	Aqueous solution	As(III)	Initial concentration = 50 mg/L Adsorbent = 5 g pH = 6.5	-	30.7 mg/g	[130]
Iron oxide amended with rice husk nanoparticles	Aqueous solution	As(V)	Temperature = 303 K Reaction time = 60 min Initial concentration = 10 mg/L Adsorbent = 2.5 g/L pH = 10.75	95	82 mg/g	[126]
Calcium chloride impregnated rice husk carbon	Aqueous solution	As(III)	Temperature = 301 K Initial concentration = 1 mg/L Surface area = 171 m ² /g Adsorbent = 40 g/L pH = 5	85	0.0182 mg/g	[125]

Table 11. Cont.

Type of Adsorbent	Type of Water	Type of Arsenic	Experimental Conditions	Maximum Removal (%)	Adsorption Capacity	References
Iron–Manganese oxide incorporated active rice husk silica	Aqueous solution	As(V)	Temperature = 298 K Reaction time = 24 h Initial concentration = 5 mg/L Surface area = 366 m ² /g Adsorbent = 0.3 g/L pH = 5	-	11.9 mg/g	[127]
Iron–Manganese oxide incorporated active rice husk silica	Aqueous solution	As(III), As(V)	Temperature = 298 K Reaction time = 24 h Initial concentration = 2–40 mg/L Surface area = 366 m ² /g Adsorbent = 0.4 g/L pH = 7	-	19.1 mg/g, 20.3 mg/g	[127]

5.2. Rice Straw and Rice Bran as Adsorbents for Removal of Arsenic

The efficiency of As(V) removal from aqueous solution was investigated using iron-modified biochar derived from rice straw and synthesized using FeCl₃ as iron source [119]. The authors compared the arsenic removal efficiency of raw biochar and iron-modified biochar. The study revealed that the ability of arsenic removal is better for iron-modified biochar with respect to raw biochar at the initial pH of 5.0. Ranjan et al. [131] carried out an experiment to study the optimal parameters for arsenic removal from water by rice polish using a fixed bed columns system. The investigation was directed to analyze different design parameters like flow rate, bed height, initial concentration and their effect on the adsorption process, and revealed that the As(III) and As(V) uptake capacities are 66.95 and 78.95 µg/g, respectively (Table 12). Another study was carried out by Mukherjee et al. [132] in order to remove As(V) from aqueous medium by using rice straw-derived biochar produced from slow pyrolysis process at 600 °C. Batch tests were conducted at room temperature under different conditions, such as initial concentration, contact time, and adsorbent dosages. The study highlighted an adsorption capacity of 25.6 µg/g for As(V) by rice straw biochar.

Table 12. Arsenic adsorption capacities by rice straw, synthesized rice straw, and rice polish (rice bran).

Type of Adsorbent	Type of Water	Type of Arsenic	Experimental Conditions	Maximum Removal (%)	Adsorption Capacity	References
Rice straw biochar	Aqueous solution	As(V)	pH = 6.5 Temperature = 298 K reaction time = 120 min Initial concentration = 100 µg/L Surface area = 133 m ² /g Adsorbent = 0.2 g/L	-	25.6 µg/g	[132]
Iron-modified biochar derived from rice straw	Aqueous solution	As(V)	pH = 5 Temperature = 295 K Reaction time = 120 min Initial concentration = 4 mg/L	91.5	28.5 mg/g	[119]
Iron-modified rice straw derived from biochar	Aqueous solution	As(V)	Temperature = 298 K Surface area = 68.9 m ² /g	-	30.6 µg/g	[132]
Pristine/rice straw-derived biochar	Aqueous solution	As(V)	Temperature = 298 K Surface area = 68.9 m ² /g	-	25.6 µg/g	[132]

Table 12. Cont.

Type of Adsorbent	Type of Water	Type of Arsenic	Experimental Conditions	Maximum Removal (%)	Adsorption Capacity	References
Rice polish/rice bran (column bed method)	Aqueous solution	As(III)	pH = 7 Temperature = 298 K Initial concentration = 1000 µg/L Flow rate = 1.66 mL/min Column diameter = 2 cm Bed height = 25 cm	-	67 µg/g	[131]
Rice polish/rice bran (column bed method)	Aqueous solution	As(V)	pH = 4 Temperature = 298 K Initial concentration = 1000 µg/L Flow rate = 1.66 mL/min Column diameter = 2 cm Bed height = 25 cm	-	79 µg/g	[131]

6. Final Remarks and Future Outlooks

In the drinking water industry, commercially available activated carbon used in adsorption processes can cause significant operating and management costs. Biochar produced by pyrolyzing biomass, on which the scientific literature has been focusing more and more in recent years, can be a sustainable adsorbent alternative. This review paper focuses on waste deriving from the rice industry as adsorbent material because it presents a series of non-negligible advantages: (i) easily recoverable, (ii) at low cost, (iii) reusable in a circular economy perspective, and (iv) easily manageable even in rural areas of developing countries. In addition, the adsorption treatment can be (i) applied with simple plant configurations, (ii) adapted to different scales, even very small ones, and (iii) characterized by plant engineering and management simplicity.

Almost all the experimental tests showed in the scientific literature and collected in the review paper were conducted in laboratory-scale reactors with synthetic waters. At the laboratory scale, the operating conditions (such as pH, temperature, initial concentration of the pollutant tested) of the experimental tests are very controlled and, in most cases, kept constant in each test performed. In the real field, the situation can change, even significantly, also varying the efficiencies (adsorption capacities) of the adsorbent materials obtained from the controlled laboratory conditions.

In more scientific research, groundwater from existing realities should be tested, and not just synthetic waters recreated in laboratories with aqueous solutions. Usually, waters are tested with the addition of individual pollutants such as fluoride or arsenic. The removal mechanisms are studied individually without interfering substances. The next and necessary step would be to study multicomponent adsorption, to get closer to the treatments performed on a large scale on groundwater. In this way, the interaction mechanisms between different pollutants which are present simultaneously in real waters could be investigated.

There are few scientific studies conducted at the pilot scale and most are batch tests. It is important to conduct batch experiments as they allow to identify the optimal operating conditions of the adsorption mechanisms, but the next step must consist in carrying out (i) more pilot-scale studies, (ii) continuous tests, or at least semi-batch, and (iii) experiments on a scale ever closer to future real applications of the technology. Thanks to these research approaches, it is possible to get closer to the real functioning to evaluate and verify the actual application at full and industrial scale.

There are other critical issues related to the intrinsic properties of biochar that represent a limit to its application in the water sector. Some fundamental properties that must be improved are the specific surface, surface functionality, pore volume, and pore distribution to consequently increase both the adsorption and the catalytic capacity of the biochar [133,134]. There are several treatments to increase the specific surface of biochar, including vapor activation, metal doping, hydrothermal pyrolysis, and high temperature pyrolysis [133]. Studies have shown an increase in the surface area of rice straw biochar

(FeCl₃ doped pyrolysis) from 64.9 to 263.21 m²/g [135]. These values are encouraging but still lower than the specific surface of conventional carbon materials, which can exceed 2000 m²/g.

The inevitable cost increases due to these modification treatments which increase adsorption efficiency should not be overlooked. In the future, it will be necessary to identify possible compromises between the optimization of the production process and the cost reduction, with the aim of making real an effective applicability of biochar [136].

Luyen et al. [137] underlined one of the main disadvantages related to the use of fine biochar particles, that is, the difficulty of recovery/collection after being used and therefore, the possible redispersion in the environment with consequent secondary pollution. To solve this limitation and to improve the adsorption process in general, it is possible to couple the adsorbent materials with some metals (such as iron, manganese, aluminum), also in the field of nanotechnologies. This approach can be applied to exploit the excellent magnetic separation capacity and the possibility of increasing the surface area of the biochar. Future research is needed to explore and learn more about the use of metals and nanoparticles, in particular, their effective and suitable application, and their economic and environmental sustainability.

The stability of biochar is a property to be taken into consideration as there may be a possible dissolution of organic matter by the adsorbent material in the water to be treated. The stability of the biochar may depend on the type of raw material used and on the experimental conditions of the physical and chemical activation processes [138].

As Greiner et al. [139] pointed out, it would be advisable to further investigate the possible regeneration and recovery of adsorbent materials after use to make their application more sustainable, both from an economic and environmental point of view. This can represent an excellent strategy to allow both (i) the reuse of the spent adsorbent material and therefore increase its life cycle, and (ii) the study of any improvement or worsening of its adsorption capacity.

In summary, as also underlined by Palansooriya et al. [134], to ensure the up-scaling of biochar from recovered by-products, it is necessary to act following some logical steps: (i) select a local raw material with reduced environmental/economic impact, (ii) identify an advantageous thermal conversion method for the environment and with controlled costs, (iii) provide, if necessary, biochar modification treatments to improve its contaminant adsorption efficiency, and (iv) apply customized technology specific to the situation/place of intervention to maximize the results of the process.

7. Conclusions

The global problem of removing excess fluoride and arsenic from drinking water was the subject of this review, in which particular emphasis was placed on low-cost solutions applicable in both developed and developing countries. The removal of fluorides and arsenic by adsorption appears to be one of the potentially most suitable technologies, especially by virtue of the possibility of exploiting recovered and readily available adsorbent material, such as by-products deriving from the rice industry (e.g., rice husk, rice straw, rice bran).

From the studies of the scientific literature, it emerged that the adsorption capacity, with the same adsorbent material, is strongly dependent on the operating conditions (e.g., pH, temperature, contact time, dose of adsorbent material, initial concentration of pollutant) applied in the experiments. For the removal of fluoride, excluding an experiment performed with rice straw biochar loaded with La/Fe/Al oxides (adsorption capacity of about 111 mg/g), comparable adsorption capacities (in the range 10–16 mg/g) were obtained with both the use of (i) unmodified rice straw biochar and (ii) alumina/manganese impregnated on activated carbon derived from rice straw. Moreover, (i) the unmodified rice husk, (ii) rice husk treated with NaOH or Al(OH)₃, and (iii) silica nano adsorbent modified from rice husk allowed to obtain adsorption capacities generally between 8 and 15 mg/g. The highest adsorption capacity, equal to 55 mg/g, was obtained from the application

of an adsorbent material synthesized by silica nano derived from rice husk doped on calcium peroxide.

Generally, for the removal of arsenic, the lowest adsorption capacities were obtained with rice straw and rice bran (in the range 25.6–79.0 $\mu\text{g/g}$), while the highest was with iron oxide amended with rice husk nanoparticles (up to 82 mg/g), both cases with synthetic water. On the other hand, using unmodified rice husk biochar, excellent results were obtained (adsorption capacity up to 19.3 mg/g).

Although the rice industry by-products represent a promising adsorbent material, they should be studied in more detail as several aspects need to be better clarified, such as (i) the application to contaminated groundwater to study the complexity of multiple coexisting pollutants, (ii) experimental test at pilot scale in continuous conditions for a significant time, (iii) the improvement of some characteristics of the biochar such as surface area and porous structure with specific treatments (among others, metal coupling and chemical modifications), (iv) cost analysis on the effective full-scale applicability of biochar modifications treatments, and (v) the stability of the biochar during water treatment and its possible regeneration or recovery after use. Greater clarity on these aspects can lead to the identification of positive environmental/economic trade-offs, which can make real-scale implementation of these by-products as adsorbents in the drinking water industry feasible.

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