



# **Development of Ecological Strategies for the Recovery of the Main Nitrogen Agricultural Pollutants: A Review on Environmental Sustainability in Agroecosystems**

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**Abstract:** Nitrogen (N) is a fundamental nutrient for plant growth and for the performance of biological functions. In agroecosystems, nitrogen fertilization is aimed at providing a suitable N dose for crop growth, avoiding the impoverishment or the improper enrichment of nitrogen compounds in soil. The high application of nitrogen fertilizers is the main cause of the increase in nitrate leaching and loss of the quality of natural resources (groundwater and soil). In the last decades, new sustainable technological approaches have been developed and applied on laboratory and field scales to reduce the impacts of nitrogen pollution on the environmental matrices and to improve the sustainability of agricultural management. This review highlights the results of the implementation of sustainable remediation new strategies to reduce pollution from a main agricultural contaminant (nitrate) and describes the benefits obtained from the use of these solutions in agroecosystems.

**Keywords:** nitrogen fertilization; nitrate leaching; agricultural pollution; sustainable remediation strategies; biochar

### 1. Introduction

Agriculture, in the contemporary era, is characterized by a continuous supply of fertilizers and pesticides to maximize the world yield. In the past, most of the cultivated varieties have been selected and bred under optimal nitrogen conditions. The increased production of synthetic N fertilizer and the accessibility by farmers caused the increase in the use of nitrogen fertilizers as a guarantee for the agricultural harvest.

From 1930 to 1960, N fertilizer use increased from 1.3 to 10.2 million metric tons (MMt) [1]. In 2014, the global demand for N fertilizers was 112 MMt [2] and is expected to reach 240 MMt by 2050 [3]. Therefore, there was a concomitant increase in N losses to the environment, nitrate leaching to groundwater, aquatic eutrophication, ammonia and nitrous oxide emissions, and soil acidification [4,5].

The addition of nitrogen fertilizers has marked effects on the absorption of fertilizer by plants. There are different elements affecting nitrogen compounds uptake and accumulation in vegetable tissues such as environmental and agricultural factors [6]. Deficiency and excess nitrogen in plant species result in more or less evident manifestations depending on the species and climatic conditions (Table 1).



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Probable Effect of N Deficiency	Probable Effect of N Excess		
Photosynthetic rate reductions and Rubisco content decreases with a low leaf-N content	Slow plant development		
Poor growth of the plants, with reduced dimensions both at the root level (shallow and ramified roots) and at the level of the aerial part (small leaves and thin stems)	Long biological cycle		
Flowering reduction	Increase in water consumption		
Fruit helmet	Reduction of the resistance of the fruits, favoring the breaking and the phenomena of lodging (for example, in the autumn-vernini cereals)		
Reduction of the length of the biological cycle and early ripening	Reduction of resistance to climate change		
	Reduction of resistance to parasites		

Table 1. Effects of deficiency and excess of nitrogen fertilizers in plants.

Determination of actual plant consumption of nitrogen (N) is necessary to optimize fertilization efficiency and minimize the contamination of natural resources [7]. At the same times, it is necessary to find new strategies to minimize nitrogen losses, thus avoiding environmental damage.

This review explains the current state of knowledge on the latest ecological strategies for the remediation of groundwater contaminated by agricultural nitrates. In addition, the study aims to assess the application of sustainable technologies in the international scenario in order to provide a useful academic reference in favor of action programmes aimed at sustainable agriculture.

#### 2. Environmental Pollution by Agricultural Practices

Nitrogen fertilizers (N) have substantially tripled global food production over the past 50 years [8].

From 1950 to 2019, there was an increase in the global population from 2.5 to 7.7 billion, and it is expected to reach about 9.7 billion by 2050 [9], which poses a major threat to both global food security and environmental sustainability [10].

It has been estimated that, at the end of the 21st century, about 40% of the world's population will depend on inputs of fertilizers useful for food production. Therefore, the preparation of accurate fertilization plans in agroecosystems is essential for producing crops capable to meet the increase in food demand.

In agroecosystems, the mass inputs of fertilizers may lead to substantial environmental consequences, such as cascade effects of reactive N, hazardous to human well-being [11,12]. The over-application of nitrogenous compounds can lead to several problems directly related to human health (such as respiratory diseases induced by exposure to high concentrations of ozone due to greenhouse gases) and ecosystem vulnerability (as soil acidification and eutrophication of coastal systems) [13]. Additionally, the intensive use of agrochemicals (fertilizers and pesticides) compromises food safety [14].

Nitrogen is a fundamental mineral nutrient for both plant growth and agricultural yield [15]. It is absorbed by the roots in the form of ammonium or nitrate ion, assimilated by nitrate reductase, and subsequently incorporated into the amino acids [16,17].

The doses of nitrogen fertilizers depend on the crop species, soil and climate conditions, and the N content in the soil. Each culture requires an appropriate dose of nitrogenous elements concerning its plant cycle [18]. However, excessive application of N reduces crop yields [19].

An idea of the potential environmental impact of global fertilizer use is provided by the FAO data, according to which today 32% of the world's land is used for crop production. The projections are that the human population will expand to 9.2 billion in 2050 [20], which will require an increase of food by 70% and, therefore, an increase in yield, with the introduction of new high-yielding cultivars, fertilization, and other cultivation techniques [21,22].

Figure 1 shows how the production of fertilizers in the world has grown to meet the increase in food demand, with a predominant production of nitrogen fertilizers. In 2017, 119 million tons of nitrogen fertilizers were produced, 55 million tons of  $P_2O_5$  fertilizers, and 44 million tons of K<sub>2</sub>O fertilizers [23].



Figure 1. Production of fertilizers worldwide (adapted from Ref: [23]).

In line with fertilizer production, the application of fertilizers in agroecosystems worldwide has also increased. Until a few years ago, the use of nitrogen fertilizers in agricultural land was 109 million tons, followed by phosphorus and potassium fertilizers (Figure 2).



Figure 2. Use of different fertilizer types in agricultural land worldwide (adapted from Ref: [23]).

FAO described an annual growth of the three main fertilizers, namely nitrogen (N), phosphorus expressed in phosphate ( $P_2O_5$ ), and potassium expressed in potassium ( $K_2O$ ), of 1.5%, 2.2%, and 2.4%, respectively, from 2015 to 2020, with an application of fertilizers N equal to 118,763 million tons in 2020 out of 201,663 million tons of fertilizers in total [23].

As shown in Figure 3, there are other annual inputs into crop production, such as biological fixation of N (110 Tg yr<sup>-1</sup>), recycling of N from crop residues (16 Tg yr<sup>-1</sup>) and animal manure (18 Tg yr<sup>-1</sup>), atmospheric deposition, and irrigation water [24,25]. Human activity, however, through the high intake of synthetic fertilizers, has a predominant effect on the amount of bioavailable nitrogen [26].



Figure 3. The nitrogen cycle in an agroecosystem.

Agriculture is the world's main driver of environmental change, contributing to the increase in greenhouse gases (methane emissions, carbon monoxide, and nitrous oxide), the eutrophication phenomena, reduction in biodiversity [27,28], as well as air and water pollution [29,30].

One of the most important impacts of agricultural nitrogenous contaminants is the loss of surface water quality and groundwater through the increase in nitrate concentrations. Nitrogen is a key element in plant production and an inappropriate fertilization plan induces eutrophication. The development of algae and macrophytes, the resulting oxygen deficiency, and the development of toxic substances for fish and mammals represent a major global environmental problem [31].

Nitrate leaching is probably the main cause of nitrogen losses of agricultural origin [32–34]. The negative effects of excessive nitrogen fertilization are of increasing concern, stressing the importance of estimating nitrogen losses from agriculture [35] and developing practical nitrogen management strategies to reduce nitrogen leaching in favor of crop yields [36,37].

The aim of this review is to summarize current knowledge on green strategy for recovery from agricultural nitrates in groundwater, taking into account the development of the latest technologies applied for environmental sustainability. Three appropriate sustainable remediation methodologies are presented for the recovery of contaminated sites as a result of nitrate leaching of agricultural origin. In particular, a detailed focus on the ability of biochar to absorb and retain nitrogen compounds is reported.

Finally, a comprehensive European research scoreboard concerning the application of green and sustainable remediation strategies is proposed.

## 3. Green and Sustainable Strategies for Remediation of Nitrate Contaminated Groundwater

In the last century, agriculture has undergone drastic changes. There has been a reduction in pasture areas, an increase in soil tillage and the use of synthetic fertilizers, and an increase in farm animals per unit of agricultural area. Inorganic nitrogen fertilization practices have led to increased leaching of groundwater nitrates with serious environmental consequences. The results of some field experiments have advised that nitrate leaching responds exponentially rather than linearly to rising N inputs [38–40].

Groundwater is a fundamental natural source for supporting socio-economic development and ensuring the maintenance of the ecological balance of our society [41]. It offers 36% of drinking water, 42% of water for agriculture, and 24% of water for industrial use [42,43]. The qualitative property of groundwater resources worldwide is menaced by anthropogenic pollution. Therefore, there is a continuing need to develop advanced nitrogen management practices that increase N use efficiencies and reduce nitrate–nitrogen leaching.

Agricultural mitigation measures represent a set of traditional and innovative techniques aimed at protecting groundwater and increased efficiency in the use of nitrogen. Manure management and the effective use of organic fertilizers are important to reduce nitrate leaching. Precision fertilization also contributes to sustainable nitrogen application, which can lead to a reduction in nitrogen leaching [39]. Precision farming practices provide technological strategies (for example rate sowing/planting, fertilizing, and irrigation) that reduce agricultural inputs, in relation to the spatial and temporal needs of the fields, with a positive impact on both agricultural production and the environment [44]. Delgado et al. [45] demonstrated how the application of geographic information systems (GIS), global positioning systems (GPS), as well as modelling and remote sensing have maximized the synchronization of N applications according to culture needs, thus reducing losses of nitrogen compounds by leaching.

Weather conditions are crucial in nitrogen fertilization plans. For example, the application of organic fertilizers in the autumn period leads to increased nitrate leaching [46]. Harvesting crops (usually *Lolium*, forage radish, and other grassy species) represent a sustainable strategy to reduce the leaching of nitrogen compounds during autumn fertilization by sowing crops early enough [47]. The use of an intermediate crop in the autumn/winter period and the early sowing of winter cereals promote a reduction of the nitrogen surplus [48]. In addition, end-of-season intercalant crops could be an effective strategy for the conservation of N available after green fertilizer grazing [49].

Green and sustainable remediation (GSR) strategies represent a new approach in the field of soil and groundwater reclamation that has attracted global attention in recent years [50]. GSR technologies for groundwater polluted by nitrates of agricultural origin, including the use of biochar materials, green synthesis of engineered nanoparticles, permeable reactive barriers (PRB), and the release of long-term green remediation materials.

#### 3.1. Biochar

Excessive nitrogen fertilization or an unsuitable application timing of the N distribution induces nitrogen leaching, resulting in a loss of groundwater and surface water quality [51].

For a few years, biochar has been proposed as organic carbon soil (C) amendment to reduce leaching of soil nitrogen compounds [52] and increase the bioavailability of elements for plants. Biochar is a porous carbonaceous material resulting from the pyrolysis of agricultural residues and solid waste, recently widely applied to improve the characteristics of the soil and to recovery environmental matrices [53].

However, the ability of the biochar to reduce the leaching process of nitrates is influenced by type and duration of N fertilization plan, type of biochar and soil, amount of biochar applied, and the environmental conditions (e.g., temperature, humidity, etc.). In relation to the time of treatment, Bochard et al. [54] showed that nitrate leaching was decreased by 13% with biochar treatment and that the reduction of the leaching process was increased in longer experimental (>26% in 30-day times). Moreover, Beusch et al. [55] showed that the addition of specific types of biochar led to a significant decrement in nitrate leaching in long experimental times such as the use of woody biochar in a treatment time of eight months.

Studies have evidence that the biochar pre-conditioned with different nitrogen fertilizers promotes vegetative growth by reducing nitrogen nutrient leaching [56,57].

Nitrate leaching is influenced by the combination of two experimental factors such as biochar and soil type and Nguyean et al. [58] showed that the amendment with higher application rates results in a reduction of  $NH_4$  in clay soils and no change significant for nitrate. Ghorbani et al. [59] highlighted that soil properties are improved by the biochar, depending on the type of soil that has been amended. Biochar reduces nitrate leaching by 27% and 23%, respectively, in forest and agricultural soils [60].

Experiments conducted by Li et al. [61] have shown that the choice of method for the application of biochar affects the percentage of nitrate leached in groundwater. In particular, the treatment with 4% of biochar promotes a maximum reduction of leaching of nitrate of 17%, while a mix of biochar to 2% in the subsurface soil was found to be effective for the remediation. The importance of the type of treatment for remediation is also highlighted by Dorais et al. [62], who concluded that the reduction of leachate nitrate varies from 30% to 50% for soils amended with 10% and 20% of biochar, respectively.

Biochar amended soil with rain irrigation reduces the loss of nitrates compared to treatments with full and furrow [63].

Several reviews focused on the impact of biochar on nitrogen flow in agroecosystems. However, the performance of biochar amendment varies considerably with biochar properties and site environments, such as feedstock, dosage, soil characteristics, and treatment time.

According to the state-of-the-art knowledge for the evaluation of the use of biochar as a strategy for the nitrate leaching remediation (Table 2), a few studies have aimed at evaluating the advantages of biochar amendments to soil and the amount of reduced nitrate.

Table 2. Summary of the 2018–2021 latest researches or	n the biochar application re	eduction on nitrate	leaching and	experi-
mental method details.				

Biochar Source	Experiment Type	Treatment Type	Treatment Duration	Soil Depth	NO <sub>3</sub> - Leaching	Advantages	Reference
Rice husk and populous wood biochar	Soil column experiment	Biochar + urea + arbuscular mycorrhizal fungi	10 weeks	Entire depth of the soil column	63–78%	Biochar and mycorrhizal fungi decreased nitrate leaching	[57]
Wheat straw	Greenhouse study	Biochar + mineral fertilizer	9 weeks	Entire depth of the soil column	34–70%	The amount of biochar applied to soil determined a different response in terms of leached nitrate	[64]
Balsam fir + white and black spruces	Greenhouse study	Biochar + certified organic amendments	3 years	Half of the experimental units	30–50%	Biochar in several organic soils reduced the nitrogen leaching	[62]
Corn stalks	Soil column experiment	Biochar	1 year	Upper half of the columns	23–27%	Soil use and management can influence biochar action in mitigating nitrate leaching	[60]
Canola straws	Field experiment	Biochar + urea	4 months	Topsoil	23–32%	Biochar positively influenced the reduction of nitrate leaching in rice fields.	[65]

Biochar Source	Experiment Type	Treatment Type	Treatment Duration	Soil Depth	NO <sub>3</sub> - Leaching	Advantages	Reference
Feedstock of mixed hard and soft virgin wood	Cranberry farm	Biochar + compost	10 weeks	Entire depth of the soil column	22–92%	Increased biochar application decreased ammonium, and nitrate leaching.	[66]
Corncob biochar	Local landscaping	Biochar + manure or ammonium chloride or sodium nitrate	10 weeks	Entire depth of the soil column	19–25%	Treatment with biochar and sodium nitrate reduced nitrogen losses more	[67]
Apple branches	Field experiment	Biochar + urea	2 years	Topsoil	13–74%	Biochar and mineral nitrogen fertilizers under the right dosage conditions reduced the loss of nitrates.	[68]
Apple branches	Soil column experiment	Biochar + ammonium nitrate	6–20 h	Surface layer of soil; underlying soil; the plow layer of soil	8.3–17%	The biochar applied in the undersoils of orchards or during deep processing of fields is advantageous for agricultural and environmental purposes	[61]
Ranches of oriental plane tree ( <i>Platanus</i> <i>orientalis</i> ) and dead pig	Field experiment	Biochar + ammonium nitrate	20 weeks	Entire depth of the soil column	10-42%	Platanus orientalis branch biochar could be used to improve N fertilizer use efficiency by reducing N leaching loss from soils	[69]
Winter-pruned apple branches	Field experiment	Biochar + N fertilizer	48 h	Entire depth of the soil column	10–69%	Biochar and nitrogenous fertilizers in low dose were a valid strategy to reduce nitrate leaching and promote the absorption of nitrogenous elements in the plant	[70]
Spruce chips	Abandoned field and cultivated field	Biochar	19 weeks and 31 weeks	Entire depth of the soil column	5–31%	Biochar retained nitrate and total nitrogen in both soils.	[71]
Pinewood	Field experiment	Biochar + inorganic fertilizer (ammonium nitrate) or biosolids (aerobically digested Class B biosolids)	3 years	Topsoil	60%	Soils treated with biochar and inorganic fertilizers reduce nitrate loss	[72]
Runks and branches of Prosopis juliflora	Field experiment	Biochar + clay + urea	16 months	Topsoil	46%	Biochar reduced the nitrate leaching in longer experimentation time	[55]
Corncob biochar	Vegetated filter strip plots	Biochar	1 year	Entire depth of the soil column	40%	The biochar in the surface improved nitrogen retention	[73]
Pinus monticola wood	Field experiment	Biochar + vermicompost	2 months	Entire depth of the soil column	37%	Biochar and vermicompost reduced the leaching of nitrogen compounds	[74]

## Table 2. Cont.

Biochar Source	Experiment Type	Treatment Type	Treatment Duration	Soil Depth	NO <sub>3</sub> - Leaching	Advantages	Reference
Melaleuca cajuputi waste	Forest	Biochar + urea	5 months		29%	The use of biochar of 2% and 4% in clay soils reduce nitrogen losses by 29.19% and 28.65% respectively	[75]
Holm oak biochar	Greenhouse study	Biochar + NPK fertilizer	3 months	Entire depth of the soil column	26%	Biochar reduced the nitrate leaching to soil specific depths	[76]
Urban green waste	Field experiment	Biochar + urea	50 days	Topsoil	24%	Agro-waste biochar and urea reduced the use of mineral nitrogen fertilizers	[61]
Bagasse	Farm	Biochar + urea	1 year	Entire depth of the soil column	17%	Biochar application and sprinkler irrigation decreased nitrate concentration.	[63]
Pinus pinaster and <i>P. radiata</i> wood chips	Lysimeter system	Biochar + pig slurry	8 months	Topsoil	Significant decreased	Freshly added biochar has a higher adsorbent capacity than the biochar naturally aged	[77]
Rice husk biochar	Greenhouse study	Biochar	10 months	Entire depth of the soil column	Reduced	Rice husk biochar decreased nitrate leaching principally in clay soil than loamy sand	[59]
Rice husk charcoal	Field experiment	Biochar + green mulch	28 days	Soil cores	Reduced	Biochar and mulching improved the reduction of nitrate loss.	[78]
Rice husk	Field experiment	Biochar + urea	4 months	Topsoil	Reduced	Biochar and N fertilization improved rice productivity and reduced nitrate leaching	[56]
Fir woodchips	Field experiment	Biochar	1 year	Topsoil	Reduced	High temperature biochars reduce nitrate leaching	[79]
Spruce biochar	Boreal grass field	Biochar + cattle slurry	3 years	Topsoil	Decreased	The biochar retained the nitrate produced by the use of fertilizers in the soil	[71]
Rice husk and rice straw	Field experiment	Biochar + urea	5 months	Topsoil	Any influence	Soil treatment with biochar reduced leaching of ammonium nitrogen	[58]
Aspen sawdust	Soil column experiment	Biochar + urea	4 months	Topsoil	Any influence	Sawdust biochar reduced the NH4 <sup>+</sup> concentration in a rice paddy	[80]

#### Table 2. Cont.

#### 3.2. Green Synthesis of Engineered Nanoparticles

Green synthesis is a novel field aimed at the improvement of engineered nanoparticles (NPs), useful for the remediation of water and soils contaminated by heavy metals, organic pollutants, and synthetic products (for instance pesticides and pharmaceuticals). The advancement of engineered nanoparticles (NPs) has received considerable consideration in the remediation technologies area [81], and among environmental applications, it is possible to inject NP into the subsurface in order to create reducing conditions [82] or to use them as catalysts in waste water [83]. This means that the remediation capacity of NPs depends on chemical and structural properties.

To remove nitrate from aqueous solutions, several methodologies have been designed and applied, including biological denitrification, chemical reduction, ion exchange, and others.

Denitrification can be accelerated by nano-zero-valent iron (nZVI), as an electron donor with a large specific surface and other reactive activity [84]. Nitrate can then be reduced to nitrite and ion ammonia by nZVI, which in turn can be biodegraded to nitrous oxide and molecular nitrogen through the bacterial denitrification process [85–87]. Wang et al. [88] showed that *Alcaligenes* sp. TB with nZVI/Pd promotes a 31% nitrate removal in 28 h. The use of nanoscale zero-valent iron/copper supported on chelating resin removed 95% of nitrate [89]. Liu et al. [90] pointed out that among the best green synthesis strategies, the zero-valent iron-based (ZVI) material represents the most efficient solution for nitrate reduction in groundwater and surface water. Besides, they stressed that the optimization of ZVI performances can be achieved by changing the morphology and structure of ZVI.

Recent research conducted by Manikandan et al. [91] have highlighted that the green synthesis of NP Al<sub>2</sub>O<sub>3</sub> from *Prunus* x *yedoensis* leaf extract (PYLE), have promising applications in the removal of nitrates in environmental samples. The green synthesis of iron nanoparticles (INP) under aerobic and anaerobic conditions via nitrate reductase enzymes (NAP/ NAR) generated by *Proteus mirabilis* strain 10B was tested for denitrification power in wastewater samples (urban, agricultural, and industrial) [92]. The results of the study make it possible to propose the INPs as a valid candidate in bioremediation activities of nitrate pollution.

With regard to technologies to remove nitrate from water polluted by agricultural contaminants, catalytic reduction has attracted increasing attention as it is characterized by a high bioremedial capacity, with lower costs than other methods [93]. The use of biometallic catalysts based on a noble metal such as palladium (Pd) and a transition metal such as copper (Cu) represent one of the most used supports for nitrate reduction [94]. Indeed, Perez-Coronado et al. [93] demonstrated that a new approach based on the screening of active Pd sites in PdCu catalysts by sodium bis-2-ethylhexyl sulfosuccinate (AOT) causes a decrease in activity for nitrate reduction. A cost-effective and stable three-dimensional Pdoped  $Co_3O_4$ /nickel foam has been used in order to promote the electrocatalytic reduction of  $NO_3^-$  in water [95].

The addition of 2-D graphite carbon nanoparticles, produced by electrochemical processes, to fertilizer mixtures was performed during an experiment involving the cultivation of romaine lettuce [96]. Research has shown that the use of NPs could allow farmers to apply fewer fertilizers, achieving high production yields and reducing the amount of nitrates reaching the surrounding water bodies.

#### 3.3. Permeable Reactive Barriers

The methods of nitrate removal from the groundwater provide for the application of physical, chemical, and biological methodologies. The electrochemical method, mainly preferred by researchers, shows limitations including the high number of by-products [97]. The bio-denitrification process based on the permeable reactive barrier (PRB) is now considered one of the most effective and promising technologies for the recovery of nitrates in environmental matrices [98]. As shown in Figure 4, PBR is a porous reactive material positioned along the path of a plume of subterranean water in order to remove nitrates from the plume as it passes through it [99].



Figure 4. Representation of the location of the PRB relative to a high nitrate groundwater flow path.

The effectiveness of PRBs in improving the quality of groundwater contaminated by nitrogen pollutants has been proved by several authors. The barriers can be made from different types of material. In addition, factors influencing the nitrate removal capacity include carbon sources, temperature, and hydraulic conditions. Mittal et al. [100] show that absorption capacity decreases if the temperature exceeds 45 °C due to change in chemical potential at higher temperatures. Table 3 summarizes the results obtained from 2016 to date.

Substrate Type	Nitrate Removal %	References
Corncob	86-100	[101]
Fly ash and rice husk	95	[100]
Woodchip	40	[102]
Tea factory waste and hazelnut husk	40-100	[103]
Alternative latrine and waste materials	13–57	[104]
Mixture of gravel and mulching	97	[105]
Wood shavings or biochar	33–37	[106]
Mixture of Fe, activated carbon and coarse sand	92	[107]
Granular cast ZVI	15-20	[108]
Poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) and ceramsite	95	[109]

Table 3. Percentage of nitrate removed according to the type of material as a carbon source.

The use of PBR provides a viable economic and ecological alternative for the remediation of polluting groundwater from nitrogenous contaminants of agricultural origin. Studies suggest that the recovery and use of waste materials for the construction of barriers is an increasingly widespread ecological strategy.

## 4. Sustainable and Green Remediation Strategies in Europe: Research Studies and Field-Scale Applications

Clean water is a vital resource for human health and well-being, so safeguarding water quality is one of the cornerstones of European environmental policy. The 1991 Nitrates Directive is one of the first EU legislation aimed at controlling water pollution by agricultural contaminants and improving water quality [110]. Nitrogen is an essential nutrient for agricultural production and population growth is leading to the use of high concentrations of nitrogen elements in agroecosystems. The massive distribution of chemical and organic fertilizers is the main source of water pollution in Europe.

In recent decades we have already witnessed profound changes in modern society and the "green revolution" in place recalls the need to disseminate the latest sustainable technologies in both the scientific and economic system.

As shown in Figure 5, from 2000 to date, scientific research in the field of green and sustainable remediation (GSR) has increased. Among the three technologies described above, the use of biochar is the green strategy mainly researched, in Europe and around the world, to reduce pollution caused by the increase in agricultural nitrates. In contrast, the use of nanoparticles has not yet been explored by European researchers.



**Figure 5.** Number of studies on the different types of Green and Sustainable Remediation carried out in Europe (in yellow) and in the world (in green) from 2000 to today. Source: Scopus database (http://www.scopus.com/ accessed on 29 April 2021).

In particular, the GSR studies focused on the biochar's ability to bind nitrate, reducing the percentage of leached nitrogen compound in surface and groundwater. Of the 101 papers on biochar published, Europe has contributed 38 publications. The United Kingdom was the European country which published the largest number of scientific papers (9), followed by Spain and Germany (6) and Italy (5). Ireland has published five articles on the application of biochar for environmental purposes as Italy. From 2017 to today, Finland has contributed an article for each year, indicating a recent and continuous interest in the remediation strategy. Worldwide, China is the nation with the largest number of publications, as it is the world's largest producer of crop residues [111], followed by the United States.

The analysis of the keywords allows to reveal the characteristics and the tendencies of development of the field [112]. During the bibliographic study for the biochar, the words "biochar" and "nitrate leaching" were used.

In reference to published work on engineered nanoparticles (NPs) [113], the number of publications is only one. In fact, green synthesis is a new emerging field with the aim of developing and improving the production of effective and ecological nanoparticles. India is the country that contributed to deepening the challenges for the synthesis of NPs products for environmental recovery.

For the period under examination, the bibliographical search through the keywords has previewed the insertion of the words "green nanoparticles" and "nitrate leaching".

Finally, the graph in Figure 5 shows the recent attention in investigating the potential of permeable reactive barriers in the field of sustainable green technologies [114]. From 2000 to 2021, bibliographic research using the keywords "permeable reactive barriers" and "nitrate leaching" returned eight publications. China is the country that has begun to study the ability of barriers to reduce the nitrogen contamination from agricultural practices. In

Europe, the countries that are carrying out research and application studies on permeable barriers are Belgium, Italy, and the United Kingdom.

#### 5. Conclusions

The importance of sustainability in agriculture and the growth of the world's population requires the implementation of adequate nitrogen management strategies and fertilization techniques, capable of preserving both the quality of environmental matrices and crop yields.

High nitrate concentrations in water bodies due to N soil leaching cause nitrate pollution of drinking water and, as a consequence, excess N levels change the ecological balance of the natural resources. This review describes and discusses environmental pollution by agricultural practices and the most recent green and sustainable remediation (GSR) strategies developed to limit nitrate pollution, such as the use of biochar, engineered nanoparticles, and permeable reactive barriers.

Special attention is paid to biochar, employed usefully as a soil improver and to reduce the concentrations of environmental contaminants. Prior to defining the optimal remediation protocols, it is necessary to consider and study the biochar favorable properties i.e., biochar type, fertilization type, and characteristics of soil. The performance, in terms of nitrate leaching reduction percentage, achieved with the rice husk and wood biochar in urea–arbuscular mycorrhizal fungi-fertilized soils was the highest found in literature, with an average value of 70%. The fir biochar was instead found to be the most performing in experiments conducted in soil treating with organic fertilizers. In addition, several research studies have shown that the use of biochar allows for a reduction in the employment of nitrogenous fertilizers thus preserving groundwater quality.

Green synthesis is an emerging multidisciplinary area aimed at improving engineered nanoparticles (NPs) for the recovery of environmental matrices from agricultural origin organic contaminants. Among the best GSRs, zero valence, iron-based material (ZVI) is the most efficient solution for reducing nitrates in groundwater. In fact, the use of these NPs has proven highly promising, with a nitrate removal of 31–95%.

Finally, in this review, we have described how the use of PRBs is a valid ecological strategy for the remediation of water bodies polluted by N contaminants.

The highest percentage of nitrate removal has been achieved using permeable barriers consisting of corncob biochar and fly ash-rice husk biochar, confirming the carbanions soil improver as a valid green material for environmental remediation.

Using biochar is the main sustainable strategy currently adopted in Europe for the recovery of environmental matrices from agricultural pollution.

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