

Biomass for Bioenergy and Biochar Applications – 15653

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ABSTRACT

Exponential population growth is a growing challenge that will increase the global demand for both food and bioenergy, increase the pressure on land and water resources and change its availability, and also influence the pattern of biomass production. The objective of this study is to evaluate and compare the efficiency of bio-sorbents obtained from different parent materials, zeolite, and activated carbon as an infiltration media of contaminated surface-groundwater by assessing reductions of chemical oxygen demand, nitrogen and phosphorus compounds, as well as sum selected trace elements. Furthermore, the current research will investigate how long the cleaning capacity of the selected bio-sorbents lasts and how the performance of the filter changes under an increased load of contaminants. Bio-sorbents characteristics, its applications as a green environmental sorbents for the contaminated water and soil, and its importance for the soil sustainable use are also reviewed.

INTRODUCTION

Water consumption has increased and is expected to continue rising as the population increases and the availability of water becomes increasingly limited with a changing climate [1, 2]. Not only does quantity but also the quality of surface-groundwater affects the long-term sustainable use of water resources, especially in intense agricultural regions, where the urban and rural population, irrigation and industries have consumed a huge portion of major water supplies [3]. The intense applications of fertilizers in agricultural regions and the other point source discharges have resulted in severe surface-groundwater and soil contamination, particularly nutrients (nitrogen and phosphorus) and heavy metals [e.g., 4, 5, 6, 7, 8].

Nutrients (especially nitrogen and phosphorus) is an essential element of aquatic ecosystem, but excessive levels can reduce the quality of water for human uses and lead to many environmental and health problems. For example, the deleterious effects of excessive environmental N include the following: (1) an oxygen deficient condition referred to as “blue baby syndrome” in infants under the age of six months [9]; (2) the risk of non-Hodgkin's lymphoma in adults and reduced stomach acidity [10, 11]; and (3) acidification of soils and water resources [12].

High phosphate concentrations can cause kidney failure and damage the liver, and osteoporosis [12]. The increasing phosphorus concentrations in surface waters caused eutrophication phenomenon, which increases the growth of phosphate-dependent organisms, such as algae and

duckweed, which, in turn, consume great amounts of oxygen and prevent sunlight from entering the water, All these changes in the water medium, make the water fairly unliveable for other organisms [12].

The fate and transport of nitrogen and phosphorus in water have been very well studied over the world [4, 5, 13]. A number of studies conducted over the last three decades in Midwest - United States have indicated that nitrogen/phosphorus leaching is occurred to the surface water and shallow groundwater aquifers [14, 15, 16]. All the previous studies were focused on the monitoring and management methods, and despite all the efforts to establish an effective management system that can protect water quality in the Midwest - United States, more than 20% of the surface-groundwater samples in the Midwest have nitrogen/phosphorus concentrations greater than the EPA maximum contamination level (MCL) [7], which is 10 milligrams per liter (mg/L or part per million [ppm]).

Heavy metals exist extensively in the natural and human-altered environments. They are careering a risk to public health and environment because of their toxic, carcinogenic, and non-biodegradable nature. They are mainly introduced into the environment from point sources (e.g., discharges from mining, metal plating, battery, and paper industries). Lead, copper, cadmium, and nickel are among the most toxic and carcinogenic heavy metals that could cause serious environmental and health problems. The United States Environmental Protection Agency (USEPA) has established maximum contaminant level targets for these heavy metals in natural waters.

Many methods have been created to address the EPA rules and regulations which required removal of nutrients and heavy metal compounds from water. For example, precipitation, ion exchange, electro-coagulation, membrane filtration, and packed-bed filtration are some of the traditional water treatment technologies that have been found to be effective in reducing nutrients and heavy metal concentrations [17, 18, 19]. However, most of these technologies have been found to be associated with high operation cost and/or sludge disposal problems [20]. Therefore, the need has increased for developing an alternative and low-cost technology for nutrients and heavy metal removal from water. Bio-sorbents have been suggested to be a potential candidate to satisfy these needs [21].

Bio-sorbents have recently been used as a mechanical support to disperse and stabilize engineered nanoparticles to assist their environmental applications [22, 23, 24, 25]. However, these applications have been conducted mainly on small-scale models that are currently limited to specific bio-sorbent types and site locations (e.g., it is limited for aqueous solutions or batch processes) [26, 27]; also only limited information is available on bio-sorbent and metal interactions as well as the associated underlying mechanisms [28]. On the other hand, some kind of bio-sorbents can release some toxic pollutants to the environment, which have negative effects on the soil and surface-groundwater systems [29].

The overall goal of this research is to study the use of bio-sorbents as a replacement/ alternative for activated carbon and similar materials to serve as a filter material for surface-groundwater purification. The specific objectives are (i) to evaluate the chemical oxygen demand (COD), total nitrogen (Tot-N) and total phosphorus (Tot-P) reductions in surface-groundwater infiltrated filters made of bio-sorbents and activated carbon and (ii) to compare the surface-groundwater purification efficiency of bio-sorbents and activated carbon.

BIO-SORBEN EXAMPLES AND BACKGROUND

The Amazonia dark earth “Terra Preta de Indio” that formed as a result of native settlement in Brazil [30, 31] represents the first evidence of biochar use in history as a bio-sorbent. Biochar is the carbon rich, fine-grained, porous product obtained as a by-product of biomass pyrolysis, thermal/hydrothermal decomposition of plant/organic wastes-derived materials under limited supply of oxygen at relatively low temperatures (< 1000 degrees Celsius [°C]) to produce combustible gases [32, 33, 34, 35, 36, 37, 38].

The variations in the production process and the intended use are distinguished biochar types from charcoal and similar materials. Biochar can be easily obtained from many kinds of plant and waste biomass like agricultural crop residues, forestry residues, animal waste (manure), woody materials, food processing waste, paper mill waste, municipal solid waste, sewage sludge, and anaerobically digested/ undigested biomass residue materials (or the remains of biofuel production) [28, 32, 35, 39, 40, 41, 42, 43, 44, 45, 46, 41]. However, biochar may contains considerable amounts of soluble base cations (toxic heavy metals) - especially the biochar that developed from sewage sludge and municipal solid waste – that can be released rapidly into soil [35, 47, 48, 49] therefore biochar must be carefully handled before long-term application to soils.

Biochar is produced at relatively low-cost compared to activated carbon [35], because it is generally obtained at lower temperature (less energy) and without further activation processing [50, 51], and it can be used for carbon sequestration in agricultural applications and environmental management; whereas charcoal is a source of charred organic matter for producing fuel and energy.

BIOCHAR CHARACTERISTICS

Many authors have reported some of biochar general and specific characteristics and properties. The quality of biochar and its effective potential value to the environmental applications are greatly affected by the nature of the feedstock (parent material) [38, 52], and the variations in the pyrolysis process, principally temperature and furnace residence time [28]. Because biochar can be made of various plant/waste biomass sources under different processing conditions, it is therefore very important to characterize their physicochemical properties before use [53].

Biochar has a neutral to alkaline pH. The acidic neutralizing capacity of biochar and its effects on the activity of soil bacteria (liming effect of biochar) may vary based upon the mineral

deposits and oxygen-organic functional groups on biochar surfaces formed during pyrolysis processing or produced from parent feedstock [46, 54, 55, 56]. For example, Chan et al. (2007) [57] has reported the acidic media of biochar, and Zweiten et al. (2010) [58] has reported that biochar derived from paper mill waste pyrolyzed at 550 °C had a liming value around 30% that of calcium carbonate (CaCO₃).

Biochar in some cases possess large surface area, high degree of porosity [28], good ion exchange capacity, and a range in chemical compositions [24]. Higher pyrolysis temperature often results in an increase of surface area (e.g., Day et al. (2011) [59] reported that increasing the pyrolysis temperature from 400 to 900 °C caused an increase in biochar surface area from 120 to 460 m²/g), ash content, and pH, while P, calcium (Ca), and magnesium (Mg) increased as temperature increased [55].

BIOCHAR AND ENERGY PRODUCTION

Research on the environmental use of biochar in the energy applications is almost limited to the production of bioenergy during the fast and slow pyrolysis processes, through converting waste biomass to biochar [60]. Lower pyrolysis temperature (slow pyrolysis) often results in an increase of biochar yield and decrease of carbonized fraction of biochar (Table 1), i.e., biochar carbon content is inversely related to biochar yield [28, 61].

Table 1 Pyrolysis processes and biochar products distribution*

Process	Temperature (°C)	Residence time (S)	Biochar carbon (bio-oil) (%)	Biochar yield (%)	Synthetic gas (syngas) (%)
Fast pyrolysis	300-1000	Short (< 2)	75	12	13
Intermediate pyrolysis	~500	Moderate (10-20)	50	25	25
Slow pyrolysis	100-1000	Long (300-1800)	30	35	35
Gasification	>800	Moderate (10–20)	5	10	85

Table adopted from: [52, 60, 61, 107, 108]

Chen (2011) [28] showed that increasing the pyrolysis temperature from 300 to 800 °C caused an increase in biochar carbon content by about 37%, whereas the biochar yield has decreased by 41%. However, some other authors [55] have reported that biochar carbon contents significantly decreased from 36.8% to 1.67% with increasing the pyrolysis temperature from 100 to 500 °C. It was noticed that a maximum bioenergy output of 8.7 millijoules per kilogram (MJ/kg) of biomass could be obtained, with an intermediate yield of 35% biochar [40]. On the other hand, Yuan (2013) [62] used sewage sludge biochar as an efficient catalyst for oxygen reduction reaction in a microbial fuel cell (MFC), and their resulted indicated that sewage sludge biochar can be a potential alternative to platinum (Pt) in MFCs. However, industrial scale production of

biochar and/or bioenergy from biomass is still controversial, with research currently ongoing within the scientific and technological communities focusing on the most effective method of producing it on a large scale.

BIOCHAR FOR SOIL IMPROVEMENT

Because of its potential as a long-term sink for carbon, biochar has been distinguished as a considerable material in soil amendment applications to improve the physicochemical and biological properties of soils such as:

1. Improve crop production, the alkaline pH of biochar encourages a liming effect on acidic soils, thereby potential increase in plant productivity, e.g., Glaser et al. (2002) [63] have documented the positive implications of biochar in seed germination, plant growth, and crop yields. However, results of few studies on biochar effects on crop production showed no significant effects on crop productivity [64].
2. Soil fertility by applying biochar together with organic or inorganic fertilizers can enhance the retention of fertilizers (nutrient retention) and then enhance crop yields [65], e.g., Sohi et al. (2009) [52] has documented a decrease of nutrient leaching due to biochar applications. On the contrary, Cowie et al. (2012) [66] have reported that biochar obtained from kind of agricultural crops or certain type of forests may lead to a decline in soil fertility and cause an increase in soil erosion.
3. Soil-water holding capacity, e.g., Glaser et al. (2002) [63] has reported an increase in the soil-water retention capacity by 18% with biochar existence.
4. Encouraging the host of beneficial microorganism and increased its population [36, 44, 67, 68].
5. Soil amended with biochar has showed null to positive impacts on earthworm population [69], especially wet biochar that could help mitigate avoidance of earthworms by preventing desiccation [70]. However, negative effects of biochar on earthworm population are suggested to be related to rise in soil pH by biochar derived from sludge, manures or crop residue [69].
6. Serve as a recalcitrant carbon stock, and modify the soil enzymatic activities, which influences the biogeochemical processes of the soil microbial communities [67, 71], which fasten the decomposition of soil native carbon (biochar positive priming effect).
7. Applying of biochar to soil may influence its chemical properties such as changes in pH, electrical conductivity, cation exchange capacity and soil buffering, and metal sorption efficiency [72, 73, 74, 75]. Biochar could enhance the chemical hydrolysis of the soil by increasing its pH, which enhances the biochar positive priming effect [76, 77, 78].
8. It has also been suggested that biochar can even enhance crop resistance to disease [38].
9. Some other researchers, on the contrary, have reported that biochar could increase the adsorption of dissolved organic carbon [79, 80], that decreasing its decomposition rate (enhance biochar negative priming effect), which has attributed to the toxicity of biochar that resulting in a decreasing in microbial activity [80].

BIOCHAR AND SOIL REMEDIATION

It has been noticed that biochar made from a variety of sources had strong sorption ability to different types of organic contaminants and pesticides (Table 2) [81, 82, 83]. The biochar sorption ability has been shown to exceed that of the natural soil organic matter by a factor of 10–100 in some cases [84].

Cui et al. (30) [85] studied the sorption and desorption of phosphorus on ferrihydrite (Fe-oxide) in the absence or presence of biochar in soils. Results showed that the sorption of phosphorus on Fe-oxide decreased in the presence of biochar and desorption of adsorbed phosphorus on Fe-oxide was enhanced by combination with biochar. The enhanced phosphorus bioavailability in biochar amended soil may due to the changes of soil environment for microorganisms.

BIOCHAR AND CLIMATE CHANGE MITIGATION

Biochar is being considered as a potentially significant material of storing carbon (sequestering carbon in soil) for long periods [86] to reduce the emissions of greenhouse gasses from soils and sequestering atmospheric CO₂ in order to mitigate global warming [32, 33, 39, 51, 86, 87, 88]. Singh et al. (2012) [89] estimated the mean residence time of carbon in biochar between 90 and 1600 years depending on the labile and intermediate stable carbon components.

Conversely in an attempt to clarifying the key mechanisms in which biochar may act in mitigating emissions of nitrous oxide (N₂O), Cayuela (2013) [46] investigated the published literature in this matter from 2007 to 2013, which are 30 studies with 261 experimental treatments. They concluded that, (1) biochar reduced soil N₂O emissions by 54% in laboratory and field studies; e.g., Rondon et al.(2005) [90] found that N₂O emissions were decreased by up to 50% for soybean and by up to 80% for grass growing in a low-fertility oxisol from the Colombian savanna, (2) the biochar parent materials, pyrolysis processes and carbon/nitrogen (C/N) ratio were shown to be key factors influencing emissions of N₂O while a direct correlation was found between the biochar application rate and N₂O emission reductions, and (3) interactions between soil matrix and the chemical form of N-fertilizer applied with biochar were also found to have a major influence on soil N₂O emissions.

Table 2 Biochar utilization for organic/inorganic contaminants remediation in soil

Contaminant	Biochar type	Effect	References
Agro chemicals			
Atrazine	Dairy manure (450 °C)	Sorption	[54]
Chloropyrifos and carbofuran	Woodchips (450 and 850 °C)	Adsorption due to high surface area and nano-porosity	[76]
Pentachlorophenol	Bamboo (600 °C)	Reduced leaching due to diffusion and partition	[112]
Pentachlorophenol	Rice straw	Adsorption due to high surface area and microporosity	[82]
Simazine	Hardwood (450 and 600 °C)	Sorption due to abundance of micropores	[113]
Antibiotics			
Tylosin	Pulpgrade hardwood and softwood chips (850 and 900 °C)	Sorption	[114]
Other hydrocarbons			
Phenanthrene	Pine wood (350 and 700 °C)	Entrapment in micro- or meso-pores	[115]
Polycyclic aromatic hydrocarbons (PAHs)	Hard wood	Sorption and biodegradation	[73]
Polycyclic aromatic hydrocarbons (PAHs)	Sewage sludge (500 °C)	Partitioning	[116]
Heavy metals and trace elements			
Arsenic	Hard wood (400 °C)	Mobilization due to enhanced pH and DOC	[117]
Arsenic and copper	Hard wood	Mobilization due to enhanced pH and DOC	[73]
Arsenic, cadmium, chromium, cobalt, copper, nickel, lead, and zinc	Sewage sludge (500–550 °C)	Immobilization of arsenic, chromium, cobalt, nickel and lead due to rise in soil pH; mobilization of copper, zinc and cadmium due to high available concentrations in biochar	[116]
Cadmium and zinc	Hard wood	Immobilization due to enhanced pH	[73]
Cadmium, copper and lead	Chicken manure and green waste (550 °C)	Immobilization due to partitioning of metals from the exchangeable phase to less bioavailable organic-bound fraction	[118]
Copper	Broiler litter (700 °C)	Cation exchange; electrostatic interaction; sorption on mineral ash contents; complexation by surface functional groups	[72, 104]
Copper and lead	Oak wood	Complexation with phosphorous and organic matter	[119]
Lead	Dairy manure (450 °C)	Immobilization by hydroxypyromorphite formation	[55]
Lead	Oak wood (400 °C)	Immobilization by rise in soil pH and adsorption onto biochar	[107]
Lead	Rice straw	Non-electrostatic adsorption	[120]
Lead, copper, zinc and antimony	Broiler litter (350 and 600 °C)	Stabilization of Pb and Cu; desorption of Sb	[72]
Nickel, copper, lead and cadmium	Cottonseed hulls (200–800 °C)	Surface functional groups of biochars controlled metal sequestration	[104]

Some other authors have explained the mechanism by which biochar is reducing the soil N₂O emissions as that biochar is affecting soil physical properties, either by reducing soil compaction and bulk density [91] or by sorbing an excess of soil moisture [92, 93], which leads to an increase in soil porosity and aeration which is a major factor governing N₂O generation and diffusion [94] because it regulates the oxygen availability for microorganisms, and then affecting the activity/ratio of nitrifiers and denitrifiers [46, 95], which changes the microbial abundance and community composition [67].

Shang (2013) [96] studied the potential of biochar derived from camphor, bamboo, and rice hull to adsorb H₂S at various temperatures. They concluded that biochar with particle size ranging from 0.3 to 0.4 mm (rice hull) possesses a maximum H₂S sorption capacity at a pyrolysis temperature of 400 °C.

While there is a strong evidence that, in many cases, emissions of carbon dioxide (CO₂), N₂O and hydrogen sulfide (H₂S) are reduced, the potential application of biochar with regards to reducing the emissions of N₂O and other greenhouse gases such as methane (CH₄) and H₂S, and the hypothetical mechanisms by which biochar influences such processes are still less recognized and remains a difficult challenge that requires an intensive research [46, 97, 98, 99].

BIOCHAR AND WATER TREATMENT APPLICATIONS

Several authors have been studied biochar that converted from agricultural crop residues, forestry residues, animal waste, woody materials, and anaerobically digested/ undigested biomass residue materials (or the remains of biofuel production), as a low-cost sorbent material in water treatment applications (Table 3) and evaluated its capacity in removing various contaminations from aqueous solutions including heavy metals (e.g., lead, copper, nickel, and cadmium), nutrients (e.g., phosphate and nitrate), and organic and inorganic compounds, because of its carbon matrix structure that provides it with a medium-to high surface area, and for its abundance of polar functional groups, such as carboxylic, hydroxyl and amino-groups which are favorable for heavy metals removal.

Removal of heavy metal from water media is influenced by many factors, such as solution concentration and pH, contact time, carbon dosage, and sorbent surface modification procedure [100]. The efficiency of biochar in metal sorption can be enhanced by: (1) iron-impregnation [101], (2) oxidizing the surface of the carbon in order to increase the number of surface active sites, mainly given by oxygenated active groups such as carboxylic and phenolic moieties [102, 103, 104, 100]; (3) composting [105], and (4) chemical activation using hydroxides [106].

The investigations on the interaction of metal ions with the carbon surface active groups are fundamental for the development of wastewater treatment technologies based on sorption/desorption processes. However, the mechanism of metal ion adsorption is not yet adequately understood [103].

Table 3 Biochar utilization for organic/inorganic contaminants remediation in water

Contaminant	Biochar type	Effect	Reference
Agro chemicals			
Atrazine	Dairy manure (450 °C)	Partitioning into organic C/sorption	[55]
Atrazine and simazine	Green waste (450 °C)	Adsorption and partition	[121]
Chlorpyrifos and fipronil	Cotton straw (450 and 850 °C)	Adsorption due to high surface area and microporosity	[122]
Deisopropylatrazine	Broiler litter (350 and 700 °C)	Sorption due to high surface area and aromaticity; sorption on noncarbonized fraction	[104]
Pyrimethanil	Red gum woodchips (450 and 850 °C)	Adsorption due to high surface area and microporosity	[76]
Norflurazon and fluridone	Grass and wood (200–600°C)	Sorption on amorphous C phase	[123]
Antibiotics			
Sulfamethazine	Hardwood (600 °C)	Adsorption due to p–p electron donor–acceptor interaction; negative charge assisted H-bonding	[124]
Sulphamethoxazole	Bamboo (450 and 600 °C)	Sorption	[22]
	Pepperwood (450 and 600 °C)		
	Sugarcane bagasse (450 and 600 °C)		
	Hickory wood (450 and 600 °C)		
Tetracycline	Rice husk (450–500 °C)	Formation of p–p interactions between ring structure of tetracycline molecule and graphite-like sheets of biochars	[125]
Other hydrocarbons			
Brilliant blue and rhodanine dyes	Rice and wheat straw	Electrostatic attraction/repulsion and intermolecular hydrogen bonding	[126]
Catechol and humic acid	Hard wood, softwood and grass (250, 400 and 650 °C)	Adsorption due to presence of nano-pores	[127]
m-Dinitrobenzene	Pine needles (100–700 °C)	Transitional adsorption and partition	[28]
Methyl violet	Crop residue (350 °C)	Electrostatic attraction; interaction between dye and carboxylate and phenolic hydroxyl groups; surface precipitation	[112]
Naphthalene	Pine needles (100–700 °C)	Transitional adsorption and partition	[28]
Naphthalene	Orange peel (250, 400 and 700 °C)	Adsorption and partition	[28]
Naphthalene and 1-naphthol	Orange peel (150–700 °C)	Adsorption and partition	[28]
Nitrobenzene	Pine needles (100–700 °C)	Transitional adsorption and partition	[28]
Phenanthrene	Soybean stalk (300–700 °C)	Partitioning	[128]
p-Nitrotoluene	Orange peel (250, 400 and 700 °C)	Adsorption and partition	[28]
Pyrene	Corn stover (600 °C)	Adsorption due to nano-porosity	[129]
Pyrene	Saw dust (400 and 700 °C)	Sorption	[27]
Trichloroethylene	Soybean stover (300 and 700 °C)	Sorption	[107]
	Peanut shell (300 and 700 °C)		
Heavy metals and trace elements			
Chromium	Oak wood (400–450 °C)	Sorption	[61]
	Oak bark (400–450 °C)		
Chromium	Sugar beat tailing (300 °C)	Electrostatic attraction; reduction of Cr(VI) to Cr(III); complexation	[130]
Copper	Crop straw (400 °C)	Adsorption due to surface complexation	[131]

Contaminant	Biochar type	Effect	References
Copper	Pecan shell (800 °C)	Sorption on humic acid at pH 6; precipitation of azurite or tenorite at pH 7, 8 and 9	[103]
Copper and zinc	Hardwood (450 °C) Corn straw (600 °C)	Endothermic adsorption	[28]
Copper, cadmium, nickel and zinc	Broiler litter (500 °C) Alfalfa stems (500 °C) Switch grass (500 °C) Corn cob (500 °C) Corn stover (500 °C) Guayule bagasse (500 °C) Guayule shrubs (500 °C) Soybean straw (500 °C)	Adsorption onto inorganic fraction of biochar	[132]
Lead	Dairy manure (200 °C)	Precipitation with phosphate	[55]
Lead	Sewage sludge (550 °C)	Adsorption due to cation release, functional groups complexation, surface precipitation	[49]
Mercury	Soybean stalk (300–700 °C)	Precipitation, complexation and reduction	[128]

BIOCHAR ECONOMIC VALUE

The growing price of waste disposal is likely to make the production and application of biochar for electricity and waste management economically viable. The cost of biochar production from agricultural by-products (agricultural residues, animal waste, and woody materials) is mainly associated with the processing (machinery and heating), which is only about \$4 per gigajoule [43]. Biochar economic value is influenced by energy supplies and demand, the supply and demand for low emissions technologies, the availability of alternative biochar technologies and global policy responses to climate change [87].

METHODS

A plug-flow reactor (PFR) will be designed in order to evaluate the efficiency of some NanoBio-sorbent materials in surface-groundwater treatment, and compare its performance in sorption of nitrogen and phosphorus with the activated carbon.

EXPERIMENTAL SETUP

1. Material preparation and packing: sieve analysis and particle size distribution of the NanoBio-Sorbents and activated carbon will be determined.
2. Fill four of the (4.5 cm diameter x 60 cm long) PFR, two with NanoBio-Sorbents and the other two with the activated carbon (Figure 1). PFRs will be filled up to 2.5 cm with bottom silica sand and/or zeolite, then 50 cm of the well mixed filter material (packed them as densely as possible). A layer of 2.5 cm top silica sand and/or zeolite will be added and finally the whole PFR will be packed into aluminum foil in order to prevent light penetration. Throughout the PFR packing process, the individual weights of the different fractions will be recorded (column, gravel, filter material) in order to calculate bulk density, particle density and total porosity in a later step. NanoBio-Sorbent

3. Bulk density, particle density, and total porosity of each PFR will be determined, using standard procedures of soil physics. Moreover, the tracer residence time will be determined using electrical conductivity and a sodium chloride tracer in the outflow.
4. Surface-groundwater samples will be distributed through the PFR (using low rate flow meters) by a rate around 5ml/min.
5. The effluent water from the activated carbon and NanoBio-sorbents PFR will be sampled continually, and it will be tested for pH, electrical conductivity (EC), alkalinity, chemical oxygen demand (COD), biological oxygen demand (BOD), methylene blue active substances (MBAS) as indicator for anionic surfactants, nitrate ($\text{NO}_3\text{-N}$), ammonium ($\text{NH}_4\text{-N}$), total nitrogen (Tot-N), phosphate ($\text{PO}_4\text{-P}$) total phosphorous (Tot-P), in addition to the major cations and anions and common trace elements using ion chromatography (ICs), and integrated coupled plasma mass spectrophotometer (ICP-MS).

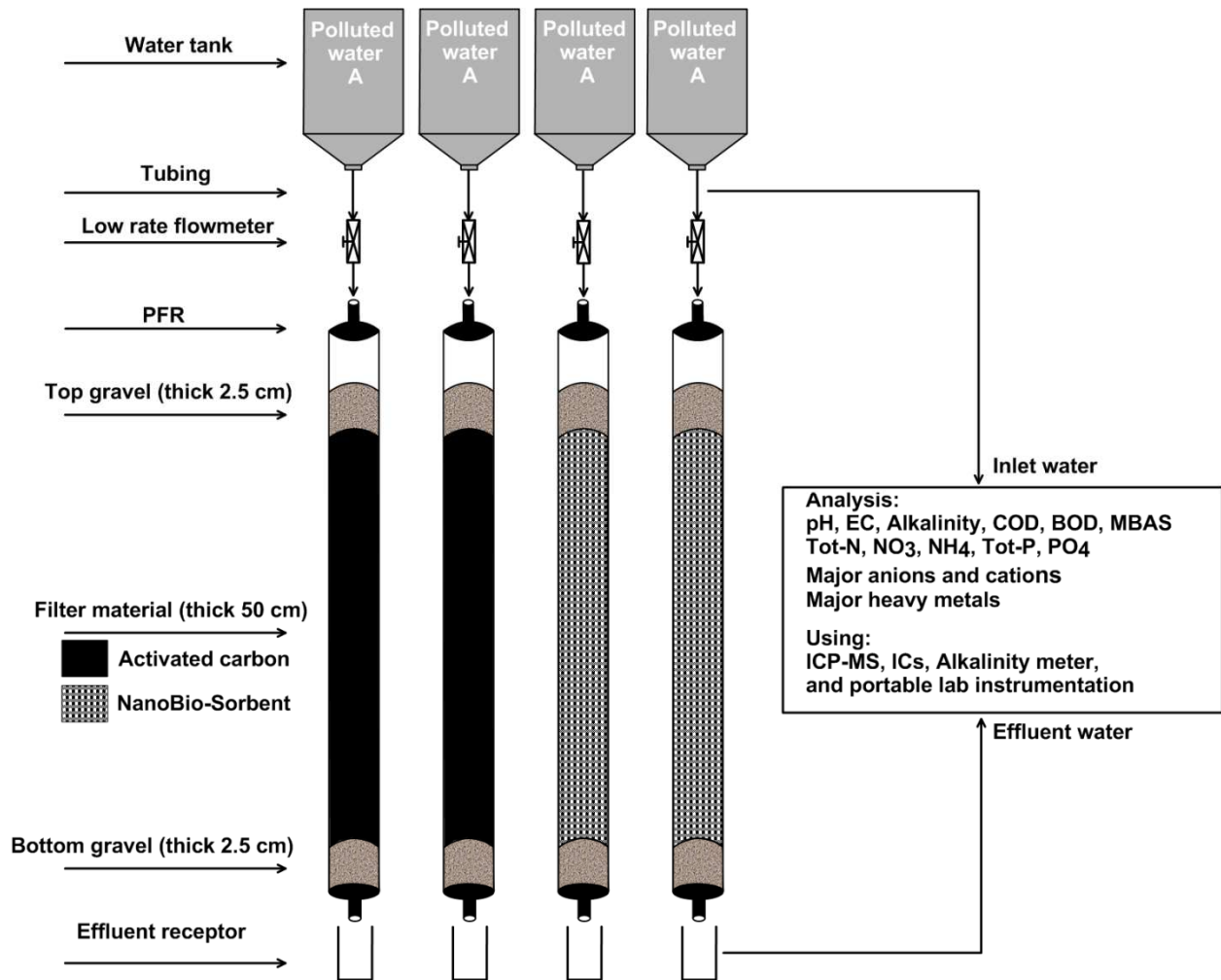


Figure 1. Experimental plan shows the NanoBio-Sorbents and activated carbon PFR design construction and dimensions, as well as the feeding process.

DETERMINATION OF THE PHYSICAL PARAMETERS

Equations [1, 2, 3, 4, and 5] will be used for the determination of, respectively, water contents, particle density, water density, bulk density, and total porosity of the materials in the PFR. Standard procedures of soil physics were followed can be found in Hillel (1982) [109]. For the determination of particle density and gravimetric water content, samples were taken from the excess of the filter materials that had been mixed at the ratio 2:3.

The gravimetric water content (w) of the air dry filter materials was determined on dry base by applying the following formula:

$$w = Mw/Ms \quad (\text{Eq. 1})$$

Where:

W: gravimetric water content (g/g)

Mw: mass of water (g)

Ms: mass of solids (g)

The air dry materials will be dried for 24 hours in a furnace at 105 °C. The mass of water will be calculated by subtracting the weight of the oven dry material from the weight of the air dry material. The particle density of solids (ρ_s) is determined by applying the following formula:

$$\rho_s = Ms/Vs \quad (\text{Eq. 2})$$

Where:

ρ_s : Particle density (g/cm³)

Ms: mass of solids (g)

Vs: volume of solids (cm³)

Water density at a certain temperature is determined using two volumetric flasks filled up to a third with the oven dried materials, one with bio-sorbent, and the other one with granular activated carbon. The flasks then will be filled with deionized water that already had settled for three days until up to the half. Then the flasks will be placed for boiling on a hot plate for around 10 minutes, until no more air bubbles came up. The cooled and covered flasks remained standing in the lab for 24 hours and then they will be filled up with deionized water to the volume line. The weight of the flasks should be recorded for all steps and at the end also the temperature of the water in the flask must be recorded. According to Tanaka et al. (2011) [110], the following formula can be used to get the water density.

$$\rho_w(t) = a_5 \cdot \left[1 - \frac{(t+a_1)^2 \cdot (t+a_2)}{a_2 \cdot (t+a_4)} \right] \quad (\text{Eq. 3})$$

Where:

$\rho_w(t)$: Density of clean water, free from air (Kg/m³), having the isotopic composition of the Standard Mean Ocean Water (SMOW) at $p_0=101325$ Pa.

t: temperature (°C)

- a1: coefficient (-3.983035) (°C)
- a2: coefficient (301.797) (°C)
- a3: coefficient (522528.9) (°C)
- a4: coefficient (69.34881) (°C)
- a5: coefficient (999.974950) (Kg/m³)

The density of the water at the measured temperature can be compared with a water density table for pure water [111]. In order to obtain the volume of water, multiply the water density by the mass of water. By abstracting the volume of water from the total volume, the volume of solids is calculated. The mass of solids is then divided by the volume of solids to obtain particle density. The bulk density (ρ_b) can be determined by applying the following formula:

$$\rho_s = M_s/V_s = M_s/(V_s + V_a + V_w) \quad (\text{Eq. 4})$$

Where:

- ρ_b : bulk density (g/cm³)
- M_s : mass of solids (g)
- V_s : volume of solids (cm³)
- V_t : total volume of the representative soil body (here: carbon) (cm³)
- V_a : volume of air (cm³)
- V_w : volume of water (cm³)

The total volume (V_t) is the part of the PFR that is filled with the filter material (excluding top and bottom silica sand). The PFR is filled with 50 cm of filter material and had a diameter of 4.5 cm. The mass of solids is determined by subtracting the mass of water from the air dry filter material in the PFR. The mass of water is calculated by multiplying the air dry weight of the filter material by the gravimetric water content. The total porosity is calculated with the formula:

$$f = 1 - \rho_b/\rho_s \quad (\text{Eq. 5})$$

Where:

- f : porosity (cm³/cm³)
- ρ_b : bulk density (g/cm³)
- ρ_s : particle density (g/cm³)

The efficiency in reduction of the measured substances was calculated with the following formula:

$$E = \frac{C_{in} - C_{out}}{C_{in}} \quad (\text{Eq. 7})$$

- E : Efficiency
- C_{in} : Influent concentration (mg/L)
- C_{out} : Effluent concentration (mg/L)

CONCLUSIONS

Researchers have documented the effects of NanoBio-Sorbents amendment to soil on the vegetation growth for quite some time, but its development for environmental management on a global scale is quite recent. NanoBio-Sorbents might be a costly effective material to be used for soil improvement, waste management, climate change mitigation and energy production, alternative to replace the industrial activated carbon and similar materials, which has long been used for water treatment. NanoBio-Sorbents applications have been conducted on water treatment mainly on small-scale models that are currently limited to specific NanoBio-Sorbents types and site locations.

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