

APPROPRIATE WASTEWATER MANAGEMENT TECHNOLOGIES USING PEAT*

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ABSTRACT

This article deals with uses of peat in wastewater treatment. The following topics are considered: i) peat and its properties; ii) pre-treatment of peat; iii) impurity removal by peat; (iv) applications of peat in wastewater treatment. Particular attention is given to the principles underlying the uses of peat in removing impurities from wastewaters, and on practical examples.

INTRODUCTION

Peat has been the subject of many experimental studies during the past two decades. This interest stems from the fact that peat is a cheap raw material with distinct characteristics such as porosity and polarity and is easy to use [1]. Natural peat can adsorb many elements due to its polarity and porosity. As a result of this, low content of heavy metals (Zn, Pb, Cr, Cu, Hg) has been found in peatland waters [2]. Peat is also able to adsorb other contaminants, e.g., I, Se, Cs, U and Pb, from groundwater and atmosphere [3]. As an effective adsorbent [4] and filtration medium in the purification of wastewaters [5-13], peat has been proven successful in removing impurities such as suspended solids, odors, organic matter, oils, nutrients, ranging in scale from the laboratory to practical application. Moreover, peat has greater adsorption capacity [14] than other adsorbents (such as carbon, silica, and alumina), and is more economical (\$88 per metric tonne compared to \$4400 to \$22,000 per metric tonne for commercial ion exchange resins, and \$1100

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per metric tonne for activated charcoal) (in 1991 U.S. dollars). Peat is itself convertible to activated carbon with good physico-chemical adsorption properties [15, 16], and can be used as fuel [17].

This review covers the properties of peat, its practical uses in wastewater treatment, and the scientific principles of impurity removal with peat. Studies of mechanisms of kinetic and mass transfer within peat beds [18-22] are not included in this review.

PEAT AND ITS PROPERTIES

The Muskey engineering Handbook includes an extensive review of the available data and the geotechnical properties of peats [23]. Peat is partially fossilized plant matter in wet areas where there is a lack of oxygen and the accumulation of plant matter is faster than its decomposition. Typically dark brown, peat is a complex material containing lignin and cellulose as major constituents [24]. The lignin has polar functional groups (Figure 1) such as alcohols, aldehydes, ketones, acids, phenolic hydroxides and ethers, which are involved in chemical binding [25]. The lignin and humic fractions contain predominantly p-hydroxyl units [26]. Adsorption capacity for transition metals and polar organic molecules is quite high. On the other hand, microscopic studies have revealed that peat is a highly porous material [27]. Lightly decomposed peat can have about 95 percent porosity and a specific area of $200 \text{ m}^2 \cdot \text{g}^{-1}$ [28].

Peat can be regarded as an organic soil capable of exchanging cations. When determining the specific surface of a sphagnum peat by dye adsorption, Poots and McKay obtained a much higher value with basic dye than with acidic dye [29]. For the particle size range of 150-250 microns, $122.2 \text{ m}^2 \cdot \text{g}^{-1}$ was given by basic dye and $11.8 \text{ m}^2 \cdot \text{g}^{-1}$ by acidic dye compared to $27.3 \text{ m}^2 \cdot \text{g}^{-1}$ by nitrogen adsorption. Peat strongly attracts cations of basic dye, due to the negatively charged groups in fulvic and humic acids of peat, and to considerable exchange adsorption occurring with hydrogen ions. With the use of an acidic dye, the repulsion between anions and the negatively charged groups present in peat results in a low specific surface value. Peat possesses a high cation exchange capacity but a very low anion exchange capacity, as shown by Valentin [30].

Many properties of natural peat depend on the extent of its decomposition and on its environment during formation [31]. Harvesting affects the properties of peat [32]. For example, the concentration of Ba, Ca, Cd, Co, Cr, Fe, La, Mn, Ni, Ti, Zn, Al, Be, Cu, Pb, Mg, Na, and Sr in peat varies with depth [33]. Peat becomes more amorphous with decomposition. The higher degree of decomposition enhances the sorption but lowers draining capacity. Partially decomposed peat is more fibrous and has better hydraulic and adsorptive properties. Undecomposed peat has a high total pore volume capable of holding a large amount of water. Drying peat teases apart fibers and screens out fine particles. This gives peat a high void ratio. The

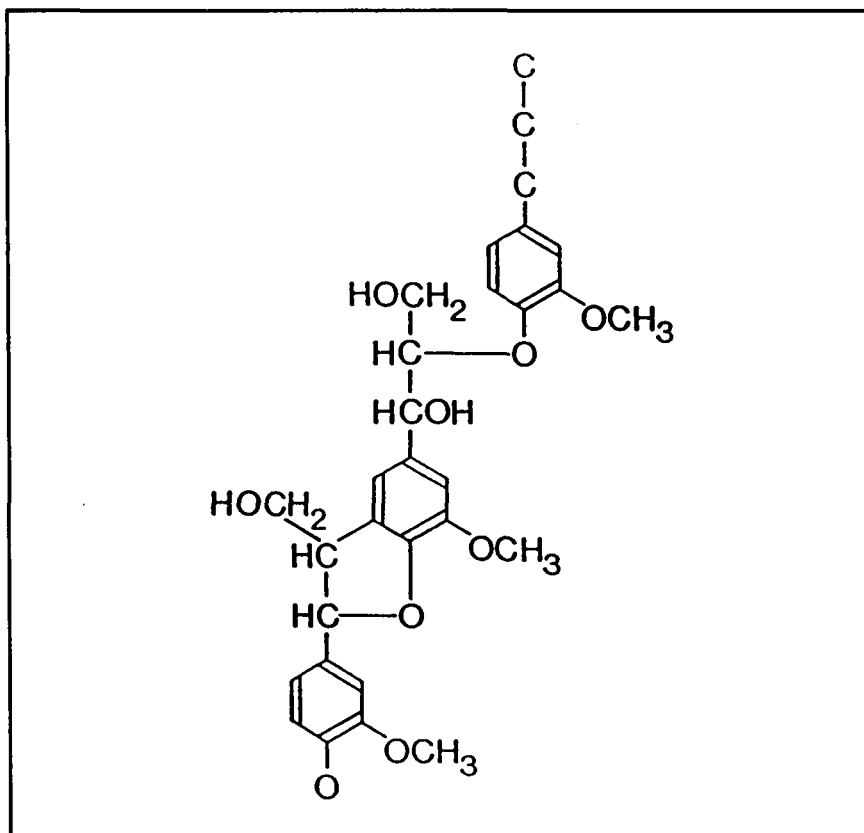


Figure 1. The structure of lignin.

properly separated fibers ensure even permeability. Peat with high porous structure is a coarse-fibered material.

Peat generally contains a large amount of water (90% typically) due to its porous structure. The moisture in peat affects microbial activity. When the moisture levels exceeds 85 percent, microbial activity drops slightly, and ceases at moisture levels below 30 percent [30]. In any event, water storage capacity of peat is critical in designing peat-lands for wastewater treatment [34].

The pH value influences the structure and properties of peat. Peat generally has a pH around 4, due to the presence of humic acids [30]. At pH above 9, the destruction of the structure of peat occurs and at pH below 3, the chelating capacity of peat decreases [35]. At pH < 3, therefore, the removal of most metals by peat will not be efficient. For example, the Cu²⁺ adsorption on 1 g of peat decreased from AC (Adsorption Capacity) of 0.4 millimoles at pH = 5 to AC of 0.14 millimoles at pH = 1 [39].

PRETREATMENT OF PEAT USED IN WASTEWATER TREATMENT

Peat is generally treated by washing and sieving prior to use. Although the use of natural peat without further treatment generally gives good results for removing contaminants from waters and wastewaters [36], efficiency is sometimes limited by low mechanical strength, high affinity for water, tendency to shrink and/or swell, and poor chemical stability. To overcome these problems, some methods of peat pre-treatment have been used, such as thermal and chemical treatment.

Thun et al. have treated peat by surface thermolysis to improve peat's mechanical strength and obtain filtration beds less susceptible to clogging [37]. Ekman and Asplund [38] confirmed the high oil-sorbing potential of peat rendered hydrophobic by heat treatment, compared to agents made of plastic, mineral, wood, and wood hydrolysis waste. Dissanayake and Weerasooriya have treated peat with acid [39]. They introduced additional sulphonic acid and carboxylic groups into peat and improved the sorption capacity and mechanical strength. Smith and co-workers [40-43] have studied chemically treated peats with sulphuric or phosphoric [41] acids to enhance the cation exchange capacity of peat. They converted the peat into an anion exchanger by coupling an amine and ethylenediamine onto the peat modified previously by H_2SO_4 . The sulphuric acid-treated peat could remove 90 percent of oil [40] and potentially cationic species [42] from water. In general, acid and steam heat fragment peat, increasing its specific surface and adsorptive capacity. However, Poots and McKay revealed that adsorptive capacity can decrease in drying [29]. They attributed this to a reduction in effective surface area, due to the shrinkage of pores during drying and the cross-linking of bonds as a result of the elimination of water from neighboring hydroxyl groups. Gravelle and Landreville have reported that chemical modification might reduce the efficiency of natural peat to adsorb organic matter [44]. Kosarevich treated peat with NaOH or NaOH/HCl and obtained peat suspensions with substantially altered rheological properties [45]. These studies suggest that peat pre-treatment is of value if proper conditions are maintained.

IMPURITY REMOVAL BY PEAT

Peat removes impurities such as suspended solids, organic matter and heavy metals, from wastewaters (through various interactions and in different ways). All solids larger than the interstitial channels of peat are filtered. Other impurities are removed principally by two mechanisms: ion-exchange and chelation.

Bel'kevich et al. have suggested four possible types of interactions between peat and impurities: 1) the H-exchanges with cations via the -COOH, phenolic hydroxyl and heterocyclic groups of peat, as well as the OH-exchanges; 2) the formation of chelate complexes due to the interaction of peat with metallic cations; 3) the formation of hydrogen bonds with polyvalent cations via

hydroxyls, lignin, celluloses, and hemicelluloses within porous peat complex; and 4) the formation of anion-cation bonds due to the presence of various ionogenous groups containing coordinately non-saturated oxygen atoms [46]. The occurrence of these interactions depends on the properties of peat and impurities. The surrounding conditions can affect the exchange capacity of peat. For example, heating can make some functional groups free and increase available sorption centers for other groups to be exchanged. On the other hand, the nature of impurities to be exchanged influences the exchange capacity of peat. Thus, cations are selectively adsorbed by peat [46, 47]. Bel'kevich et al. reported the following orders of affinity of cations to their peat: $\text{Ag}^+ > \text{Ti}^+ > \text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ and $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Ba}^{2+} > \text{Si}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ [46]. Pakarinen et al. observed a selective adsorption order of $\text{Pb} > \text{Cu} > \text{Zn}, \text{Mn}$ [48]. A similar order of metallic cation-exchange such as $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Fe}^{3+} > \text{Ca}^{2+}$ has been given by Maslennikov and Kiseleva [49]. But the selective adsorption of granulated peat with respect to heavy metals follows the order $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ [50]. A study of iodine release to a Canadian peat bog [51] demonstrated that K^+ is capable of displacing major cations from reaction sites in the peat. The adsorptive selection of cations by peat is derived from differences in: a) binding capacity of cations into ion pairs; b) hydration types of these cations; c) relative energy levels of the functional groups and peat; d) the structure of the electron shell of cations, and e) the interaction types (i.e., coulomb and/or electrostatic, polar) etc. [46].

The difference in affinity of cations to peat should be derived from (i) differences in binding capacity of cations into ion pairs, including hydration types of these cations, and the energy level between the functional groups and peat; and (ii) differences in the structure of the electron shell of cations and the interaction types (i.e., coulomb and/or electrostatic, polar) [46]. Few detailed studies have been undertaken to address the effects of each of these differences. However, it is probably due to these effects that K^+ is capable of displacing major cations from reaction sites in the peat [3] and that peat could be used as a natural sorbent for extracting non-ferrous metals from wastewaters [50] and polyvalent metal cations from solutions [49].

In addition, the nature of adsorbed cations also influences the ion-exchange efficiency. Comparing the ion-exchange capacity with peat of alkali, alkali earth and ammonium ions, Tummavuori and Aho found that the adsorption of $\text{K}^+, \text{Na}^+, \text{Ba}^{2+},$ and Ca^{2+} on peat is faster than trivalent metallic ions [52]. They attribute this to the difference in ionic radii. The equilibrium time varies also in different cases. When Cr^{6+} was adsorbed on a sphagnum peat, it took several hundred hours to reach the equilibrium [53]. Tinh et al., however, demonstrated that the equilibrium was attained in about 30 minutes with a municipal wastewater [27]. This is probably due to the difference in the nature of cations and peat involved in these two cases. These studies have shown the effects of the nature of impurities to be removed on exchange capacity and efficiency.

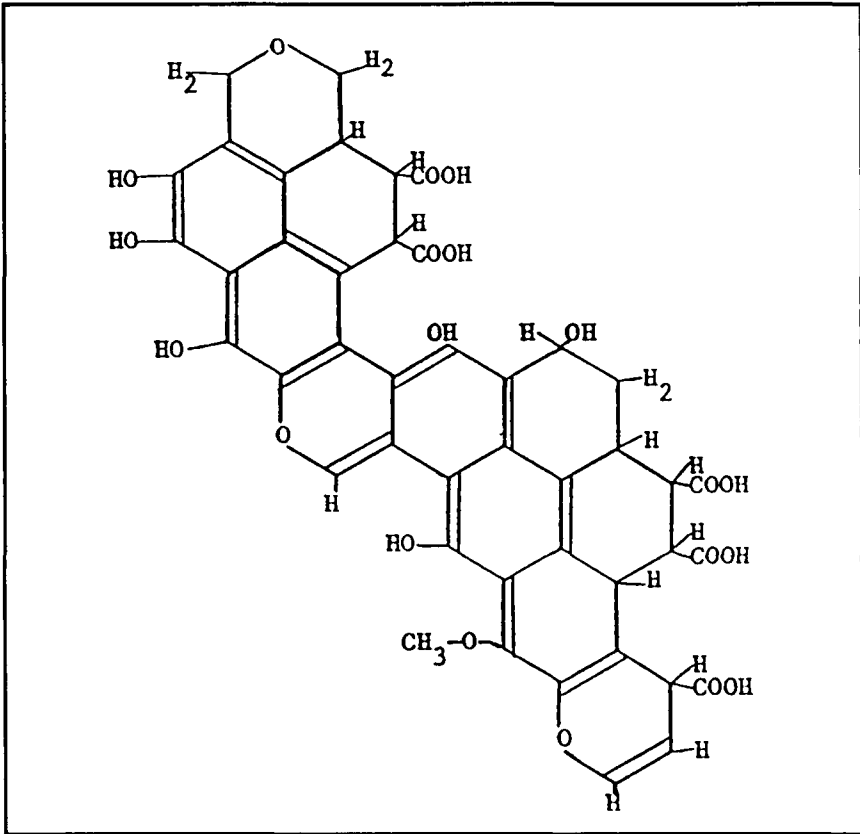


Figure 2. Chelating structure of peat.

Among the four proposed types of interaction, the chelation and formation of complexes through chemical binding during adsorption is considered to be the major interaction between the polar groups of peat and cations [25, 35, 39]. The chelation capacity of peat with metallic ions depends on the presence of polar groups (called chelating agents) (Figure 2), such as alcohols, aldehyde, and on the type of metallic ion. Coupal [35] found an order of chelation capacity of peat for cations as $\text{Fe}^{3+} > \text{Pb}^{2+} > \text{Ba}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$, which is similar to the selective adsorption order given by Chistova et al. [50]. Since peat is polar, it can adsorb large amounts of most metals [54] and hence is competitive with other adsorbents [55]. Thus peat can be used as a natural sorbent for extracting non-ferrous metals from wastewaters [50] and polyvalent metal cations from solutions [49]. Making use of the high chelation capacity of peat, Coupal and Lalancette [25] have devised methods for removing Hg, Cd, Fe, Zn, Ni, Cr^{3+} , Cr^{6+} , Ag, Pb, Sr, phosphates, and organic matter (oils, detergents, dyes).

The humic acid groups of peat play an important role in removing metallic ions. Dissanayake and Weerasooriya removed the humic acids from peat and observed a reduction of metals trapping capacity [39]. The di/trivalent ions can be removed by binding with aromatic carboxylate hydroxyl groups of humic acids through the chelation and formation of complexes. Besides being excellent chelating agents, the humic acids are also capable of retaining large quantities of metals by cation exchange and surface adsorption. The retention of cations by peat takes place in an inner hydration sphere. The surface organic matter has a negative charge and so primarily cations are adsorbed.

It should be noted that the pH value can substantially affect the retention capacity of peat for metals [52, 56]. Coupal has illustrated the vital role of pH in chelation and indicated that peat's chelation capacity is high between pH = 3 and pH = 9 [35]. Over this range, the chelation capacity increases with pH because the peat at a high pH has a tendency to become soluble and its structure loosens. Cameron treated landfill leachate with peat and found that the best adsorption of metals occurred at pH = 7.1 [57]. The carboxylic groups of peat take part in the ion-exchange reaction by binding cations (e.g., Cu^{2+}) with the release of H^+ [52]. A high level of H^+ concentration will, therefore, hinder the ion-exchange reaction. However, at high pH, metal removal is helped by precipitation of metal oxides.

Peat, by itself, cannot remove substantial amounts of phosphorus [58-60]. The required precipitation reactions must be provided by added aluminum, calcium and iron. The phosphates replace water molecules and hydrous groups coordinated with Fe, Ca, and Al to form precipitates. The phosphate precipitates are retained by the peat, as suspended solids during filtration. Nitrogen is removed and returned to atmosphere by denitrification, under anaerobic conditions, carried out by grass vegetation. The mechanisms of nutrient removal by natural wetlands have been reviewed by Nichols [59, 61].

Various types of interactions occur between peat and the impurities to be removed. Removal can be achieved by ion-exchange (H-exchange, OH-exchange), chelation with metallic cations, and the formation of various bonds (hydrogen and anion-cation), as well as by the precipitation of Al, Ca, and Fe compounds. These mechanisms have been confirmed by experimental studies. Dufort and Ruel [62] studied the removal of coloring materials by peat and attributed the good results obtained for the removal of basic and acid dyes to chemisorption. Langmuir isotherms of Zr and Ti adsorption on peat [63, 64] are consistent with the process of chelation. A Freundlich isotherm of copper adsorption on peat [19] indicated the occurrence of chelation and formation of complexes along with other interaction types (e.g., ion-exchange). Additionally, in a study of oil removal from produced waters by peat, Viraraghavan and Mathavan [65] showed that the adsorption pattern generally followed the Langmuir and Freundlich isotherms. The two main types of interaction (i.e., ion-exchange and chelation) may participate together in adsorption. Based on a study of the sorption characteristics for slaughterhouse impurities, Gravelle and Landreville concluded

that chemical reactions with carboxyl groups, physical sorption, filtration, and precipitation occur simultaneously [44]. The R-COOH groups in natural peat first release hydrogen ions (indicated by a pH decrease), then the chemical activity drops, followed by physical sorption and filtration. In general, the predominant of interaction type is determined by the properties of both peat and impurities (cations to adsorb), as well as by surrounding conditions.

As a filter, peat can remove the solid matter from wastewater [66]. Chaney and Hundemann used peat as a filter to remove suspended Cd precipitates from simulated hypo-chloride-oxidized cadmium cyanide electroplating wastewater and, as a sorption medium for dissolved Cd [54]. The concentration of dissolved Cd has been reduced from $560 \mu\text{g}\cdot\text{l}^{-1}$ to $< 3 \mu\text{g}\cdot\text{l}^{-1}$. Using peat columns, Viraraghavan and Kikkeri removed 94 percent suspended solids from slaughterhouse wastewater during a 5 day period at a rate of $3.55 \text{ m}^3\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ and 99 percent from dairy wastewater at the end of 81 hours at a rate of $2.13 \text{ m}^3\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ [67].

APPLICATIONS OF PEAT IN WASTEWATER TREATMENT

Since the beginning of the nineteen-seventies, peat has been widely used to remove various impurities such as oil [38, 65, 68-70], heavy metals [57, 71-73], odor [74], pesticides [75, 76], and nutrients from industrial and municipal wastewaters [22, 36, 77-80], from slaughterhouse wastewater [44, 81, 82], and animal wastes [58, 83]. Peat has proven to be an effective and efficient medium for wastewater treatment [84, 85].

Oil Removal

Viraraghavan and Mathavan used a horticultural peat to remove oil from waters and obtained 80 percent oil removal during 8-h runs with flows of 12 to 48 $\text{ml}\cdot\text{min}^{-1}$ [65]. In another study, these workers obtained 90-99 percent oil removal when treating oil-in-water emulsions [86]. They found that the oil-binding capacity of their peat was 7.5 to 7.8 times its weight.

Heavy Metal Removal

Heavy metal removal by peat has been found to be very efficient [35, 71, 72, 87, 88]. Eger et al. removed more than 99 percent Cu [89]. Bencheikh-Lehocine have reported an efficiency of 93-96 percent of Zn removal by peat [63]. Lalancette and Coupal have proven that peat is efficient in controlling Hg in water and at the same time is a potential adsorbent of Cd, Zn, Pb, Cu sulphides from polluted water [71]. Rozmej and Kwiatkowski studied metallic ion removal from wastewater and demonstrated that peat, with a higher extent of decomposition, had a higher adsorptive capacity for metal [90]. In the United States, twenty five wetlands

have been constructed to treat acidic mine water [91], and a 50-96 percent reduction of iron and acidity was obtained at most sites. Peat was also used to reduce Se, Cr, As, Be, and Ag, and to adsorb Zn, Ni, Cu, and Hg from sanitary landfill leachate [92].

Organic Matter Removal

Many studies have been undertaken on the removal of organic matter using peat [66, 67, 72, 93-97] including phosphorus [59, 67, 94, 95, 98-102] and nitrogen compounds [59-61, 97, 99, 102-104]. Nichols and Boelter treated a secondary effluent for eight years with a peat-sand filter and monitored the efficiency to remove impurities [105]. They have obtained complete removal of phosphorus and fecal coliform bacteria and 90 percent removal for N during the first three years, with 50 percent N removal by the 5th year. They also observed the particular effectiveness of grass vegetation in microbial immobilization of N and P, as outlined by Farnham and Brown [106]. Sixty to eighty percent phosphorus removal occurred [67, 94, 95]. Nevertheless the presence of small amounts of Fe, Ca, and Al in peat can greatly improve phosphorus removal [107, 108]. The addition of 0.4 percent iron in peat can achieve 99 percent phosphorus removal [100]. Nichols and Boelter believe that the consumption of soluble organic compounds by micro-organisms in peat and the filtration of suspended materials result in a treated wastewater with very low BOD and turbidity [105]. Narasiah and Hains have confirmed this [109]. The BOD was reduced more than 90 percent [72, 95-97], but some authors have obtained less reduction [66, 67, 94]. In the case of coliform bacteria, removal by peat is considered to be excellent (>99%) [97,99].

As previously mentioned, the P removal is correlated with the iron, aluminum, calcium and ash content of the peat. This means that one peat may have good P removal characteristic but another, apparently similar peat may not. This fact is borne out frequently in the literature. An easy way to cope this phenomenon would be to use any commercial peat and to add a boosting agent. The use of a waste from the aluminum industry (red muds) has been investigated at the INRS-Eau laboratory. The red muds were added, as doping agent, to a commercial peat. Based on a column study, the phosphorus removal efficiency was raised from ~20 percent to over 95 percent and the effluent P concentration was less than 0.15 mg·L⁻¹. This boosting effect seemed to decrease with time and, especially, the hydraulic loading. For a load of 30 cm·day⁻¹, the P removal met governmental guidelines (effluent < 1 mg·L⁻¹) for about 50 days. Other classic efficiency parameters were not altered. After this period of time, a quantity of red mud was added to the filter and the P removal efficiency regained the initial efficiencies. The added waste appeared not to increase the level of any toxic heavy metals in the effluent since peat itself is a good metal removal agent. With good P removal, the peat filter system is cheap, efficient, and easy to operate, and would be of great interest to small communities with eutrophication problems.

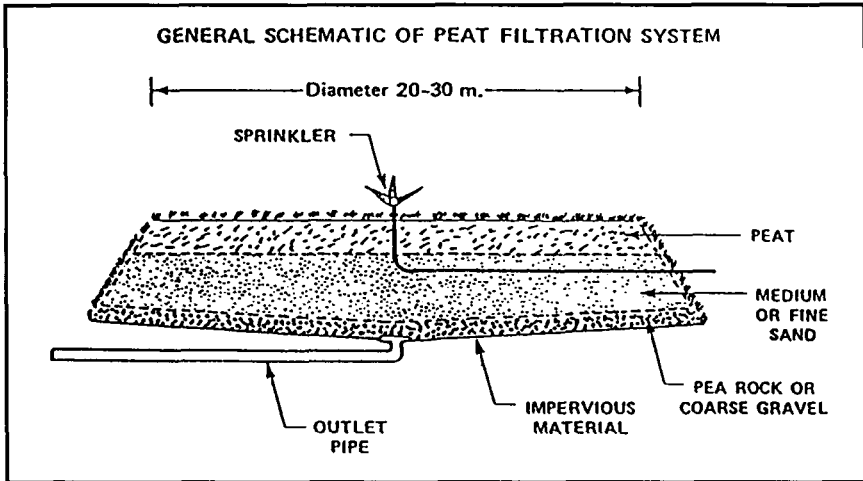


Figure 3. Peat-soil filter system proposed by Farnham and Brown [106, 110].

PEAT BED APPLICATIONS

Several peat filter beds have been developed in the USA, Canada, Finland, and Ireland [89, 97, 105, 106, 110-115]. These test beds have been built to treat effluents from domestic wastewaters on small scales. The construction of these beds is virtually the same, with sometimes only a minor difference in equipment. The bed usually has four layers: at the bottom, a layer of coarse gravel; overlain by one of sand, one of peat and finally a top layer of grass (Figure 3). One pipe introduces the effluent, another drains out the treated effluent. The sand and gravel layers retain the peat bed. The sand layer also creates a suction effect at the sand-peat interface and helps the effluent flow through the bed. The grass helps retain more nitrogen and phosphorus. The peat sometimes is mixed with lime to precipitate more phosphorus. Most of these beds have given promising results. Some of those studies are cited in Table 1, which lists bed features and principal results. The beds are easily maintained but may become clogged. Clogging may be overcome by turning the peat or changing it. A bed can last five to ten years [105]. Dubuc et al. studied the treatment of domestic wastewater by peatland in a northern climate, and concluded that the peatland was effective in treating domestic settled wastewater in a cold climate [36].

CONCLUSION

Peat is an effective medium with great potential for the removal of a variety of impurities from wastewater. This is by virtue of its double effect: adsorption and

Table 1. Features and Results of Some Studies

Wastewater Treatment	Surakka and Kamppi, 1971 [97]	Nichols and Boelter, 1982 [105]	Brooks et al., 1984 [95]	Meunier, 1985 [66]	Fana and Viraraghavan, 1987 [58]	Narasih and Hains, 1988 [109]	Buelna and Belanger, 1989 [11]
	T & S	T	T	T & S	S	T	S & T
H (cm)	2,000	25	60	75	35-50	—	80
Peat type	—	Reed-Sedge	Sphag.	Brown	Brown	Sphag.	Sphag.
BOD ₅ (%)	80-95	—	91	73	92	50	95
COD (%)	—	—	84	64	75	—	—
TSS (%)	—	—	90	83	91	80	98
Bacta (%)	95-99	99	>99	—	99	95-99	98
P (%)	39-82	99	60-96	—	14	10	10-50
N (%)	62-90	46-93	83	—	53	—	20-95
Bed age (year)	14	12	8	25-45 days	1	>85 days	—

S = secondary treatment of wastewaters, T = tertiary treatment of wastewaters, TSS = total suspended solid, Sphag. = Sphagnum peat, H = thickness of peat, BOD₅ = biochemical oxygen demand through five days, COD = chemical oxygen demand, Bacta = bacteria.

filtration, due to its porous and polar characteristics. The adsorption of impurities from wastewaters is principally accomplished through ion-exchange and/or chelation and formation of complexes, depending on the properties of both peat and impurities, as well as on the surrounding conditions. Researchers must now figure out how to remove the impurities from the peat for reuse.

After use in wastewater treatment, peat can be dewatered and burned as a heat source. It also can be used as a fertilizer if contamination is low. Used peat also may be regenerated by releasing metal ions from it.

The advantages of peat for the treatment of wastewaters should not suggest the use of natural systems for this purpose. The use of natural ecosystems such as peatlands for wastewater treatment raises complex biological and ecological questions. Although these natural systems appear to some workers and decision-makers as attractive, inexpensive alternatives to advanced treatment plants, the long-term cost of using peatlands for this purpose has not been evaluated. Alteration of the structure or function of the biotic and abiotic components of the system may be irreparable. Complex, diverse systems may be changed irrevocably to simple systems which would interact with other units of the landscape. The long term response of peatland ecosystems to sewage effluent disposal must be assessed. It would be preferable that the use of natural peatlands should not become the focus of a classic confrontation between immediate priorities of profit and long-term productive sustainability. Therefore, I would recommend the use of peat in contained (artificial and controlled systems) man-made systems, for the treatment of wastewater, until the response of peatland ecosystems to sewage effluent disposal has been fully assessed.

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