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Environmental Pollution 107 (2000) 187–197

ENVIRONMENTAL POLLUTION

www.elsevier.com/locate/envpol

On-site biological remediation of contaminated groundwater: a review

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"Capsule": *Many types of bioreactors have been widely used, but their use is limited by high operational costs.*

Abstract

On-site biological treatment has been used for groundwater cleanup from industrial and agricultural chemicals. The pump-and-treat efficiency is controlled by retardation of contaminants by sorption onto the saturated subsurface solids and by the presence of non-aqueous-phase liquids in the aquifer. On-site bioreactors have been widely used for treatment of contaminants such as petroleum hydrocarbons, monoaromatic hydrocarbons, chlorinated aliphatics and aromatics. The most commonly used reactor types for groundwater include the following: trickling filter, upflow fixed-film reactor and fluidized bed reactor. Bioreactor processes have limitations mainly because of their design to operate at elevated temperatures and thereby by high operational costs.

Keywords: Biodegradation; Bioreactor; Bioremediation; Groundwater; Contamination; On-site treatment

1. Introduction

Groundwater contamination by various anthropogenic organic compounds is a widespread problem in agricultural and industrialized environments (Westrick et al., 1984; Storck, 1987; Anonymous, 1996; Hirata et al., 1992; Barbash and Roberts, 1996; Trauth and Xanthopoulos, 1997). Several organic environmental contaminants are persistent in the subsurface environment (e.g. Knuutinen et al., 1990; Ellis et al., 1991). Groundwater pollution often results in further migration of contaminants and contamination of drinking water supplies. Contaminated groundwater is of concern due to the toxicity towards humans and the ecotoxicity (Piver, 1992).

Bioreactors have been used for treatment of wastewater for over 100 years (for reviews, see Czysz et al., 1989; Degremont, 1991; Tchobanoglous and Burton 1991). Types of bioreactors for groundwater treatment has been adopted from wastewater treatment processes. The contaminant concentrations in groundwater are typically one to two orders of magnitude lower than those of the wastewater treatment influents (Bouwer et al., 1988). Effluent concentrations from groundwater treatment should fulfill drinking water standards at μg l^{-1} level as compared to mg l^{-1} level from wastewater treatment. Therefore, groundwater treatment process designs differ considerably from those used for wastewater in order to achieve low effluent concentrations.

During the last two decades different groundwater cleanup technologies have been developed. In many applications, prior to treatment, contaminated groundwater is pumped above ground. One benefit of this approach is that pumping may prevent further migration of contaminants. The benefits and shorthands of on-site bioremediation of contaminated groundwater are the main topics of this review.

2. Fate of organic compounds in the subsurface

Sources of environmental contamination by xenobiotics are multiple. Industries use toxic organic compounds in large amounts and several industrial sectors can be identified with typical contaminants of the subsurface (Crosby, 1981; Dowd, 1984; Luthy et al., 1994; Mueller et al., 1989; Schaefer et al., 1997). The contaminant migration in the subsurface is controlled by both the contaminant (Table 1) and the site characteristics (Fig. 1).

The unsaturated (vadose) zone, reaching from the soil surface down to the saturated zone, can be contaminated by dissolved and volatilized organic compounds

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0269-7491/00/$ - see front matter
PII: S0269-7491(99)00137-2

Table 1
Typical physico-chemical properties of contaminants and their effect on remediation

Physico-chemical properties	Range	Behavior in the subsurface	Possible mobilization/separation process	Example compound		
				Benzene	Acetone	Tetracloroethylene
Density (kg dm^{-3})	< 1.0	Floating at the water table	Gravity separation possible	0.876	0.79	
	> 1.0	Sinking to the bottom of the aquifer	Gravity separation possible			1.63
Solubility (mg l^{-1})	Immiscible (NAPL)[a]	Free product pooling, migration with/against groundwater flow	Difficult to pump up	1750–1808		150–200
	Miscible	Migration with groundwater flow	Can be pumped up		1000.000	
Vapor pressure Henry's law constant (atm)	< 50	Partition in the water phase	Vapor extraction and air-stripping of dissolved contaminants cannot be applied		0–1.0	
	> 50	Volatilization through the unsaturated zone	Air-stripping can be applied	230–240		1035–1100
Octanol/water partion coefficient ($lg_{10}K_{ow}$)	< 10	Hydrophilic, high water solubility	Can be flushed out of the saturated subsurface	1.8–2.1	−0.24 – −0.6	2.6–2.88
	> 10.000	Hydrophobic, adsorption onto soil matrix	Retardation for long periods			

[a] NAPL, non-aqueous phase liquids.

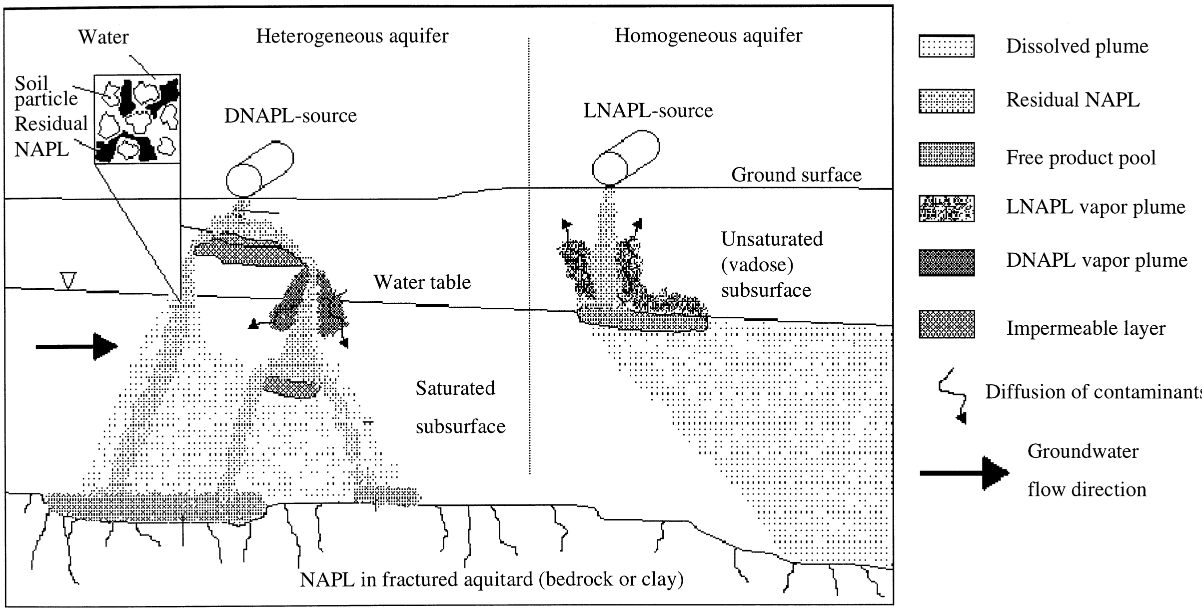

Fig. 1. Different fates of organic environmental contaminants in subsurface. NAPL, non-aqueous phase liquid; DNAPL, dense non-aqueous phase liquid; LNAPL, light non-aqueous phase liquid.

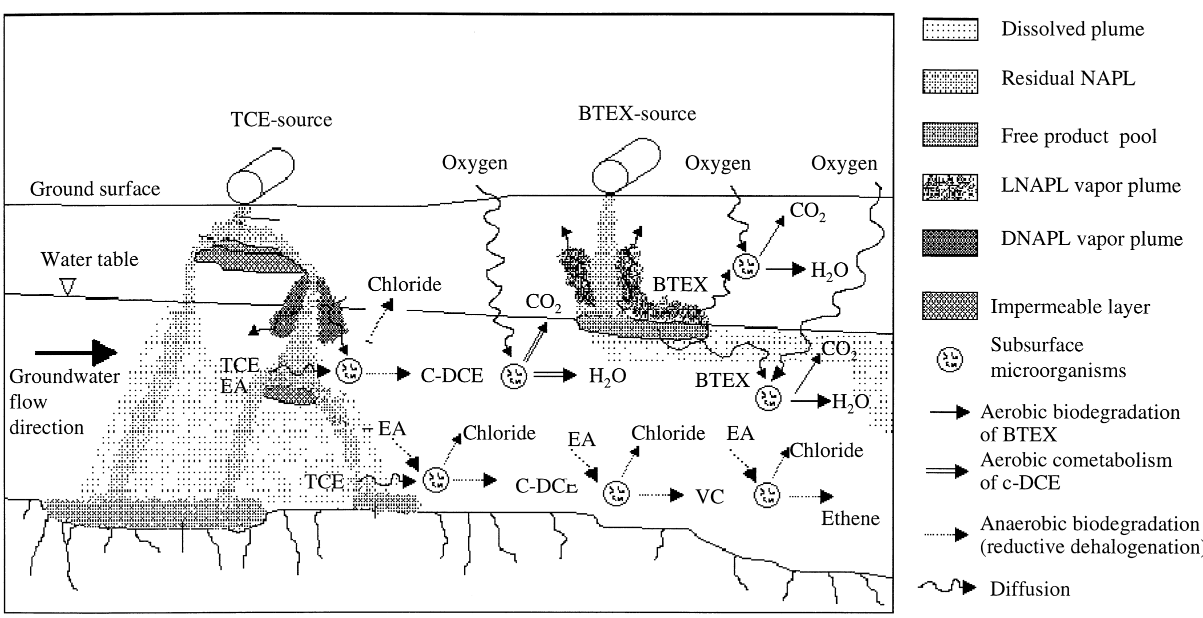

Fig. 2. Biodegradation of contaminants in the subsurface. EA, electron acceptor; NAPL, non-aqueous phase liquid; DNAPL, dense non-aqueous phase liquid; LNAPL, light non-aqueous phase liquid; C-DCE, *cis*-dichloroethylene; VC, vinyl chloride; TCE, tetrachloroethylene; BTEX, benzene, toluene, ethylbenzene, xylene.

Table 2
Stoichiometries of toluene mineralization

Electron acceptor	Reaction	Reference
O_2	$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$	Borden et al. (1995)
NO_3^-	$C_7H_8 + 7.2\ NO_3^- + 7.2\ H^+ \rightarrow 7\ CO_2 + 3.6\ N_2 + 7.6\ H_2O$	Dolfing et al. (1990); Ball and Reinhard (1996)
SO_4^{2-}	$C_7H_8 + 4.5\ SO_4^{2-} + 3\ H_2O \rightarrow 7\ HCO_3^- + 2.25\ HS^- + 2.25\ H_2S + 0.25\ H^+$	Haag et al. (1991); Edwards et al. (1992)
Fe(III)	$C_7H_8 + 36\ Fe^{3+} + 21\ H_2O \rightarrow 7\ HCO_3^- + 36\ Fe^{2+} + 43\ H^+$	Lovely et al. (1989)
H_2O	$C_7H_8 + 5\ H_2O \rightarrow 4.5\ CH_4 + 2.5\ CO_2$	Grbic′-Galic′ and Vogel (1987)

Table 3
Mechanisms of microbial degradation of typical groundwater contaminants[a]

Contaminant(s)	Condition	Degradation mechanism	Degradation products	Benefit for the organism	For review, see
Toluene	Aerobic	Mineralization	CO_2, H_2O	Carbon and energy	Borden et al. (1995)
Tetrachloroethylene	Anaerobic	Reductive dechlorination	TCE, c-DCE, VC, ethene	Energy	de Bruin et al. (1992)
Trichloroethylene	Aerobic	Cometabolism	TCE epoxide[b]	None	McCarty and Semprini (1993)

[a] TCE, Tetrachloroethylene; c-DCE, *cis*-dichloroethylene; VC, vinyl chloride.
[b] TCE epoxide is unstable and readily chemically degraded into easily biodegradable forms.

and non-aqueous phase liquids (NAPLs) (Norris et al., 1994). In the saturated zone groundwater flows due to gravity above an impermeable layer, the aquitard. Aquifers can be contaminated by water soluble organics which migrate with the groundwater flow in the saturated zone and by NAPLs. Light non-aqueous phase liquids (LNAPLs) and dense non-aqueous phase liquids (DNAPLs) migrate with and also separately from the groundwater flow. DNAPLs may also contaminate the capillary system of fracturated aquitard below the aquifer.

3. Biodegradation of contaminants

Many organic environmental contaminants are biodegradable under aerobic and/or anaerobic conditions. Biodegradation of these contaminants in groundwater is a complex process and may be limited by the toxic contaminant itself or other inhibitory substances, contaminant or nutrient (N and P) bioavailability, physical conditions (e.g. temperature, salinity, pH) or microbial competition (Fig. 2).

Contaminants may serve as electron donors or acceptors in biochemical redox reactions. They may be partially transformed or become mineralized to innocuous end products. Oxidative processes utilize available oxidants (electron acceptors) in the aquifer, e.g. O_2, NO_3, SO_4, $Mn^{(IV)}$ and $Fe^{(III)}$ (Table 2).

The biodegradation end products can be intermediate/dead-end metabolites that can be less or more toxic and more soluble/mobile than the parent compounds, or in mineralization to carbon dioxide and water (Table 3). Highly chlorinated compounds such as tetrachloroethene are very oxidized. Therefore, anaerobic reduction of contaminants combined with oxidation of electron acceptors are the only possibility for microbes to generate energy for growth.

The principle of bioremediation is to utilize microbial degradation processes in technical and controlled treatment systems.

4. Bioreactor development

Bioreactors have been utilized with success for wastewater treatment for over 100 years (for reviewers, see e.g. Alleman and Prakasam, 1983; Peters and Alleman, 1983). Bioreactor processes can be distinguished on the basis of biomass retardment mechanism. Biomass grows on a carrier in attached growth, i.e. biofilm systems or as a suspension in sludge processes. Early bioreactor tests were done by Alexander Mueller in 1865 and resulted later in the trickling filter design, which was based on attached growth on a support material in trickling filters (Corbett, 1903). Rotating biological contactor was patented by Weigand in Höchst (1900). The first suspended bioreactor was the activated sludge processes introduced by Ardern and Lockett (1914). Rotating biological contactors have been used in Germany since the 1920s (Glaze et al., 1986). The next steps in bioreactor development were completely mixed stirred tank reactors in the late 1950s (Bazyakina, 1948), fluidized-bed reactors in the 1970s (Jeris et al., 1974) and the upflow anaerobic sludge blanket reactor in 1978 (Lettinga et al., 1980).

Different bioreactors can be operated under aerobic or anaerobic conditions. Anaerobic bioreactors have been used since the 1880s to treat wastewater with high organic solid concentrations (Admussa and Korus, 1996).

The continuous flow system can be plug-flow or completely mixed. Schemes of bioreactors in current use are presented in Fig. 3.

These basic bioreactor types have also been applied for groundwater treatment. The process designs, however, are very different from those applied in wastewater treatment.

For groundwater remediation, bioreactors require specific designs to fulfil the technical, environmental and economical requirements (Table 4). The process must function at low contaminant concentration, which causes slow biomass accumulation and possible start-up problems. Very low contaminant concentrations have to be achieved to meet regulatory goals. The system must reliably operate under varying conditions, especially at very low feed concentrations towards the end of remediation action. Operational costs have to be low to allow long-term operation.

5. Bioreactors based on attached microbial growth

Bacteria have a tendency to grow in interfaces. In flowing environments, this interfacial growth gives a

Table 4
Benefits and shorthands of different bioreactor designs in groundwater treatment

Process	Aerobic/anaerobic	Full-scale experience in groundwater treatment	Major benefits	Major shorthands
Attached growth				
Trickling filter	Aerobic	Yes	Simple to design, operate and maintain	Poor effluent quality
Rotating biological contactor	Aerobic	Yes	Simple and inexpensive design, low energy consumption	Poor effluent quality
Upflow fixed-film reactor	Aerobic	Yes	Adjustable retention time	
	Anaerobic	No	Reductive dehalogenation of contaminants possible	High temperature and high organic carbon supplementation needed
Fluidized-bed reactor	Aerobic	Yes	Reliable operation, low effluent concentrations, dilution of toxic contaminant, easy to start-up	Relatively high energy consumption
Suspended growth				
Activated sludge	Aerobic	Yes	None	Difficult to generate and maintain the biomass, high energy consumption
Upflow anaerobic sludge blanket	Anaerobic	No	Reductive dehalogenation of contaminants possible	High temperature and high organic carbon supplementation needed

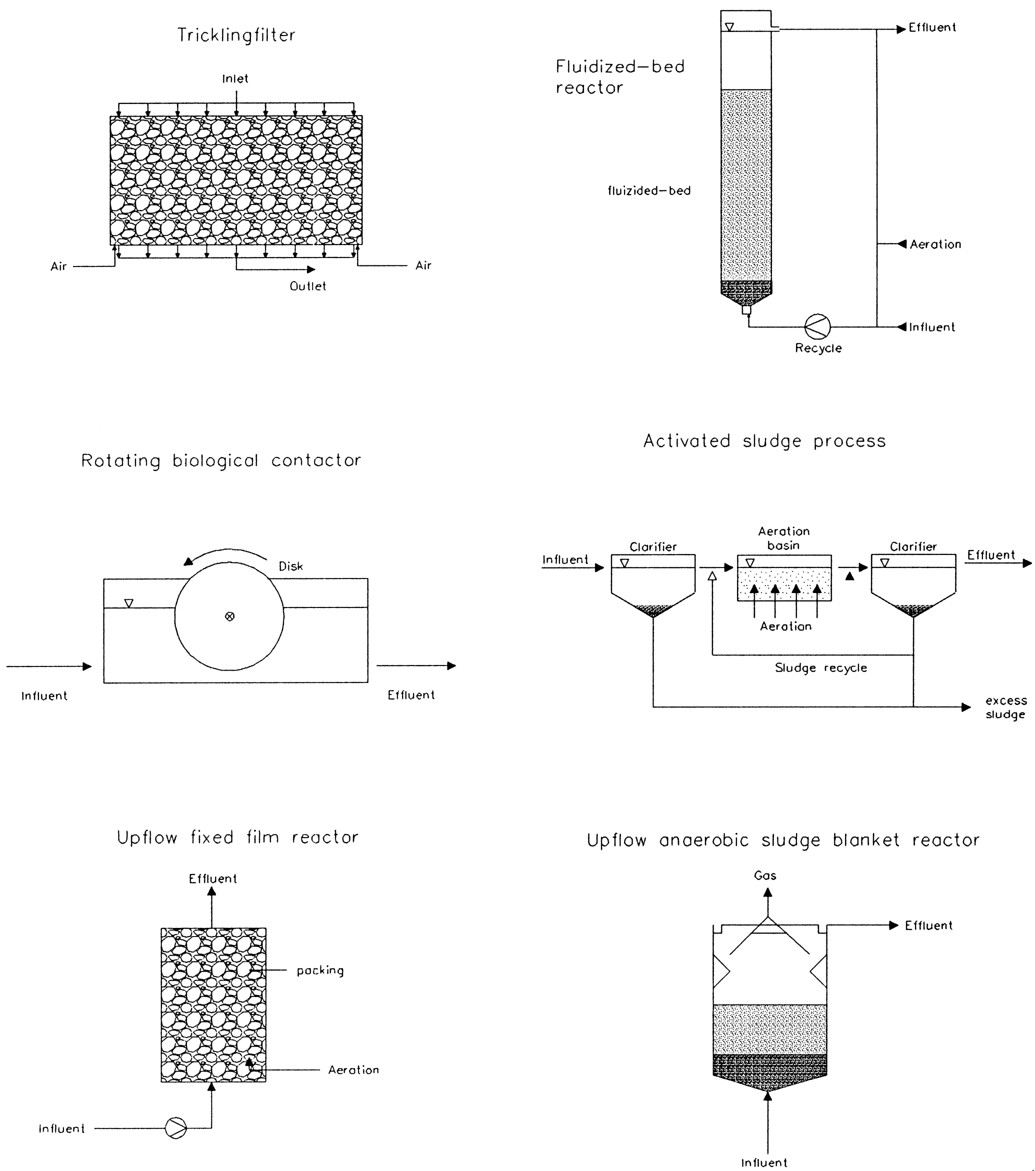

Fig. 3. Schemes of bioreactors.

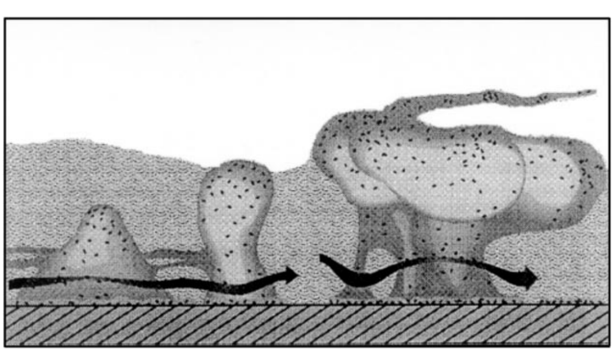

Fig. 4. Current biofilm model (from Costerton et al., 1995).

growth benefit. For attachment, bacteria produce exopolymer-based gelatinous material which together with cells form a biofilm on the carrier material. Bacteria also use specific cell surface structures, i.e. pili and fimbriae, to stick to surfaces. Dissolved contaminants and oxygen diffuse throughout the biofilm. The outer layers of the biofilm protect the inner cells from toxicity and reduce soluble contaminant concentrations by adsorption (Hu et al., 1994).

Bacteria attached to a support material usually show higher specific activity than those observed in suspended growth. Holladay et al. (1978) and Rittmann (1982) showed that from different biofilm reactor types fluidized-bed reactors operated at the highest loading rates and achieved the lowest effluent concentrations. The modern understanding of biofilm structure describes it as a non-homogenous porous matrix which allows non-uniform liquid flows through the matrix, as shown in Fig. 4 (Costerton et al., 1995).

5.1. Trickling filter

The principle of a trickling filter is to support attached growth of bacteria by allowing the contaminated water to trickle through the support material (inert packing) due to gravity. Trickling filter is aerated from the bottom mostly by natural draught, but in some cases also with air blower. Trickling filters can be categorized on the basis of the support material. Typical support materials include traditional fill, like lumps of crushed rocks, slag or pumice, and plastic fills (Admussa and Korus, 1996).

Bench-scale tests with a trickling filter were carried out by van der Hoek et al. (1989) to remove polycyclic aromatic hydrocarbons, benzene, toluene, ethylbenzene, xylene and phenols from groundwater. The test showed that trickling filters are less effective than upflow fixed-film reactors. Trickling filters have been used to treat dichloroethylene-contaminated groundwater under aerobic conditions in laboratory-scale by Koziollek et al. (1998). Trickling filter treatment has been used in full-scale, but to our knowledge, not reported in scientific periodicals.

5.2. Rotating biological contactors

In rotating biological contactors microorganisms grow on the surface of rotating disks. The disks are partially immersed into the water and are partially in contact with the atmosphere. Rotation of the disks brings the attached biomass alternately in contact with the water to be treated and the air.

Use of rotating biological contactors for treatment of contamined groundwater has been rare. Rotating biological contactors were compared with upflow fixed-film reactors in a laboratory study, showing that the aromatic hydrocarbons and phenols removal efficiencies were lower than in an upflow fixed-film reactor (van der Hoek et al., 1989). Enrichment of 1,2-dichloroethane mineralizing biomass on the rotating disks was a long-term process shown also in a full-scale application where biomass build-up required 1 year (Stucki and Thüer, 1995). A rotating biological contactor has also been used to treat vinyl chloride contaminated groundwater under methanotrophic conditions in an air-tight pilot-scale system (Belcher et al., 1997).

5.3. Upflow fixed-film reactor

In an upflow fixed-film reactor bacteria are growing on submerged inert packing. The upflowing water provides microorganisms in the biofilm with substrates and nutrients. If aerobic conditions are required oxygen is often added by air sparging. The hydraulic conditions in the reactor may cause some expansion of the packing, but not fluidization. Upflow reactors are widely used for cleanup of contaminated groundwater with mixed or pure cultures. Especially, fixed-film bed reactors with granular-activated carbon used as packing provide benefits for microbial growth due to sorption of contaminants on the granular-activated carbon (for reviews, see Weber et al., 1970; Bouwer and McCarty, 1982). In laboratory-scale studies anaerobic upflow fixed-film reactors were also used, but not at ambient groundwater temperatures (Hendriksen et al., 1991; Juteau et al., 1995; Komatsu et al., 1997). Aerobic-fixed film reactors are common reactors for groundwater treatment (Lenzo and Ward, 1994; Skladany, 1994). This bioreactor design has been successfully applied at bench, pilot and full scale (Marsman et al., 1993).

5.4. Fluidized-bed reactor

In fluidized-bed reactors the biomass grows on granular support material. The main principle of this reactor type is the fluidization of the bed by high recirculation rates of the water to be treated. Recirculation of the water dilutes the concentration of the influent to a non-toxic level for bacteria and provides completely mixed conditions. Aeration of the groundwater is often designed to the recycle line. High biomass concentrations can be achieved in this process.

Fluidized-bed reactors are successfully used for cleanup of groundwater (Ahmadvand et al., 1995; Gandee et al., 1995; Massol-Deyá et al., 1997), also at low groundwater temperatures (Järvinen et al., 1994; Puhakka and Melin, 1998). Especially, fluidized-bed reactors with granular-activated carbon as support material have the advantage of establishing rapid microbial growth due to sorption of contaminants on the granular-activated carbon (for reviews, see Edwards et al., 1994; Sutton and Mishra, 1994). In laboratory scale, fluidized-bed processes have been also used for anaerobic treatment (Ballapragada et al., 1997; Magar et al., 1999).

6. Bioreactors based on suspended microbial growth

Microorganisms grow in suspension in concentrated substrate solutions. The bacteria form flocs or granules which can be separated from the purified water by sedimentation. In most groundwater contamination cases the contaminant concentration is too low to allow biomass buildup in suspended systems. Therefore, the suspended growth applications are limited to situations where contaminated groundwater is treated ex-situ/off-site in existing wastewater treatment plants. In these applications groundwater contaminants are minor constituents of the organic feed and, therefore, the process performance cannot be optimized for contaminant degradation.

6.1. Activated sludge process

The basic design of an activated sludge process includes an aeration basin and a mechanical clarifier to separate the sludge from the effluent for recycle. Aeration of the water can be done by various types of air blower and aeration nozzles. The design of the settling tank is adapted from wastewater cleaning processes. An example of municipal activated sludge experience in groundwater treatment was described by Ettala et al. (1992) confirming that, as shown in laboratory-and pilot-scale studies (Petrasek et al., 1983; Melcer and Bedford, 1988), the trace toxic organic removal is low and cannot be optimized.

6.2. Upflow anaerobic sludge blanket reactor

In upflow anaerobic sludge blanket (UASB) reactors suspended granular biomass degrades the contaminants by production of methane and carbon dioxide. Main limitations of the technology for groundwater treatment are, so far, the requirements of elevated temperatures ($\geqslant$28°C) (Hendriksen et al., 1992; Mohn and Kennedy, 1992) and high organic carbon concentration (Woods et al., 1989) which were not the conditions for groundwater treatment. Therefore, treatment of contaminated groundwater has not yet been reported in pilot or full-scale.

New bioreactors like the expanded granular sludge bed reactors allow anaerobic treatment of low strength wastewater at low temperatures (Lettinga et al., 1997) but, so far, are not applied for groundwater treatment.

7. Pump-and-treat systems

7.1. Contaminant retardation

Pump-and-treat systems for remediating groundwater came into wide use in the early to mid-1980s. The traditional pump-and-treat system contains a series of recovery (extraction) wells or interceptor trenches to pump the contaminated groundwater from the subsurface (Fig. 5). The contaminated groundwater is usually treated chemically, physically or biologically. The purified groundwater is reinjected through injection wells to the aquifer. Continuous pumping of contaminated groundwater provides hydraulic control of subsurface contaminants to prevent their migration.

The contaminant availability in bioreactors is limited to the water-soluble fraction. Pump-and-treat groundwater remediation has frequently proven inefficient due to slow desorption, diffusion and dissolution processes of NAPLs and residual contaminants trapped in soil (Mackay and Cherry, 1989; Travis and Doty, 1990; Nyer, 1993). Slow desorption of contaminants like polycyclic aromatic hydrocarbons (PAHs) correlate with the organic carbon content of the soil and the properties of the organic compounds. Slow diffusion of contaminants is of concern especially if low-permeability layers or lenses are present and the site has been contaminated for long periods prior to start-up of remediation (Grathwohl, 1998; Griffioen and Hetterschijt, 1998). Slow dissolution, especially by chemicals such as PAHs and NAPLs (Freeze and Cherry, 1989), cause immiscible plumes of contaminants. In heterogeneous aquifers, the groundwater flows mainly in the high-permeability zones which

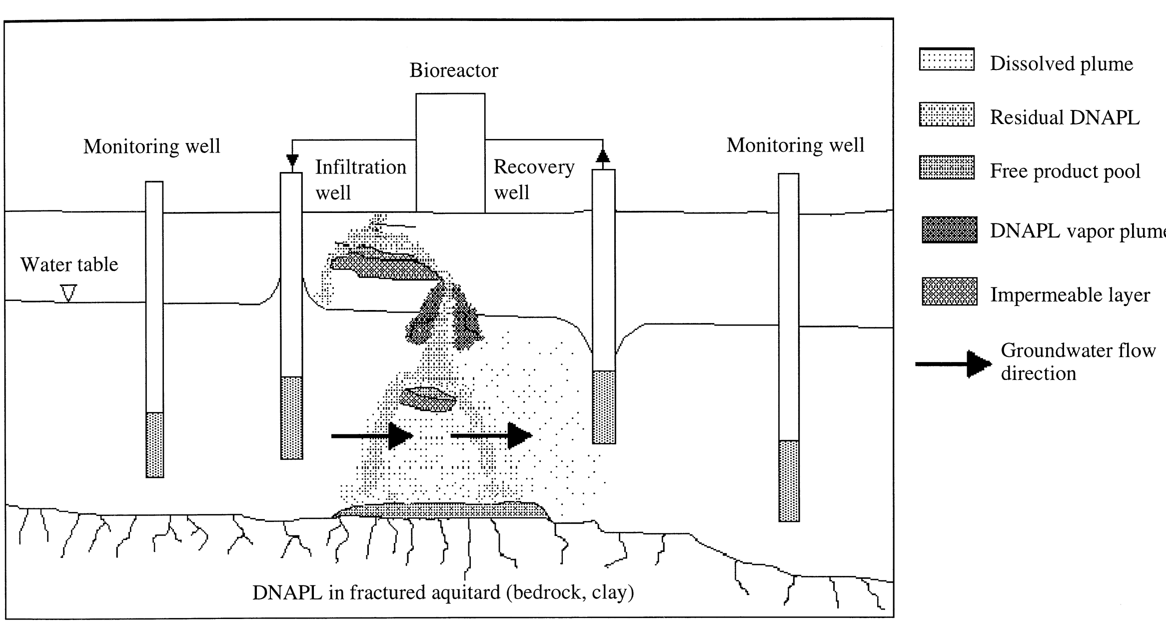

Fig. 5. Schematic set-up of a pump-and-treat system. DNAPL, dense non-aqueous phase liquid.

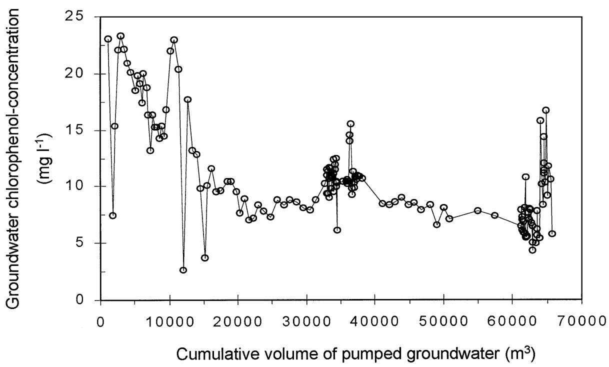

Fig. 6. Tailing of chlorophenol concentrations in groundwater during operation of a pump-and-treat system in Kärkölä, Finland.

reduces the flushing of low-permeability layers and lenses (Berglund and Cvetkovic, 1995). These mass transfer limiting processes require that a large number of pore volumes of groundwater has to be pumped up to meet cleanup requirements resulting in long pumping times (Borden and Kao, 1992; Bouwer et al., 1988). An example of pumping inefficiency is shown in Fig. 6. Therefore, most contaminated groundwater sites cannot be remediated with this approach alone and regulatory cleanup standards cannot be achieved in a reasonable time and cost frame.

7.2. Bioprocess design limitations

The design development of bioreactors to clean up contaminated groundwater has similar trends with the design development for wastewater treatment. Simple bioreactors like trickling filters and rotating biological contactors were used in the 1980s with limited success resulting in low removal efficiency, poor effluent quality and sensitivity to shock loadings. Application of more efficient designs like upflow fixed-film and fluidized-bed reactors improved cleanup efficiencies, but did not eliminate the general limitations associated with the groundwater pumping.

The main limitation of the bioprocesses applied for groundwater treatment has been thought to be the groundwater temperature which causes slow degradation rates (Melin et al., 1998), low loads and slow biomass build-up. Heating of the groundwater is not economically reasonable (Valo et al., 1990; Stinson et al., 1991; Piotrowski et al., 1994). Therefore, bioprocesses operating at low temperatures have been developed (Puhakka and Melin, 1996, 1998). Anaerobic bioreactors are believed to be difficult to operate at low groundwater temperatures and limited experiences of this approach exist, so far. Enrichment of contaminant-degrading microorganisms from contaminated groundwater can be a long-term process, because 97–99% of subsurface bacteria are attached on soil particles (Harvey et al., 1984; Bouwer, et al., 1988). Use of pure cultures to degrade harmful organic compounds has had limited success. Indigenous bacteria have been shown to degrade lower contaminant concentrations than pure cultures (Massol-Deyá et al., 1997).

8. Conclusions

Pump-and-treat technologies have been used to clean up the source zone or plume of the contaminants to avoid further contamination of the groundwater by dissolution and dispersion. NAPLs, especially DNAPL, can migrate as free phase by gravity and capillary forces to the saturated zone. Hydraulic containment for the control of a plume migration is possible with a pump-and-treat approach, but total cleanup of a contaminated aquifer by this method requires long treatment periods resulting in high total costs. Pump-and-treat processes may be enhanced by using surfactant to increase DNAPL solubility, groundwater circulation wells for enhanced flushing and by varying the pumping rates to minimize operational costs. Bioreactors are succesfully applied for cleanup of readily biodegradable contaminants but often require pretreatment, e.g. heating of the water, At many contaminated sites, autochthonous bacteria can be used to remove the contamination. In future, in-situ applications combined with a pump-and-treat process and especially low cost and less maintainance-requiring-processes like natural attenuation and passive bioremediation technologies, e.g. permeable reactive barriers, will be utilized to overcome the on-site bioremediation limitations.

Acknowledgements

This work was funded by the Academy of Finland.

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