Co-funded by the Erasmus+ Programme of the European Union

Masterclass: WATER REMEDIATION

E-LIBRARY CONTENT

Assoc. Prof. Lidia Hrncevic, PhD

Prof. Katarina Simon, PhD

Katarina Peric, mag. eng. petrol.

Faculty of Mining, Geology & Petroleum Engineering

UNIVERSITY OF ZAGREB

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

NAPLs-	*Nonaqueous- Phase Liquids*
DNAPLs-	*dense NAPLs*
LNAPLs	*light NAPLs*
EOC's-	*Emerging Organic Contaminants*
SVE-	*Soil Vapour Extraction*
ERH-	*Electrical Resistance Heating*
RFH-	*Radio Frequency Heating*
TCH-	*Thermal Conduction Heating*
ISCO-	*In Situ Chemical Oxidation*
MnO_4-	*Permanganate*
H_2O_2-	*Hydrogen peroxide*
O_3-	*Ozone*
S_2O_8-	*Persulfate*
PRB-	*Permeable Reactive Barrier*
ISCR-	*In Situ Chemical Reduction*
H_2S-	*Hydrogen Sulfide*
CWs-	*Constructed Wetlands*
EFB-	*Ecological Floating Beds*

1. INTRODUCTION

Water is one of the most valuable resources of mankind. Due to population and economy growth and climate changes, resulting with the increase of water consumption, pollution of water resources and scarcity of it, but especially scarcity of available fresh water, nowadays more than ever there is urgent necessity of water quality management and management of water resources in general.

Water pollution is, alongside air pollution, one of the biggest ecological problems of the modern world. The unique properties of water make it an universal solvent, but also get water easily polluted. Compared to groundwaters, surface waters, due to their availability, are more prone to pollution, but also generally more easily to remediate. Under certain conditions, any surface water body (river, lake, pond etc.) in certain extend will go through the process of self- purification.

In case of surface water pollution several zones can be distinct. These are (Figure 1):

1. Zone of degradation- When polluter/ contaminant enters the water body, it usually changes its turbidity. Water becomes more turbid and that prevents penetration of sunlight to the bottom of water body (river, stream, or lake). The lack of sunlight affects green plants, which by process of photosynthesis use carbon dioxide from the water and produce oxygen. Without sufficient sunlight the green plants extinct. In time, with the decrease of oxygen concentration, aerobic conditions turn to anaerobic resulting in blooming of anaerobic microorganisms. The anaerobic microorganisms produce hydrogen sulphide (H_2S), which, along with solids dispersed in water, settles to the bottom, and forms a sludge. The settled solids soon decompose, forming gases such as ammonia, carbon dioxide, and methane (marsh gas). The oxygen resources become exhausted and life in such waters is limited to mentioned anaerobic bacteria, larvae of certain insects such as mosquitoes, and a certain type of worms.

2. Zone of decomposition-With time more solids settle down and water turbidity decreases. With water becoming more clearer, sunlight can again penetrate it near the surface. In that phase, at the air-water interface, oxygen is absorbed from the atmosphere enabling the growth of aerobic bacteria. The aerobic bacteria convert organic matter into nitrates, sulphates, and carbonates, which, together with the carbon dioxide produced by decomposition, are food sources for algae, which flourish and form a green scum over the surface.

3. Zone of recovery- Algae become more numerous and self-purification proceeds more rapidly. Green plants start the process of photosynthesis and produce more oxygen than is consumed.

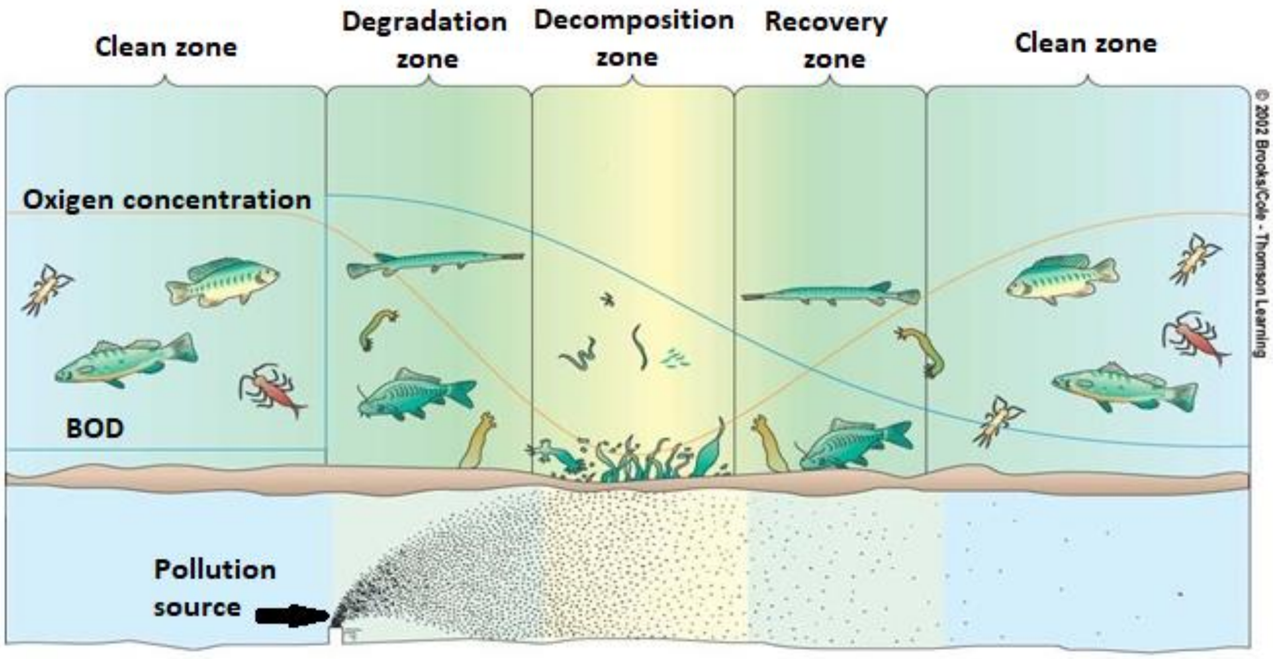

Figure 1 Zones of pollution and self-purification process (adapted from https://slideplayer.com/slide/10227627/)

Since self- purification processes are generally slow (they can take years), anthropogenic remediation processes are applied. Water remediation process implies removal of pollutants/ contaminants from water system. All anthropogenic remediation processes can be classified into several methods such as physical, chemical, electrochemical and biological. The methods can be applied either in situ (on site of the pollution) or ex situ (in special treatment plants).

2. GROUNWATER REMEDIATION METHODS

Protected by overlying sediments, compared to surface waters, groundwater is less exposed to most types of pollutants/ contaminants that usually end up in surface waters. Even though it is of relatively good quality and constant temperature, groundwater systems also get polluted/ contaminated. When polluted, groundwater systems are difficult to remediate, and the remediation processes are usually long-lasting.

Main causes of groundwater pollution are leaching from municipal or industrial landfills or illegal dumpsides, accidental oil or chemical spills, accidental spills of domesitc or industrial wastewaters and acricultural acitvities (leaching from animal waste lagoons, runoff from agricultural fields where chemical fertilizers or pesticides are used etc.). Significant threath to groundwater pollution pose so-called nonaqueous- phase liquids (NAPLs), that is the substances nonsoluble (or it could be said, slightly soluble in water due to water acting as universal solvent) in water. Due to their insolubilty in water and the fact that underground water flow is slow (generally in the order of 10^{-1} to 10^{-3} cm/s (Mayer, 1993)), these pollutants, if not treated, remain in underground aquifers for long time degrading the quality of groundwater. There are two types of nonaqueous-phase liquids. These are so-called dense NAPLs (DNAPLs), the substances which density is greater than waters' (e.g., chlorinated solvents), and light NAPLs (LNAPLs), the substances which density is less than waters' (e.g. crude oil or petroleum products).

In last few decades significant environmental challenge regarding water pollution pose so- called emerging organic contaminants (EOC's) like medicines, personal hygene products, pharmaceutical products, etc.

2.1. PUMP & TREAT

Pump & treat is one of the most applied methods for groundwater remediation. The method is used for removal of dissolved pollutants/ contaminants from groundwater. The method implies pumping (extraction) of the polluted/ contaminated groundwater from wells to the surface, its treatment in the surface treatment system, where the pollution/ contamination is removed, after which the cleaned groundwater is either injected back to the aquifer or discharged to the surface water body or sewer system. Groundwater remediation by pump & treat method are shown in Figure 2.

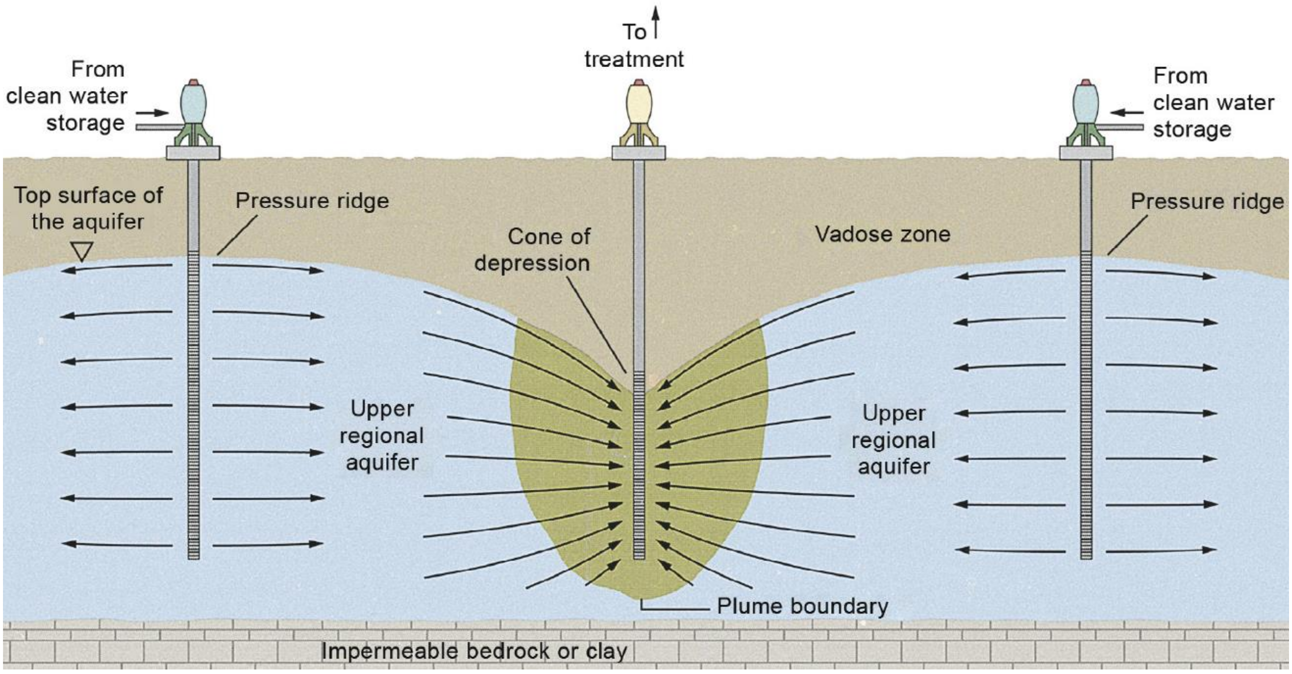

Figure 2 Groundwater remediation by pump & treat method (Brusseau et. al., 2019)

Beside used as a remediation method, this method is also used for prevention of spreading of the polluting plume. Namely, putting the pumping (extraction) wells within the polluted/ contaminated area it will cause drawdown of the groundwater table, the groundwater flow will be directed into the extraction wells, thus minimizing, or preventing further migration of the plume away from pollution source or polluted area. The method is often combined with use of physical barriers (slurry walls, sheet pile walls). The example of using pump & treat method as containment method is shown in Figure 3.

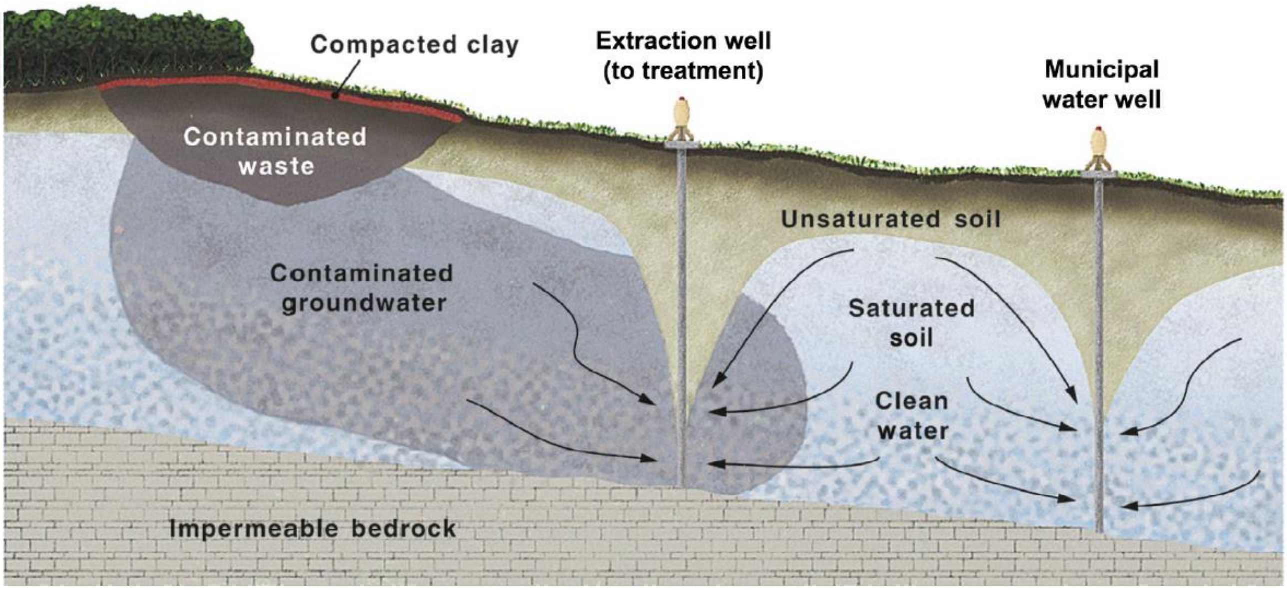

Figure 3 Containment of a groundwater contaminant plume with the use of Pump & treat method (Brusseau et. al., 2019)

The surface treatment system may involve single (air stripping or activated carbon) or combination of several methods. The method is often combined with other groundwater remediation methods (for instance bioremediation) or it is use as soil remediation method (removal of contaminants from the vadose zone). In this case it is called *in-situ* soil washing.

2.2. AIR SPARGING

Air sparging is used to remove volatile and semivolatile pollutants/ contaminants from the saturated zone. Air sparging is based on air injection into the polluted/ contaminated zone. The injected air takes up volatile and semivolatile pollutants/ contaminants from the groundwater and, due to buoyancy, the air bubbles move upward into the vadose zone from where is removed by a soil venting method (Soil Vapour Extraction (SVE)- a soil remediation technique based on injection of air, hot air or steam into the vadose zone to enhance pollution/ contamination removal). When combined with microbiological methods, air sparging is called biosparging. The contaminated air, extracted from the vadose zone by extraction wells, is treated in surface system by different methods (e.g. adsorption by activated carbon, biofiltration, etc.). Air sparging as a method of groundwater remediation is shown in Figure 4.

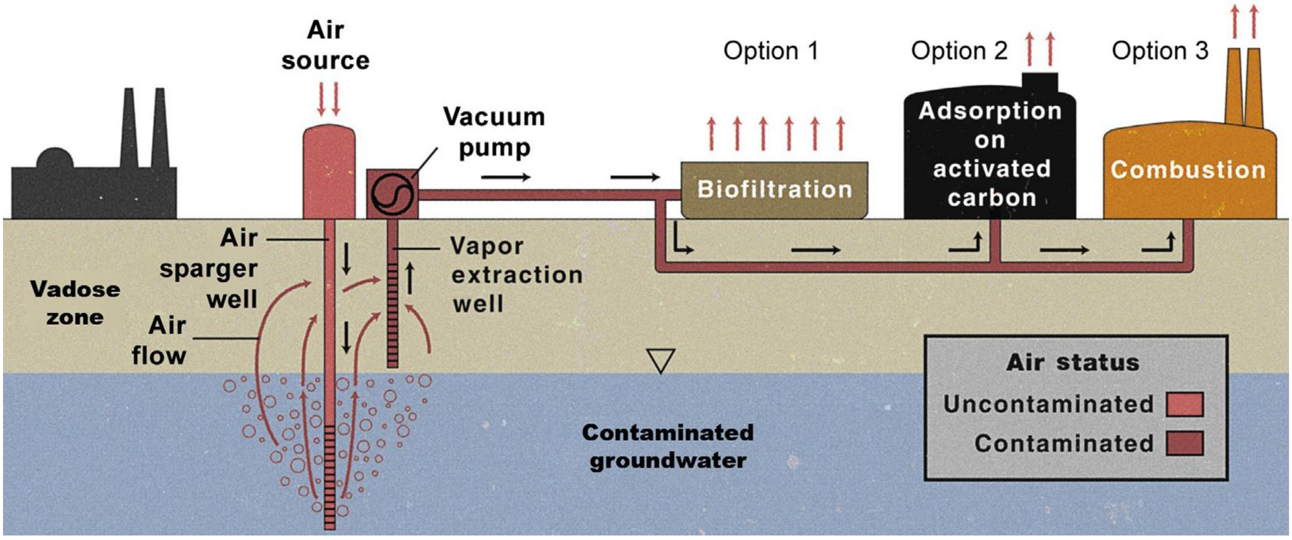

Figure 4 Air sparging (Brusseau et. al., 2019)

Special implementation of air sparging method is in-well air stripping or in- well aeration (Figure 5). As the name suggests, in this variation of air sparging, aeration of groundwater (air stripping) takes place in well and not in the saturation zone. In order to perform this, special well construction is required (two well screens that are separated by several meters) (Brusseau et. al., 2019). In this method polluted/ contaminated groundwater is extracted from the bottom screen, pumped to the top of the well and freely released down the well casing. During the free fall down the casing, groundwater is naturally aerated.

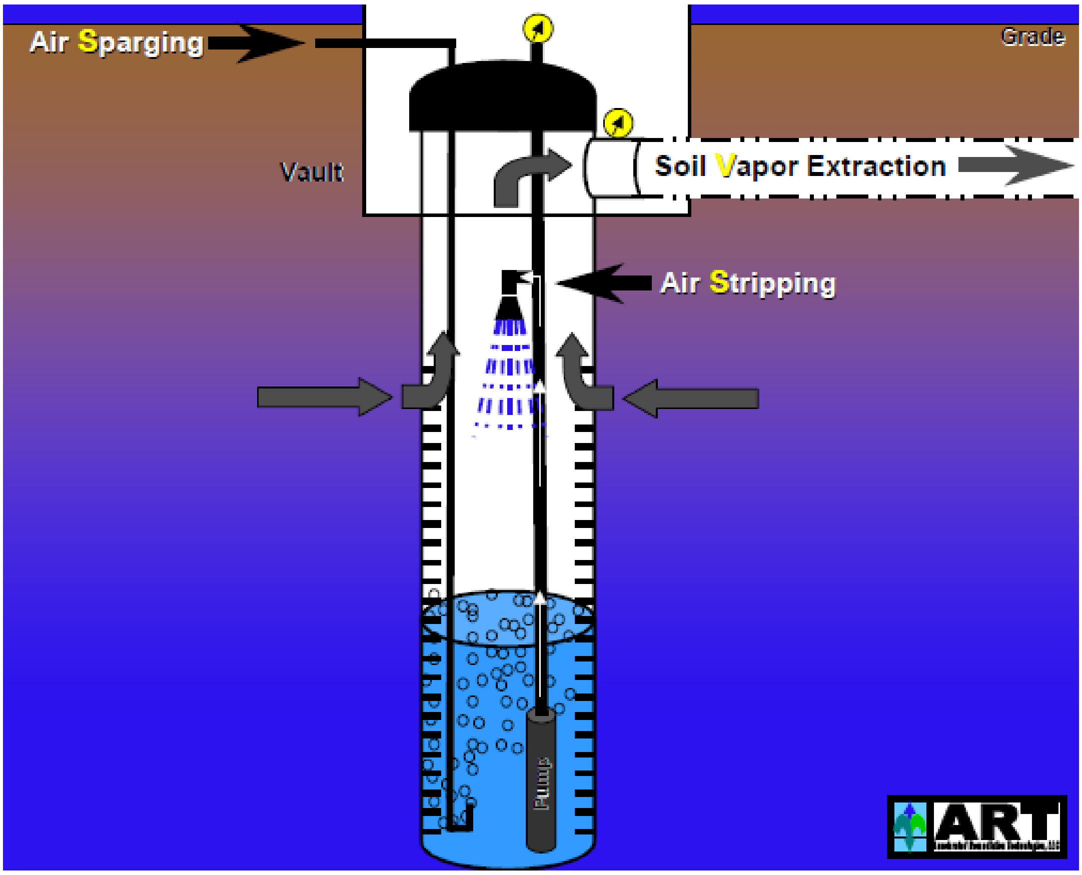

Figure 5. In-well air stripping (Pucke et. al.)

2.3. THERMAL METHODS

Thermal methods are based on increasing temperature in the polluted/ contaminated area in order to improve pollutants/ contaminants removal. Temperature increase enhances volatilization, dissolution, desorption, and evaporation. These methods are used as soil and groundwater remediation methods. Thermal methods are often combined with previously mentioned groundwater remediation methods (injection of hot water, injection of hot air or steam during pump & treat, SVE or air sparging) or are applied as standalone methods (in-situ heat generation). Compared to injection of hot water, air or steam during pump & treat or soil venting, in-situ generation of temperature using heating methods creates much higher temperature but is also more energy intensive and expensive.

In general, there are three methods for in-situ heat generation (Brusseau et. al., 2019):

1. Electrical resistance heating (ERH)- use of electrodes to create flow of electric current in the polluted/ contaminated area. Resistance to electric current flow in soil generates heat up to 100 ˚C. (Figure 6)

2. Radio frequency heating (RFH)- use of radiowaves or microwaves to generate heat (up to 300 ˚C).

3. Thermal conduction heating (TCH)- use of heaters in wells to generate heat (up to 900 ˚C) (Figure 7).

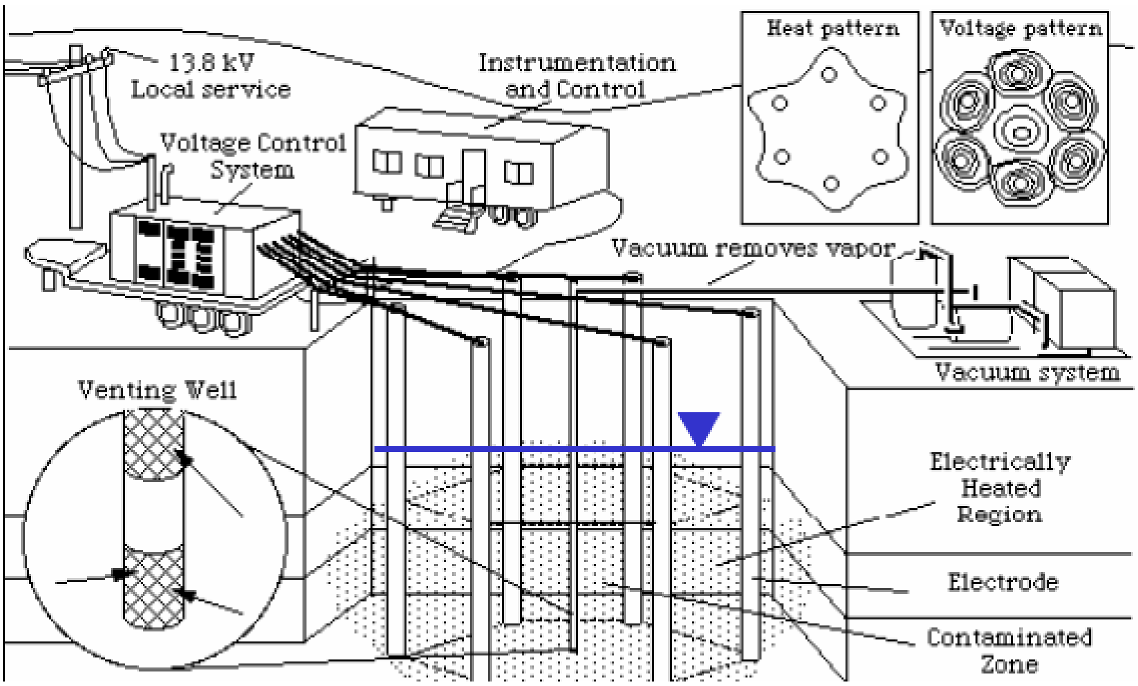

Figure 6. Scheme of electrical resistance heating method (Columbus, 2007)

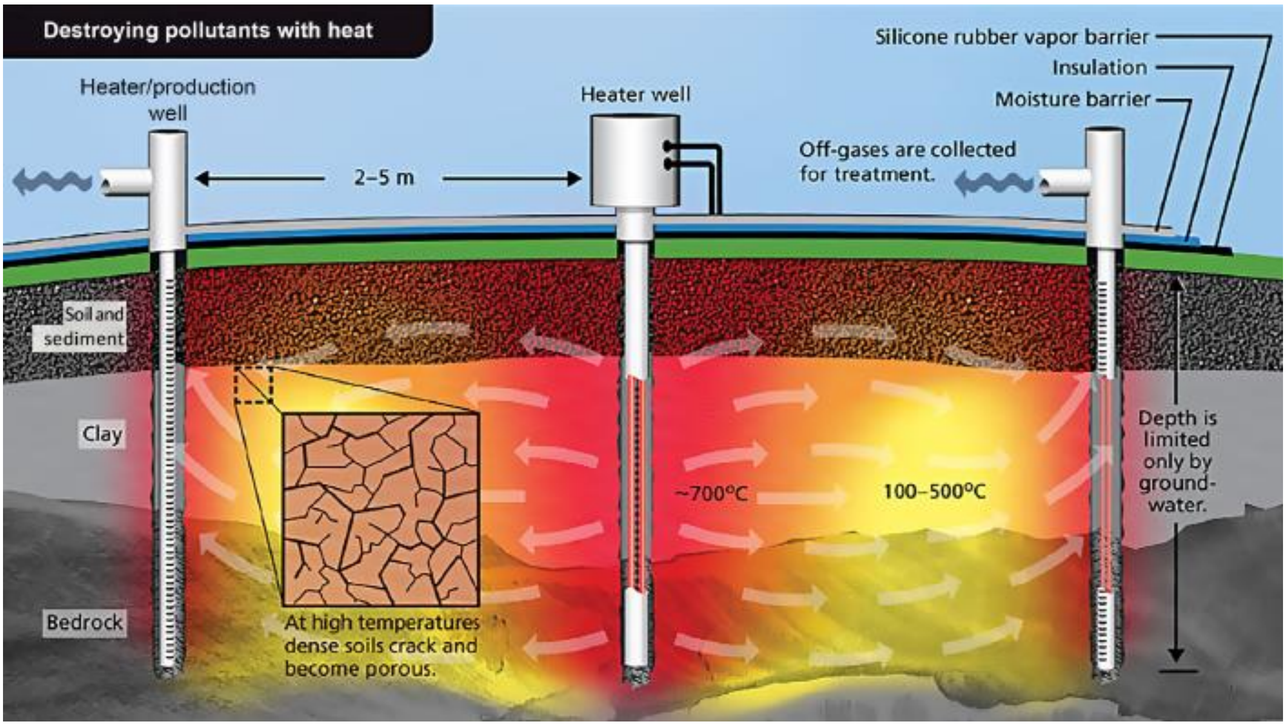

Figure 7. Thermal conduction heating as groundwater remediation method (Brusseau et. al., 2019)

2.4. BIOREMEDIATION

Bioremediation is based on enhancement of activities of naturally occurring microorganisms (biostimulation) or using selected microorganisms to biodegrade present pollutants/ contaminants. Namely, some microorganisms (like certain bacteria) can degrade certain pollutants/ contaminants by metabolizing it. The in situ method involves injection of selected microorganisms (in that case the method is called bioaugmentation), nutrients and oxygen through the well or leaching the mentioned mixture from surface lagoons into the polluted/ contaminated area. In situ biodegradation is primarily used to remove organic substances like hydrocarbons. Ex situ biodegradation is commonly used in wastewater treatment facilities. The method is often combined with other groundwater and soil remediation methods.

2.5. IN SITU CHEMICAL METHODS

In situ chemical methods are based on oxidation, reduction, or hydrolysis of the pollutants/ contaminants in the polluted/ contaminated area by using chemical reagents. The methods can be characterized as active (injection of reagent into the polluted/ contaminated area) or passive (placement of permeable barrier downflow). One of the frequently used active methods is in situ chemical oxidation (ISCO) by using permanganate (MnO_4), hydrogen peroxide (H_2O_2), ozone (O_3) or persulfate (S_2O_8) as oxidizing reagent. In situ chemical reduction (ISCR) is based on injection of reductant or reductant generating substances into the polluted/ contaminated area. As a reductant zero valent iron is commonly used. Passive chemical methods involve placing a permeable reactive barrier (PRB) (trench filled with permeable material) downgradient of the polluted/ contaminated area (Figure 8). The method is primarily used as pollution containment method.

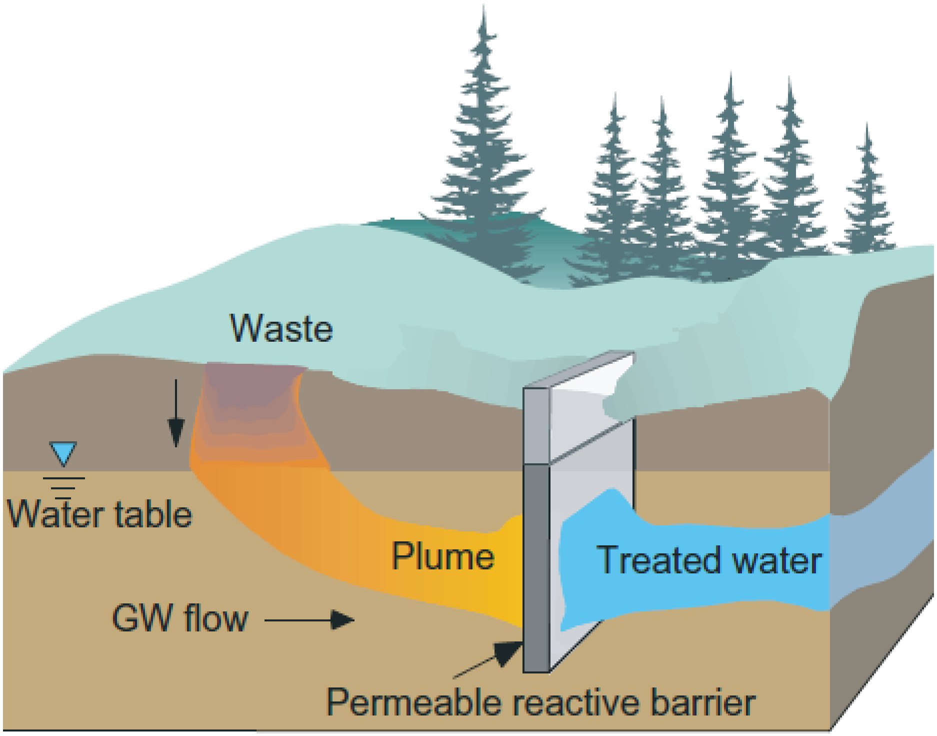

Figure 8. Use of permeable reactive barrier as groundwater remediation method (Brusseau et. al., 2019)

2.6. PHYTOREMEDIATION

Phytoremediation is a term that covers group of soil, groundwater and surface water remediation methods that are based on use of specific plants. Phytoremediation showed good results in cleaning up both inorganic and organic pollutants/ contaminants. Phytoremediation processes are (Lim et. al., 2016; Brusseau et. al., 2019; Ojuederie & Babalola, 2017):

1. Phytoaccumulation/ phytoextraction- accumulation/ extraction of the pollutant/ contaminant from soil/ groundwater through plant roots into plants
2. Phytostabilization- containment of pollution by plants' roots
3. Phytostimulation- enhancement of microorganisms' activities
4. Phytodegradation- degradation of the pollutant/ contaminant by plants' metabolism
5. Phytovolatilization- absorption of contaminants, metabolization and volatilization from plant
6. Rhizodegradation- degradation of the pollutant/ contaminant by plant metabolism.

Phytoremediation processes in case of heavy metal removal are shown in Figure 9.

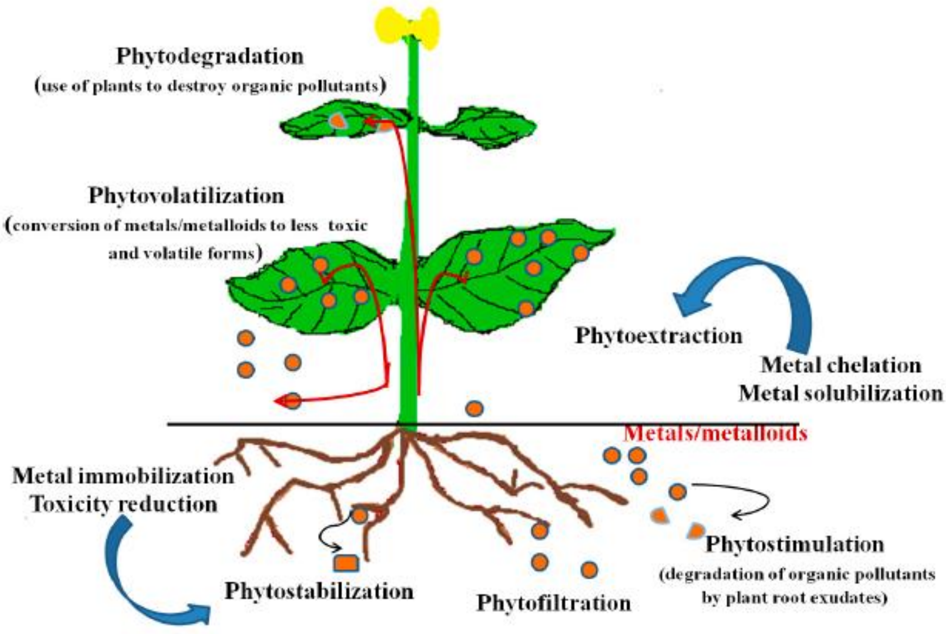

Figure 9. Phytoremediation processes in case of heavy metal removal (Ojuederie & Babalola, 2017)

3. SURFACE WATER REMEDIATION

In comparison to groundwater, surface water (rivers, streams, lakes) can be more easily polluted because it is more accessible to the polluters/ contaminants. Oceans/ seas will be covered in next chapter. Surface water remediation methods can be classified as in situ (in-stream) and ex situ remediation methods. The methods that can be applied for remediation of polluted/ contaminated surface water bodies can be categorised as (Anawar & Chowdhury, 2020):

1. Physical methods
   a. mechanical aeration process
   b. water transfer or diversion and dilution
   c. mechanical algae removal
   d. building hydraulic structures
   e. riverbank filtration
   f. dredging river sediment

2. Chemical methods
   a. enhanced flocculation
   b. chemical precipitation
   c. chemical oxidation
   d. chemical algae removal (use of algaecides)

3. Biological- ecological methods
   a. phytoremediation
   b. microbial bioremediation
   c. biofilms
   d. constructed (artificial) wetlands
   e. ecological floating beds
   f. contact oxidation
   g. membrane bioreactor technology

Chemical methods are usually applied ex situ. Since chemical methods imply using various chemicals like iron and aluminium salts for flocculation, lime for precipitation or hydrogen peroxide or ozone for oxidation, they have a great impact on the environment and are thus only used as emergency methods. Biological methods are more environmentally friendly and less expensive than the physical and chemical methods. They enhance self- purification processes. Their disadvantage, compared to physical and chemical methods, is longer implementation time (several months to years) and greater sensitivity to different environmental factors such as temperature. Usually during polluted water remediation there is always a combination of several mentioned methods. Also, depending on type of water body, pollutant/ contaminant characteristics and conditions at which pollution/ contamination happened, water bodies usually also undergo through a self-purification process. Ex situ remediation usually implies treatment in the wastewater (sewage) facility.

3.1. PHYSICAL METHODS FOR WATER REMEDIATION

3.1.1. AERATION

Aeration is a process based on either natural aeration or air injection into the water body by which oxygen concentration in water is increased. The increased concentration of oxygen enhances microbial activity by which organic compounds are degraded. There are two aeration approaches that could be applied for surface water body remediation. The water body aeration system can be designed as a fixed or mobile system (Figure 10). Aeration method is simple, widely applicable and easy to operate, but in case of air injection, can be quite energy intensive and thus expensive.

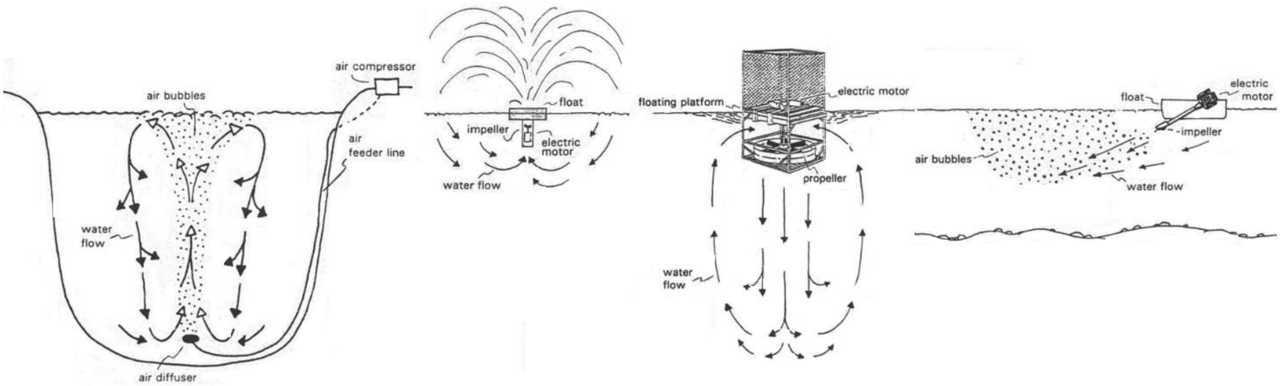

Figure 10. Various types of in- stream aeration systems (adapted form Hudson & Kirschner, 1997)

The aeration processes are often combined with biological methods as floating beds or constructed wetlands. Fixed point is approach usually applied in sediment-rooted constructed wetlands, while mobile point approach is characteristic for floating bed wetlands. The typical application of the aeration processes combined with biological remediation methods is shown in Figure 11.

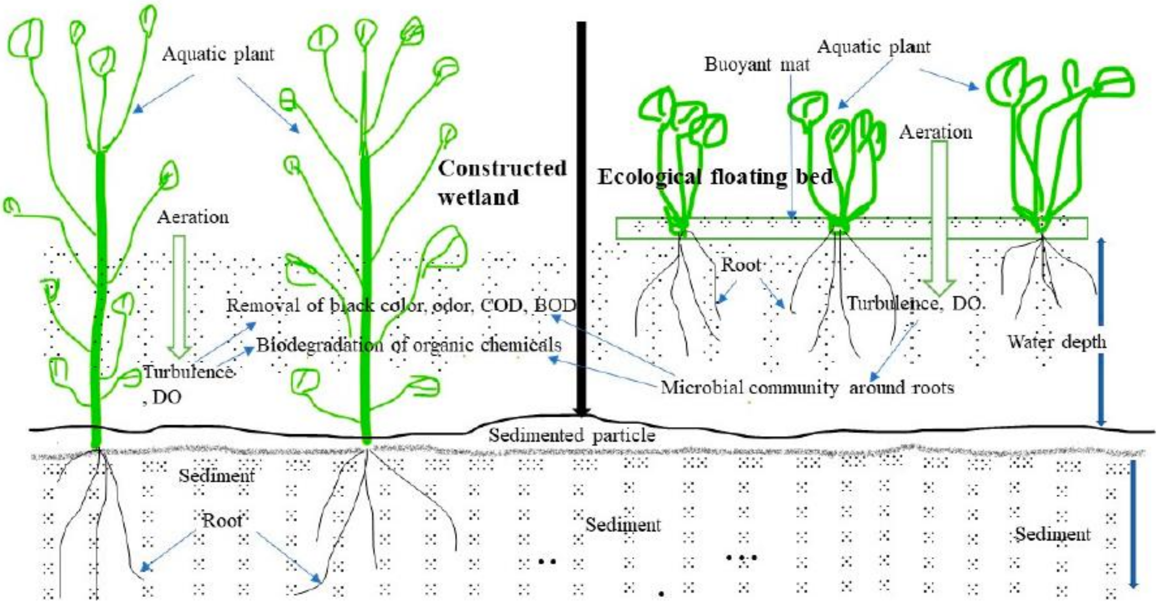

Figure 11. Schematic diagram of application of the aeration processes combined with biological remediation methods (Anawar & Chowdhury, 2020)

3.1.2. WATER DIVERSION AND WATER TRANSFER

Water transfer is based on mixing the polluted water with clean water in order to dilute the pollution. Water diversion enhances water body self- purification processes. This method is usually used as an emergency strategy due to the fact that it is expensive, it impacts the environment (moving organisms from one ecosystem to another), and it is labour intensive (Anawar & Chowdhury, 2020).

3.1.3. BUILDING HYDRAULIC STRUCTURES

Construction of hydraulic structures, like irrigation systems (irrigation weirs or irrigation infrastructure), on rivers can improve its quality. Irrigation infrastructure rivers slows down river flow and increases retention time which enables better sedimentation, aeration and better sunlight penetration and enhances self-purification processes (Figure 12).

Figure 12. Irrigation weir (www.pumpindustry.com.au/weir-upgrade-supports-irrigation)

Also, protection of bank slopes of water bodies of erosion by planting certain vegetation, hard armouring (protecting bank slopes by stones) or using specially designed geotextiles can, beside preventing erosion of the bank slopes, also improve biodiversity of the area and contribute to remediation process (Figure 13).

Figure 13. Hard armouring as riverbank protection (https://trapbag.com/natural-materials-for-riverbank-protection)

3.1.4. RIVERBANK FILTRATION

Riverbank filtration is based on drilling one or more vertical or horizontal wells near a surface water body (river or lake) and producing (pumping out) water from it. Construction of a well causes decrease of groundwater potential and groundwater, but also river water, flow to the well. By flowing through sediments, river water is filtered and thus cleaned primarily of suspended, bus also dissolved, pollutants/ contaminants. The successfulness of water remediation largely depends on type of sediments through which the flow takes place. This method is primarily used for heavy metal and pathogens removal. Schematic diagram of riverbank filtration is shown in Figure 14.

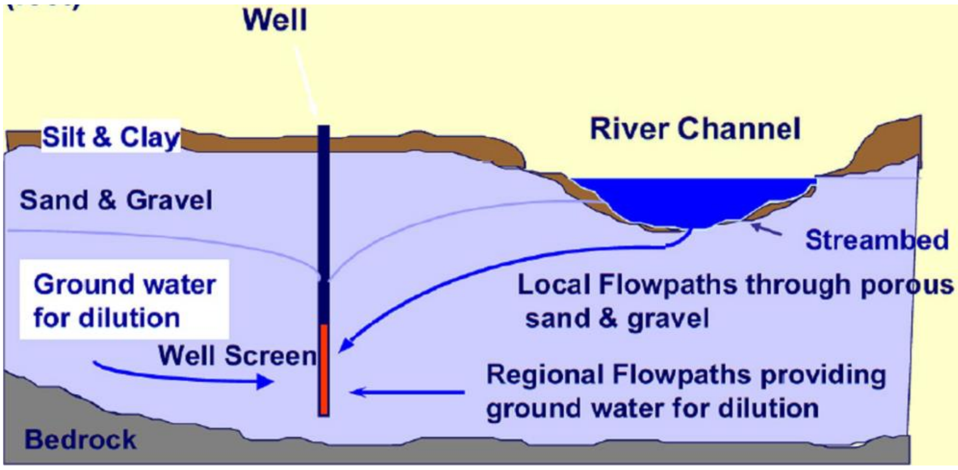

Figure 14. Schematic diagram of riverbank filtration (Abdalla & Shamrukh, 2010)

Table 1. Comparison of different physical/ engineering methods of in- stream water remediation (adapted from Anawar & Chowdhury, 2020)

METHOD	ADVANTAGES	DISADVANTAGES
ARTIFICIAL AERATION- air flow into water body increases oxygen concentration which enhances microbial activities (organic matter degradation)	Simple, easy to operate, sustainable, widely applicable, effectively improve water quality	Expensive
WATER TRANSFER/ DIVERSION- mixing of clean water with polluted water body which results with dilution of pollution	Improve water quality, water supply, pollution control, enhance self-purification processes	Potential destruction of ecosystem, expensive and labour intensive
MECHANICAL ALGAE REMOVAL- removal of algae by mechanical process	Improve water and sediment quality	Expensive
BUILDING HYDRAULIC STRUCTURES- building irrigation weirs or infrastructure on river	Improve water quality for irrigation purposes	Potential destruction of ecosystem, expensive
RIVERBANK FILTRATION- flow through riverbed and groundwater aquifer to the pumping wells	Improve water quality by removal of inorganic and organic pollutants through natural filtration process	Slow
DREDGING RIVER SEDIMENT- removal of polluted sediment by dredging machine	Improve sediment and river water environment	Potential increase of pollution, expensive

3.2. BIOLOGICAL METHODS

Biological methods for water remediation are based on using either selected plants or microorganisms, or most commonly use of both, for pollutant/ contaminant removal. These methods are often combined with other methods of water remediation. The methods can be applied in situ (in stream) (phytoremediation, floating wetlands or floating beds) or ex situ (for instance use of microbiological degradation in bioreactors). Biological methods are more environmentally friendly, easily and widely applicable and usually less expensive than physical and especially chemical methods, but their disadvantage is that it takes a long time for the methods to show some results.

3.2.1. PHYTOREMEDIATON

As previously mentioned, phytoremediation is based on using plants to purify the water body. Plants remove pollutants/ contaminants by adsorption, absorption, accumulation and/ or degradation. Some plants have a high capacity to remove nutrients (nitrogen and phosphorus) from water and thus prevent eutrophication. Plants, by their roots, also provide suitable environment for the growth of microorganisms, which additionally contribute to water remediation (removal of organic pollutants/ contaminants).

The simple phytoremediation is usually applied along the bank slopes of the water body or at point sources of water pollution/ contamination (wastewater discharge point). Some of the plants that have shown good results in water remediation are reed (*Phragmites australis*), water hyacinth (*Eichhornia crassipes*), alligator weed (*Alternanthera philoxeroides*), water lettuce (*Pistia stratiotes*), whorl-leaf watermilfoil (*Myriophyllum verticillatum*), pondweed (*Potamogeton spp.*), cattail (*Typha latifolia*), duckweed (*Lemna gibba*) and canna (*Canna indica*) (Abdalla & Shamrukh, 2010).

3.2.2. MICROBIOLOGICAL METHOD

Microbiological method for water remediation is based on use of microorganisms to biologically remove pollutants/ contaminants from water. Microbiological method for polluted/ contaminated water remediation is commonly used in secondary wastewater treatment processes in wastewater treatment plants. In situ microbiological method is based on enhancing naturally present (native) microorganisms' activity by creating favourable conditions, or by application of microbial agents. The method, as phytoremediation, is economically feasible and widely applicable. The in situ method is usually applied alongside phytoremediation in form of floating beds and constructed wetlands. Microorganisms used for bioremediation of polluted/ contaminated water are shown in Table 2.

Table 2. Microorganisms used for bioremediation of polluted/ contaminated water (adapted from Singh et. al. 2021)

MICROORGANISM	TYPE	POLLUTANTS/ CONTAMINANTS
Pseudomonas	Bacteria	Pb, Zn
Aspergillus flavus* complex and *Bacillus cereus	Bacteria	Hydrocarbons
Pseudomonas sp., Sphaerotilus sp., Janthinobacterium sp., Corynebacterium aurimucosum	Bacteria	Ammonium ions
***Cupriavidus sp*. PDN3 1**	Bacteria	Ammonium, nitrate, and nitrite
EDB-L11 (*Novosphingobium* JEM-1)	Bacteria	17β- estradiol (E2)
Pseudomonas aeruginosa	Bacteria	Cd
***Cupriavidus metallidurans* CH34**	Bacteria	Cd
Escherichia coli, Staphylococcus epidermidis	Bacteria	Zn(II)
S. epidermidis	Bacteria	Cr(VI)
Acinetobacter sp. Bacillus megaterium and Sphingobacterium sp.	Bacteria	Fe, Mn
***Rhodococcus rhodochrous* BX2**	Bacteria	Acetonitrile
***B. cereus* P1 (KP241859)**	Bacteria	Fe, Mn
***Bacillus subtilis* (N4-pHT01-nit)**	Recombinant Bacteria	Acetonitrile
***B. subtilis* N4/pHTnha-ami**	Recombinant Bacteria	Organonitrile
Aspergillus niger	Fungi	Pb(II), Cd(II)
Penicillium simplicissimum	Fungi	Pb(II)
Aspergillus fumigatus	Fungi	Cr(VI)
Termitomyces clypeatus	Fungi	Cr(VI)
Penicillium brevicompactum	Fungi	Co(II)
Saccharomyces cerevisiae	Fungi	Cu(II)
Trichoderma	Fungi	Cd(II)
Candida humicola	Fungi	As
***Mucor hiemalis* EH8**	Fungi	Hg

3.2.3. BIOFILMS

Biofilms are microbial communities composed of different types of microorganisms like bacteria, fungi, and some cyanobacteria and mycoalgae (fungi + algae) that adhere to inert or active entities and are encased by a substrate that can be hydrated. Biofilms are commonly used in secondary treatment processes in wastewater treatment plants. The commonly used forms of biofilms are static biofilms, particulate biofilms, and flocs that are used in trickling filters, fluidized bed reactors, and in activated sludge processes, respectively (Singh et. al., 2021). The method could be also applied in situ. There are several different biofilm technologies used for the remediation of polluted river water, such as gravel contact oxidation, aerated bio-filter biological fluidized bed, artificial packing contact oxidation, thin layer flow method, underground stream purification method and suspended carrier biofilm reactors (Anawar & Chowdhury, 2020).

3.2.4. CONSTRUCTED (ARTIFICIAL) WETLANDS

Constructed wetlands (CWs) are artificially made wetland systems consisting of different plant species, microorganisms species and bed materials used to remediate polluted/ contaminated water. The basic forms of constructed wetlands regarding the water flow are (www.globalwettech.com; Samal et. al., 2019):

1. Constructed wetlands with horizontal flow-polluted water flows horizontally over and around the bed media. Wetlands with horizontal flow can be constructed as systems with horizontal surface flow (Figure 15) or systems with horizontal subsurface flow (Figure 16).

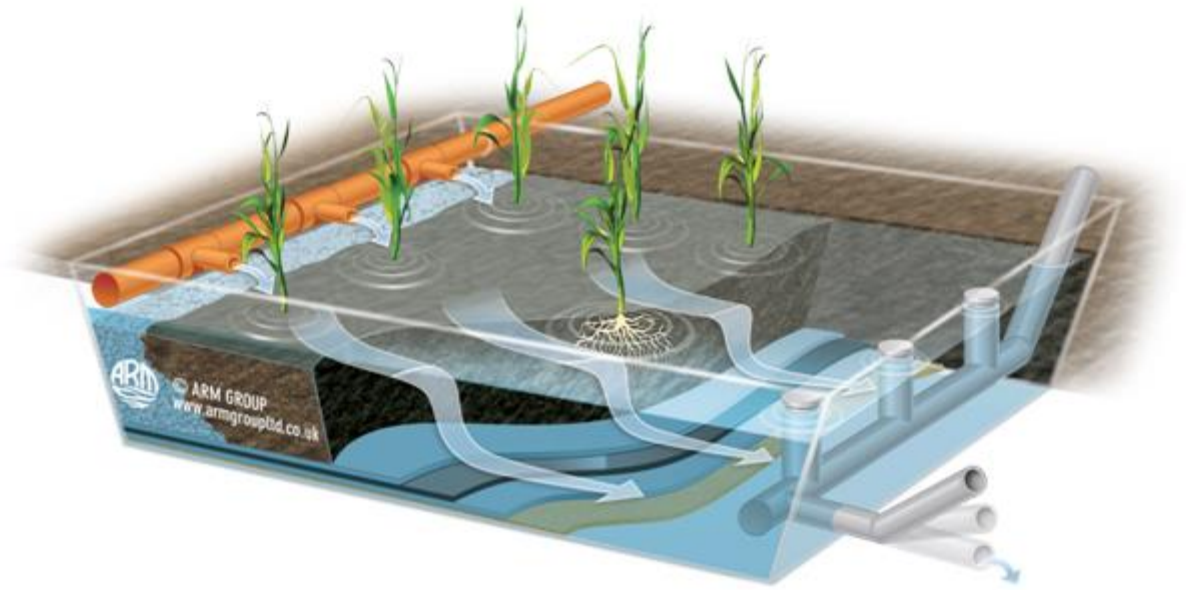

Figure 15. Horizontal surface flow constructed wetland (www.globalwettech.com)

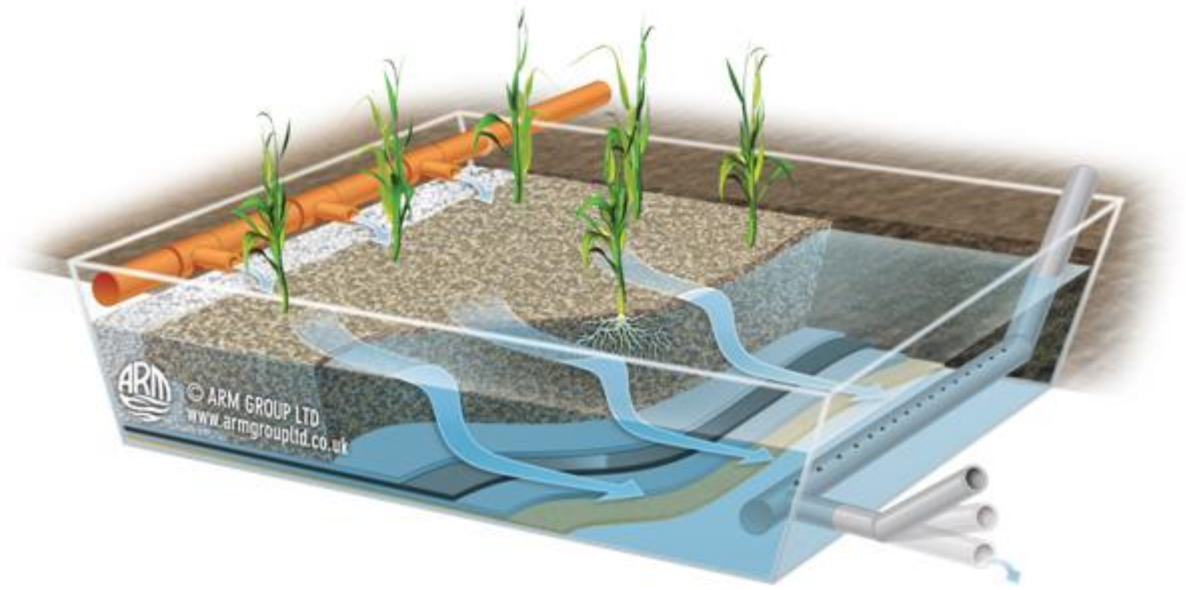

Figure 16. Horizontal subsurface flow constructed wetland (www.globalwettech.com)

2. Constructed wetlands with vertical flow (Figure 17)

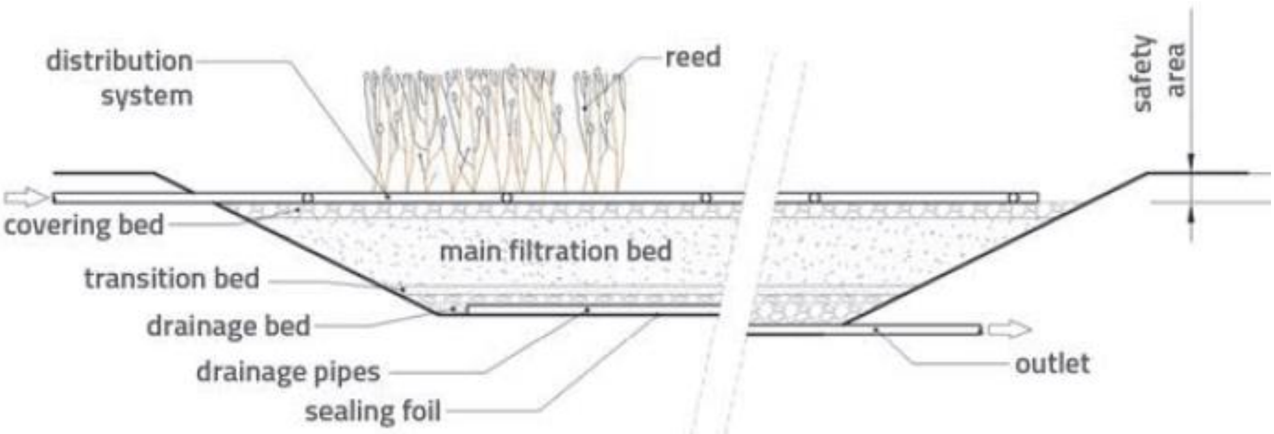

Figure 17. Schematic diagram of a vertical flow constructed wetland (Stanković, 2017)

3. Hybrid systems- combination of vertical and horizontal flow wetlands

3.2.5. ECOLOGICAL FLOATING BEDS

Ecological floating beds (EFB) are relatively new method for polluted/ contaminated water remediation. As the constructed wetland method, the method combines phytoremediation and microbiological bioremediation. The method is based on planting selected plants on a substrate, which is a synthetic buoyant mat, in a way that the plants' roots extend freely into the water body creating suitable rhizosphere which enables growth and reproduction of both aerobic and anaerobic microorganisms, which utilize, and thus degrade, organic substances from the water. Scheme of ecological floating bed is shown in Figure 18.

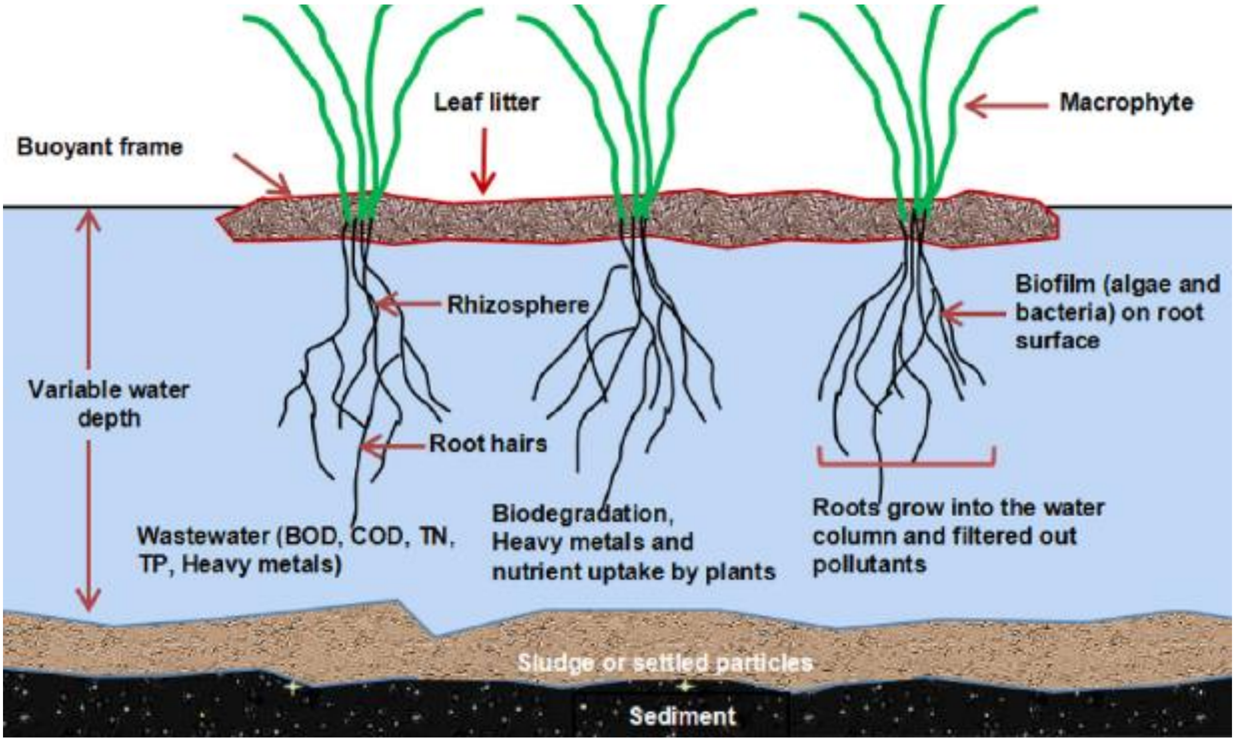

Figure 18. Scheme of an ecological floating bed used for polluted/ contaminated water remediation (Samal et. al., 2019)

Figure 19. Ecological floating bed (www.aquabiofilter.com)

4. REMEDIATION OF OIL SPILLS IN MARINE ENVIRONMENT

When crude oil or petroleum products are spilled on water, two mutually influenced sets of processes take place. These are spreading and movement (drifting) of oil and set of processes called weathering. Oil spreading is primarily caused by gravity and surface tension, with the speed of spreading being the function of spilled volume. There are several factors affecting the movement of oil slick, with wind, water currents and waves being the most important ones. Weathering of oil is a term that covers a set of processes that, depending on type of hydrocarbons and conditions in which the spill took place, in different scopes take place after the spill causing the change of physical and chemical properties of the spilled hydrocarbons. The processes are evaporation, creation of water-in-oil emulsion ("chocolate mousse"), natural dispersion of oil, dissolution, photooxidation, adhesion, sedimentation, microbiological degradation and tar balls formation. All the mentioned processes impact spilled oil behavior on water, but also its effect on the environment and thus determine the remediation actions. The extend of processes that affect behavior of spilled oil are shown in Figure 20.

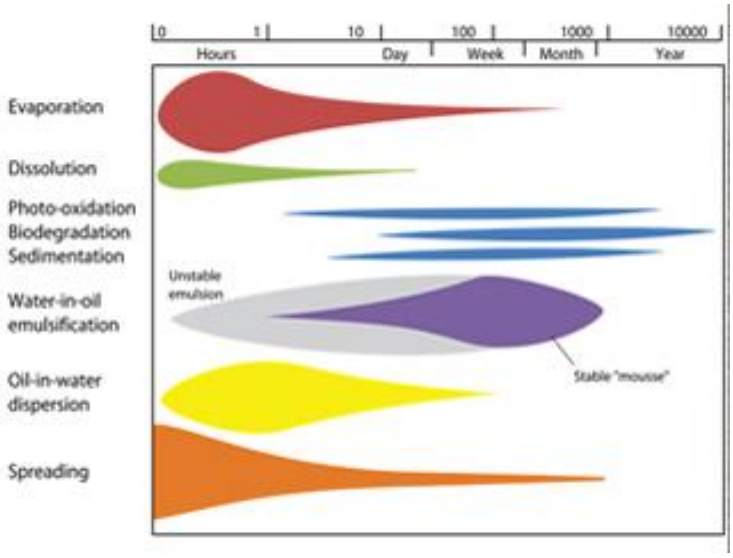

Figure 20. Typical behavior of spilled crude oil (www.itopf.org)

The first thing that should be done in case of an oil spill is to put the source of spill under control and at the same time to contain the spill (to prevent oil slick spreading and movement). The equipment used for oil slick containment, but also diversion of oil slick and protection of certain areas, are called booms. The booms vary in forms (fence booms, curtain (containment) boom, external tension booms) and sizes (depending on location of application) and are the first and the last equipment used in case of a marine oil spill. There are also several special- purpose types of booms like bubble booms, sorbent booms and fire- resistant booms. The most commonly used booms in case of marine oil spill are so- called curtain booms (Figure 21). An illustration of different boom deployments is shown in Figure 22. After the oil slick is contained by booms, the remediation activities start.

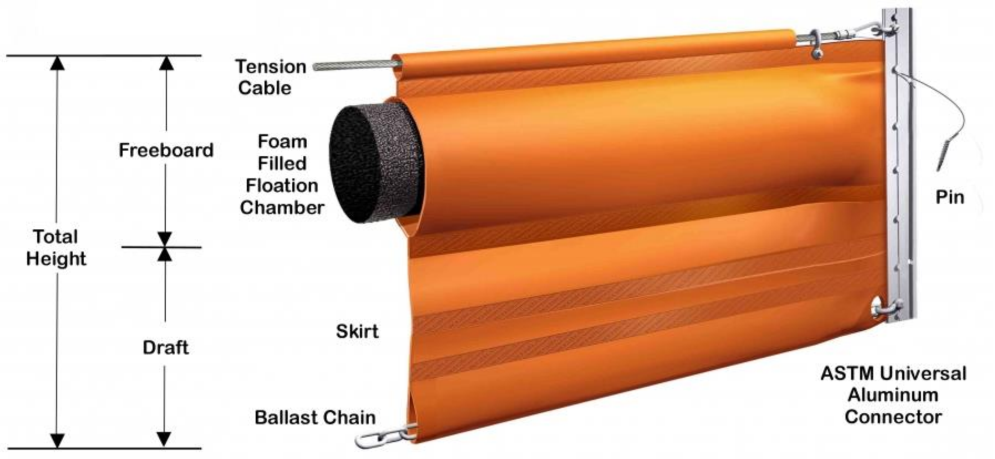

Figure 21. Oil spill containment boom (https://texasboom.com)

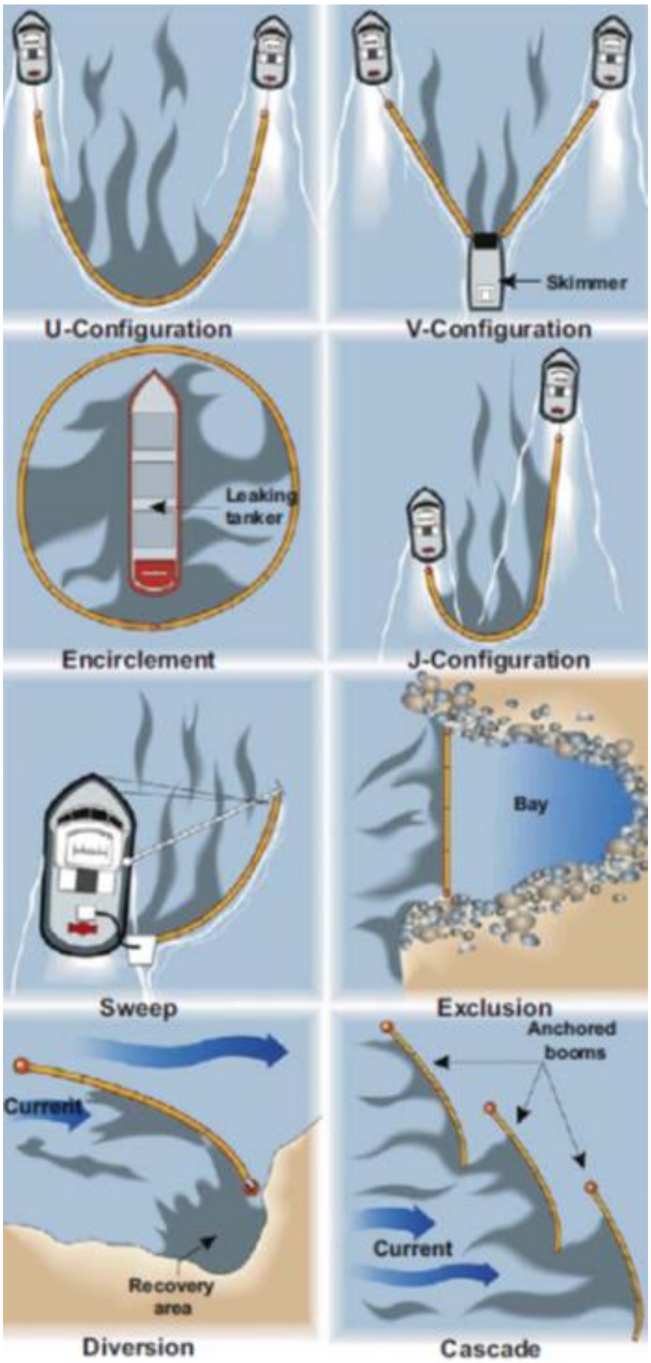

Figure 22. Typical deployments of oil booms (Fingas, 2011)

The methods for marine oil spill remediation can be classified as:

1. physical methods- The methods are based on physical recovery of spilled oil by manual collection (usually applied at shore) or by use of mechanical devices called skimmers. The main characteristic of physical methods of oil spill remediation is that spilled hydrocarbons are removed from water surface in unchanged form (except weathering effects). Skimmers come in variety of forms and sizes and are classifies according to their working principles as: weir skimmers, suction (vacuum) skimmers, centrifugal (vortex) skimmers, submersion skimmers, elevating skimmers and oleophilic surface skimmers. Due to their insensitivity to floating debris and waves, the oleophilic surface skimmers are widely used during oil spill remediation. Illustration of various types of oleophilic surface skimmers are shown in Figure 23.

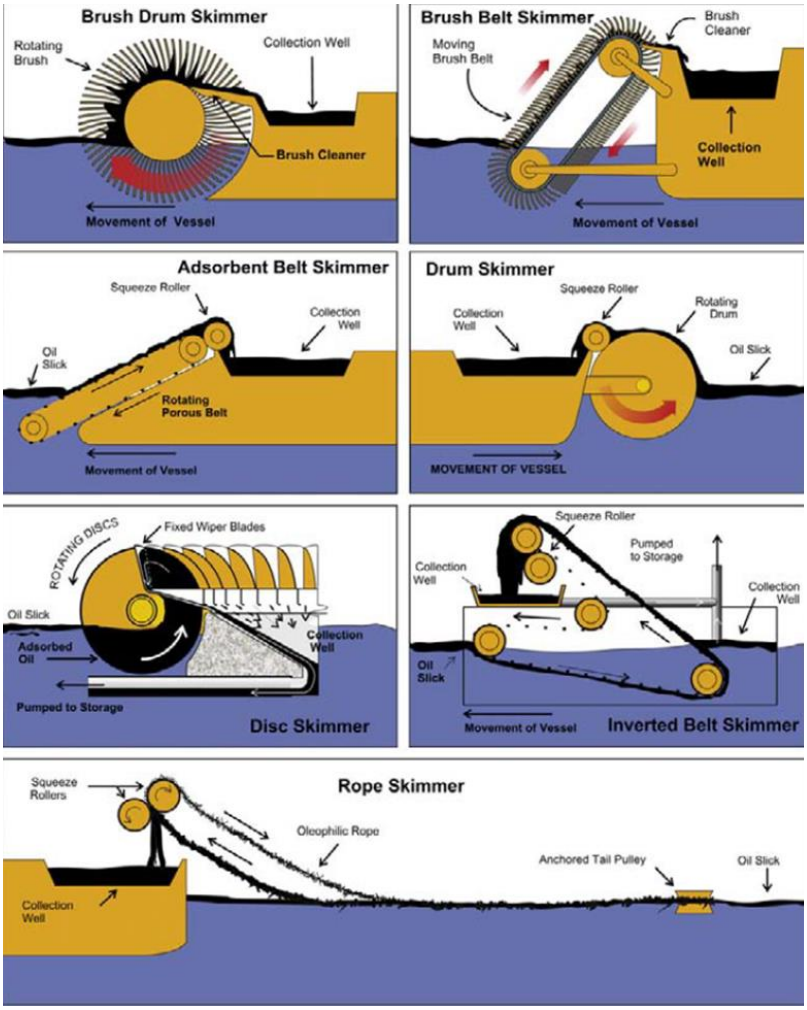

Figure 23. Various types of oleophilic surface skimmers (Fingas, 2011)

2. physically- chemical methods- These methods imply use of various types of treating agents which are classified as solidifiers (gelling) agents, recovery enhancers, sorbents and sinking agents (not often used anymore). In Figure 24 the use of sorbents is show.

Figure 24. Use of sorbents for oil spill recovery (https://foxdesignsg4fong.weebly.com/chemical-clean-up-methods.html)

3. chemical methods- The methods imply application of different chemical treating agents. The application of chemical methods undergoes strickt regulations and must be approved by appropriate authorities. The chemical methods use for oil spill remediation are use of emulsion breakers or inhibitors, use of dispersants and use of in situ burning agents (Figure 25).

Figure 25. Burning of multiple pools of skimmed oil. BP Deepwater Horizon Oil Spill, Gulf of Mexico, June 2010. (Farrington, 2014)

4. microbiological method- use of biosurfactants, biostimulation and bioaugmentation.

5. CONCLUSION

Population and economy growth, alongside climate change consequences, put an imperative on water resources quality management and management of water resources in general. Since water pollution inevitably followed industrialization and urbanization, the growth of environmental awareness resulting with environmental standards and regulation also prompted the development of water pollution remediation methods. Polluted water bodies, under certain conditions and in various extends, undergo through process of self-purification. The self- purification process is generally slow and can take for years, and even several decades, thus the water pollution issues cannot be left to nature to deal itself.

Compared to surface water bodies, groundwater systems are more difficult to remediate, and the remediation activities are time intensive. The most applied method for groundwater remediation is so-called pump & treat method, which involves pumping (extraction) of the polluted/ contaminated groundwater from wells and its' in situ or ex situ treatment. The method is often combined with other remediation methods. Other groundwater remediation methods include air sparging (or combined with biological methods-biosparging), various thermal methods, biological methods (bioremediation and phytoremediation) and chemical methods.

Surface waters remediation methods are also classified as physical, chemical, and biological (ecological) methods. Chemical methods, since they are, compared to physical and biological ones, more environmentally intensive, are usually applied ex situ in wastewater treatment plants. In last few decades great emphasis, has been put on biological methods which include use of plants, microorganisms, or combination of both, for surface remediation. Compared to physical and chemical methods, the biological methods are more environmentally friendly and less expensive since they support water self- purification processes.

6. REFERENCES

1. Mayer, D., 1993, Kvaliteta i zaštita podzemnih voda, Zagreb, Hrvatsko društvo za zaštitu voda i mora
2. Brusseau, M. L., Pepper, I. L., Gerba, C. P., Ed., 2019, *Environmental and Pollution Science*, Third Edition, Academic Press, 2019
3. Pucke, S., Odah, M., Reed, C., *The Art in-Well Technology – An Effective and Cost-Efficient Remedy For Soils and Groundwater in Fractured Bedrock Formations,* available at https://clu-in.org/products/siteprof/2004fracrockconf/cdr_pdfs/indexed/group1/059.pdf
4. Columbus, B., 2007, *Electrical Resistance Heating (ERH): Design and Performance Criteria*, available at https://clu-in.org/download/contaminantfocus/dnapl/Treatment_Technologies/RITS_2007A_ERH.pdf
5. Lim, M. W., Lau, E. V., Poh, P. E., 2016, *A comprehensive guide of remediation technologies for oil contaminated soil—Present works and future directions,* Marine Pollution Bulletin, Elsevier
6. Anawar, H., Chowdhury, R., 2020, *Remediation of Polluted River Water by Biological, Chemical, Ecological and Engineering Processes*, Sustainability 2020, 12, 7017, 1-18, MDPI, Switzerland
7. Hudson, H., Kirschner, B., 1997, *Lake Notes: Lake Aeration and Circulation*, US Environmental Protection Agency, Illinois, USA
8. Abdalla, F., Shamrukh, M., 2010, *Riverbank Filtration: Developing Countries Choice for Water Supply Treatment, Egypt Case*, The 1st IWA Malaysia Young Water Professionals Conference (IWAYP2010), 1-4 March 2010, Kuala Lumpur, Malaysia, available at https://www.researchgate.net/publication/268924778_Riverbank_Filtration_Developing_Countries_Choice_for_Water_Supply_Treatment_Egypt_Case
9. Ojuederie, O. B., Babalola, O. O., 2017, *Microbial and Plant-Assisted Bioremediation of Heavy Metal Polluted Environments: A Review*, International Journal of environmental Research and Public Health, 2017,14,1504, 1-27, MDPI, Switzerland, available at https://www.researchgate.net/publication/321781831_Microbial_and_Plant Assisted_Bioremediation_of_Heavy_Metal_Polluted_Environments_A_Review

10. Wang, H., Zhang, H., Cai, G., 2011, *An Application of Phytoremediation to River Pollution Remediation,* 3rd International Conference on Environmental Science and Information Application Technology (ESIAT 2011), Procedia Environmental Sciences 10 (2011), pp. 1904-1907, available at www.sciencedirect.com
11. Singh, M., Pandey, S., Kumar, A., Pandey, K. D., 2021, *Microbial biofilms for the remediation of contaminated water. Microbe Mediated Remediation of Environmental Contaminants,* Woodhead Publishing Series in Food Science, Technology and Nutrition, pp. 255–269, available at www.sciencedirect.com
12. Samal, K., Kar, S., Trivedi, S., 2019, *Ecological floating bed (EFB) for decontamination of polluted water bodies: Design, mechanism and performance*, Journal o Environmental Management 251 (2019) 109550, pp. 1-13
13. Stanković, D., 2017, *Constructed wetlands for wastewater treatment*, Građevinar 69 (2017) 8, pp 639-652
14. Farrington, J. W., 2014, *Oil pollution in the marine environment II: Fates and Effects of Oil Spills, Environment*, Vol. 56, Nr.4, pp. 16-31
15. Fingas, M. (Ed.), 2011, *Oil Spill Science and Technology: Prevention, Response, and Cleanup*, Elsevier Inc.
16. www.pumpindustry.com.au/weir-upgrade-supports-irrigation
17. www.globalwettech.com
18. www.aquabiofilter.com
19. www.itopf.org
20. https://texasboom.com
21. https://foxdesignsg4fong.weebly.com/chemical-clean-up-methods.html