# Water Treatment Technologies

On this page:

- <u>Schematic</u>
- Introduction
- <u>Other Technology Names</u>
- <u>Description</u>
- <u>Development Status</u>
- <u>Applicability</u>
- <u>Cost</u>
- Duration
- Implementability Considerations
- <u>Resources</u>

## Schematic



This information may be reproduced without restriction as long as the source attribution is included. Schematic of Common Water Treatment Technologies

### Introduction

Many remediation technologies generate an aqueous stream that may require treatment depending on contaminant type and concentration, site location, and regulatory requirements. A variety of treatment options based on physical (e.g., oil water separation, adsorption, and filtration), chemical (oxidation, ion exchange, photocatalysis), and biological (e.g., biological filtration) processes are available to treat the water generated by these remediation technologies. These treatment technologies can be applied independently or as part of a treatment train to overcome site-specific limitations and remove a wider range of contaminants of concern (COCs) of different phases (non-aqueous phase liquid [NAPL], suspended solids, and dissolved) than possible using a single treatment technology. Each type of treatment has its advantages and limitations and may or may not be applicable to all COCs at a site. This profile describes commonly used contaminant treatment technologies, presents their basic principles and applicability, and describes their limitations and other considerations for implementation. In addition, beneficial reuse or reclamation of the treated water is described, which has gained more recognition in recent years as part of a sustainable remediation management strategy.

## **Other Technology Names**

Pump and Treat Dissolved Phase Treatment Aqueous Phase Treatment

### Description

Water treatment is required for many remediation technologies that remove contaminated groundwater from the aquifer during restoration activities. Water treatment usually consists of a treatment train to remove contaminants (e.g., oil globules, hydrocarbon constituents, chlorinated solvents, metals, and inorganic ions) and return the water to a condition that can be discharged/reused. The water treatment system must be designed based on the COCs present, their concentrations, and local regulatory requirements. Systems can be portable and temporary (on-site trailer mounted) or can be large and complex for long-term projects (e.g., pump and treat systems) housed in buildings constructed for this purpose. Water treatment is accomplished using a variety of technologies based on treatment processes commonly used by municipal and industrial wastewater treatment facilities. Common classes of treatment include:

#### Absorption

Adsorption consists of solutes concentrating at the surface of a sorbent, thereby reducing their concentration in the bulk liquid phase. Adsorption mechanisms are generally categorized as either physical adsorption, chemisorption, or electrostatic adsorption. Weak molecular forces, such as Van der Waal forces, provide the driving force for physical adsorption, while a chemical reaction forms a much stronger chemical bond between the compound and the surface of the solid in chemisorption. Electrostatic adsorption involves the adsorption of ions through Coulombic forces, and is normally referred to as ion exchange. For liquids, interactions between the solute and the solvent play an important role in establishing the degree of adsorption.

Commonly used natural and synthetic adsorbents are described below.

- **Granular activated carbon (GAC)** is the most common type of adsorbent used to treat water generated at environmental restoration sites. The carbon is "activated" by being processed to create porous particles having a large internal surface area (300 to 2,500 square meters or about 3,200 to 27,000 square feet per gram of carbon) that attracts and adsorbs organic molecules as well as certain metal and inorganic molecules.
- Activated alumina is a filter media made by treating aluminum ore so that it becomes porous and highly adsorptive. Activated alumina will remove a variety of contaminants, including excessive fluoride, arsenic, and selenium.
- **Forage sponge** is an open-celled cellulose sponge incorporating an aminecontaining chelating polymer that selectively absorbs dissolved heavy metals. The polymer is bonded to the cellulose to minimize physical separation from the supporting matrix. The functional groups in the polymer (i.e., amine and carboxyl groups) provide selective affinity for heavy metals in both cationic and

anionic states, preferentially forming complexes with transition-group heavy metals.

- Lignin clays are used to treat aqueous waste streams with organic, inorganic and heavy metals contamination. The waste stream is treated by the molecular adhesion of the contaminants to an adsorptive surface.
- **Synthetic resins** can achieve higher degrees of selectivity and adsorption capacity for certain compounds than activated carbon. Resins are typically regenerated using acids, bases, or organic solvents, instead of thermal methods, so they are better suited for thermally unstable compounds such as explosives. They are resistant to deactivation due to the adsorption of dissolved solids.

Adsorbents are placed in one or more vessels and groundwater is pumped through them. The two most common configurations for adsorption systems are the fixed bed and the pulsed or moving bed. The fixed-bed configuration is the most widely used for adsorption of contaminants from liquids.

Pretreatment for removal of suspended solids from streams to be treated is an important design consideration. If not removed, suspended solids in a liquid stream may accumulate in the bed, causing an increase in pressure drop. When the pressure drop becomes too high, the accumulated solids must be removed by backwashing. The solids removal process necessitates downtime and may result in carbon loss and disruption of the mass transfer zone.

When the concentration of contaminants in the effluent from the vessels exceeds a target level, depending on the adsorbent used and the types of contamination present, it may be possible to regenerate the adsorbent, usually at an off-site facility. However, in some cases, it is not possible to regenerate the material. For example, GAC used for explosives- or metals-contaminated groundwater probably cannot be regenerated and should be removed and properly disposed.

#### **Air Stripping**

Air stripping is an ex situ technology that removes volatile organic compounds (VOCs) from pumped groundwater or wastewater by passing the water over a media having a large surface area while exposing the contaminated water to uncontaminated air flow. The VOCs are transferred (i.e., volatilized) from the groundwater or wastewater to the vapor phase in the countercurrent air stream, where the vapor is either directly discharged or routed to an off-gas treatment system. Additional air stripping design and application information can be found <u>here</u>.

#### **Chemical Oxidation and Reduction**

Chemical oxidation refers to the conversion of hazardous contaminants using oxidants to non-hazardous or less toxic compounds. Commonly used oxidizing agents are ozone, hydrogen peroxide, permanganate, hypochlorites, chlorine, and chlorine dioxide. These oxidants can degrade many toxic organic chemicals, control biological growth in treatment units, and convert metals (such as iron and manganese) into forms that are more amenable to precipitation and other physical separation processes. Oxidants are able to achieve high treatment efficiencies with very fast reaction rates (e.g., > 90 percent in minutes) for unsaturated aliphatic (e.g., trichloroethylene [TCE]) and aromatic compounds (e.g., benzene).

Commonly used oxidants include:

• Fenton's reagent, which consists of hydrogen peroxide in the presence of native or supplemental ferrous iron that catalytically reacts to form free hydroxyl radicals. These strong, nonspecific oxidants can rapidly degrade a variety of organic compounds. Fenton's reagent oxidation is most effective under very acidic pH (e.g., pH 2 to 4)



<u>1</u> and becomes ineffective under moderate to strongly alkaline conditions.

- **Ozone gas**, which can oxidize contaminants directly or through the formation of hydroxyl radicals. Like peroxide, ozone reactions are most effective in systems with acidic pH. The oxidation reaction process is extremely fast. Ozone must be generated on site and used immediately due to its short half-life, typically less than 30 minutes.
- **Permanganate**, which generally is applied in either sodium or potassium (permanganate) form. The reaction stoichiometry of permanganate in natural systems is complex. The reactions proceed at a somewhat slower rate than those of the two abovementioned oxidants. Permanganate reactions are effective over a pH range of 3.5 to 12.
- **Chlorine**, which can be applied as a liquid (e.g., sodium hypochlorite) or as a gas (chlorine gas), to control biological growth and to remove color, taste and odor compounds, iron and other dissolved inorganic contaminants such as arsenic. It should be noted, however, that chlorine reacts with natural organic compounds in water to form potentially chemical byproducts including trihalomethanes and haloacetic acids, although this may not be a significant concern for most applications for treating recovered groundwater.

Chemical reduction is the opposite of chemical oxidation. It involves reducing oxidized species of contaminants (or residual oxidants). Common reductants include ferrous sulfate and sodium sulfite. Chemical reduction is typically used in water treatment to remove oxygen, reduce hexavalent chromium, and destroy residual oxidants. In reducing oxygen, sodium sulfite or ammonium bisulfite which, although more expensive, is easier to use and has a much more extensive buffer effect. The chemical removal of total chromium involves reducing hexavalent chromium to trivalent chromium followed by precipitation as a hydroxide. The destruction of residual oxidants typically occurs after wastewater disinfection in order to limit the subsequent formation of unwanted byproducts, before processing the water through a membrane or ion exchanger resin, or before discharging or recycling gas from ozone utilization applications.

#### **Advanced Oxidation Processes (AOPs)**

AOPs refer to the destruction of organic contaminants using a form of light radiation in conjunction with oxidants (e.g., ozone or hydrogen peroxide) or a catalyst to achieve rapid and efficient destruction of COCs. AOPs can be divided into two primary types of processes including: Ultraviolet (UV) oxidation, which is a destruction process that can oxidize organic and explosive constituents in water by the addition of strong oxidizers such as ozone and/or hydrogen peroxide, and irradiation with UV light. Oxidation of target contaminants is caused by direct reaction with the oxidizers, UV photolysis, and through the synergistic action of UV light.

If complete degradation is achieved, the final products of UV oxidation are carbon dioxide, water, and salts. Systems can be configured in batch or continuous flow modes, depending on the throughput under consideration. The UV oxidation process is generally performed using low pressure lamps operated at 65 watts for ozone systems and 15 to 60 kilowatts for hydrogen peroxide systems. The duration of operation and maintenance of UV oxidation depends on influent water turbidity, contaminant and metal concentrations, existence of free radical scavengers, and the required maintenance intervals on UV reactors and quartz sleeves.

• **Photocatalysis** uses visible light and a catalyst to treat a range of organic contaminants. Light is absorbed by a substrate and the photocatalytic activity depends on the ability of the catalyst to generate free radicals (e.g., hydroxyl radicals) able to undergo secondary reactions. Photocatalysis is induced under UV, solar, and visible light and can be classified as homogeneous and heterogeneous. Photolysis is a weaker process than UV oxidation. Products of photo-degradation vary according to the matrix in which the process occurs, but the complete conversion of an organic contaminant to carbon dioxide, water, etc. is not probable.

#### Filtration (Particulate)

Filtration is the physical process of mechanical separation based on particle size whereby particles suspended in a fluid are separated by forcing the fluid through a porous medium. As fluid passes through the medium, the suspended particles are trapped on the surface of the medium and/or within its body. Common types of filtration techniques include:

- Sand filtration, which consists of a filter box filled with a bed of fine sand supported by a layer of gravel, and particulate and microbial contaminants are removed when water percolates through the filter box. It is used when water contains relatively low levels of suspended contaminants. It may involve the addition of a coagulant followed by rapid mixing, flocculation and filtration.
- **Biological filtration**, in which contaminants are removed by three main mechanisms: biodegradation, adsorption of micropollutants, and filtration of suspended solids. The filter usually consists of a bed comprised of sand or crushed gravel which hosts a community of microorganisms that degrade the contaminants as the water is passed through the filter.
- Membrane filtration occurs when particles are separated by forcing fluid through a semipermeable membrane. Only the particles whose sizes are smaller than the openings of the membrane can flow through it. Microfiltration (MF) and ultrafiltration (UF) are most commonly used in water treatment and can be operated under positive or negative pressure (i.e., vacuum pressure). Membrane pore size for MF units typically ranges between 0.1 to 0.5 micrometer (µm) while UF pore sizes range from about 0.01 to 0.1 µm. Particulate contaminants are retained by the membrane and removed during periodic backwashing of the membrane filter. Flux rates for MF and UF membranes typically range between 40 and 100 gallons per day per square foot of

membrane area. The design flux is typically determined by bench or pilot testing since it is dependent on specific water quality conditions and temperatures.

#### Membrane Separation (Dissolved)

Membrane filtration also may be used to remove dissolved contaminants. Membrane separation processes for this purpose include reverse osmosis (RO), nanofiltration (NF), electrodialysis (ED), and electrodialysis reversal (EDR):

- RO and NF both operate based on the principle of reverse osmosis. Osmosis is the natural flow of a solvent, such as water, through a semi-permeable membrane (which acts as a barrier to dissolved contaminants) from a less concentrated solution to a more concentrated solution. Flow continues until the concentrations on each side of the membrane are equal. The amount of pressure that must be applied to stop this flow of water is called the osmotic pressure. RO is the reversal of the natural osmotic process by applying pressure in excess of the osmotic pressure to the more concentrated solution. The feed pressure forces the water through the membrane against the natural osmotic gradient, thereby increasing the dissolved contaminant concentrations on one side of the membrane and increasing the volume of water with lower concentrations of dissolved contaminants on the other. The principal difference between RO and NF is the composition of the membrane, which affects the size of dissolved contaminants that can be removed. Nanofiltration membranes don't remove as small molecular weight contaminants as RO but operate at a lower pressure than RO membranes and therefore consume less power than RO membranes. However, NF can provide very high removal of multivalent ions with low to moderate removal of monovalent ions, and selective removal of organic compounds determined by molecular weight, size, and charge relative to the molecular weight, pore size, and charge of the membrane material.
- ED is an electrochemical separation process in which ions are transferred through membranes from a less concentrated to a more concentrated solution as a result of the flow of direct electric current. ED systems consist of alternating anion and cation ion exchange membranes placed between positive and negative electrodes. Applying a voltage across the electrodes causes the positively charged cations to move towards the negative electrode. Contaminants are removed from the water through the membrane, as opposed to other membrane processes where the water passes through the membrane and the contaminants are rejected by the membranes.
- **EDR** is a process similar to ED, but the electrical polarity (anode and cathode) is periodically reversed to control membrane scaling and fouling. Polarity reversal typically occurs two to four times per hour. When the electrical polarity is reversed, the product and concentrate streams are also reversed. This prevents the flow compartments from seeing streams with high dissolved solids for extended periods of time and aids in controlling fouling.

These membrane separation processes include three basic flow streams: the feed, permeate or product, and concentrate or waste streams. For RO and NF, treatment is generally in stages, wherein the concentrate from the prior stage becomes the feed for the subsequent stage. The permeate from each stage is blended together for the final product stream. The concentrate from the final

stage is usually wasted (disposed). In ER and EDR, the product from the prior stage is further treated in subsequent stages.

The concentration of other impurities (e.g., calcium carbonate, iron, organic matter, and bacteria) in the concentrate stream limits recovery by membrane systems. Temperature can significantly impact membrane performance. A decrease in temperature will result in the increase of viscosity and density, and the transmembrane pressure required to pass the water through the membrane also increases, resulting in an increase in the specific flux. Contaminant solubility also decreases as temperature decreases which may require operation at a lower recovery to prevent scaling. For ED and EDR systems, water temperature affects ion mobility. Higher temperatures can cause membrane degradation and compaction of RO and NF membranes.

Residuals generated from membrane separation systems include the concentrate from the membrane processes and spent cleaning chemicals. Chemical cleaning is required to periodically remove scale buildup and biological fouling on the membrane surface. Spent solutions are generally acidic in nature and require neutralization prior to disposal.

#### Ion Exchange

Ion exchange removes ions from the aqueous phase by the exchange of cations or anions between the contaminants and the exchange medium. It involves passing contaminated water through an ion exchange resin so that contaminants exchange on sites on the media, exhausting its capacity. After the resin capacity has been exhausted, resins can be regenerated for reuse. The resin material typically consists of synthetic organic polymers that contain ionic functional groups to which exchangeable ions are attached. Resins are categorized as strong or weak acid cation exchangers or strong or weak base anion exchangers. Cationic resins are typically used for softening (e.g., calcium and magnesium removal), while anionic resins are used to remove various anions impacting water quality (e.g., perchlorate and nitrate). Recent advances include application of contaminant-selective ion exchange resins that have high capacities for a single target contaminant and are disposed after use instead of regenerated. For example, perchlorate-selective resins and arsenicselective resins are commercially available.

#### **Metal Sequestration**

Metal sequestration is a form of treatment in which a chemical, known as a sequestrant or sequestering agent, is added to water. Most sequestering chemicals are polyphosphate compounds (e.g., sodium- and potassium-based), which provide nutrients to microorganisms and may need to be treated prior to discharging the water. The chemical forms a bond with metal ions (e.g., iron and manganese) or heavy metals, allowing them to remain in solution and prevent further reactions (e.g., oxidation and precipitation) that might interfere with the treatment process (e.g., fouling of equipment) or cause water quality problems (turbidity, color, staining, etc.). The effectiveness of sequestering agents depends on influent water quality in addition to metal levels. Bench- or pilot-scale testing typically is conducted prior to application of sequestering agents. Sequestered metals can be filtered and removed more easily in a later process. If not removed, sequestered metals may be released back to the water

stream, causing treatment or water quality problems in subsequent processes or discharge.

#### **Oil Water Separation**

Oil water separation is the process of separating oil (i.e., NAPL) from the water stream generated by other remediation technologies such as <u>multi-phase</u> <u>extraction</u> and <u>free product recovery</u>. Available methods for separating oil water mixtures include one or more physical, chemical, mechanical, electrical, magnetic, and thermal mechanisms; however, gravity differential separation is by far the most commonly used method to separate oil water mixtures generated at environmental restoration sites.

There are several types of gravity separators including American Petroleum Institute (API) oil/water separators, circular and plate interceptors, rotational separators (centrifuges, vortex flow), and gas flotation separators. Gravity separation is basic to almost all oil water separators. It is usually the first step in the treatment of oily waters and provides coarse separation of oil and water. In general, oil water mixtures will separate naturally into two distinct layers of oil and water. Oil globules and/or suspended particles will rise to the surface (e.g., light NAPL or LNAPL) or fall to the bottom (e.g., dense NAPL or DNAPL), depending on the sign of the density differential. In the case of LNAPL, oil globules rise and form a floating layer, which is easily skimmed from the surface. Ease of separation depends on the magnitude of the difference in densities of the two immiscible liquids, and size of the oil globules or droplets. Gravity separation is inefficient when the density difference is small and oil droplets are small. Devices operating on the gravity principle will not separate dissolved oil or emulsions.

#### pH Control

pH is an indicator of the acid or alkaline condition of water. The pH of a water stream is a result of natural geological and chemical conditions and any preceding remediation processes. pH control or adjustment is the alteration of pH by adding a reagent such as an acid to drive pH down or a caustic or other alkaline substance to increase pH. pH control or adjustment can be used to directly treat contaminants (e.g., metal precipitation and oil emulsion breaking) or create favorable conditions for other treatment processes (e.g., coagulation, chemical oxidation, and biological treatment). For example, the optimal pH range for coagulation is 6 to 7 when using aluminum sulfate (alum) and 5.5 to 6.5 when using iron, and the optimal pH range for treatment involving biological degradation is normally near neutral (6.5 to 7.5).

Sulfuric acid, hydrochloric acid, calcium/sodium carbonate, and sodium hydroxide are most commonly used for pH control. They can be added to the treatment process via tanks and mixers or dosed directly into the process line and mixed using static mixing elements controls, continuously or in batches.

Control of pH to near neutral can be achieved through a neutralizing filter. The filter contains a neutralizing material that dissolves in the influent water and raises its pH level. Calcium carbonate treats water with a pH greater than 6 and synthetic magnesium oxide will treat water with a pH below 6.

#### Precipitation/Coagulation/Flocculation

Precipitation, coagulation, and flocculation processes transform dissolved contaminants into an insoluble solid that is easily separated by sedimentation or filtration. Typically used to treat metals or facilitate removal of oils in contaminated water, this treatment process is often used as a pretreatment for other treatment technologies such as chemical oxidation where the presence of metals would interfere with these processes. Metals precipitation from contaminated water involves the conversion of soluble heavy metal salts to insoluble salts that will precipitate. The precipitate can then be removed from the treated water by physical methods such as settling and/or filtration. The process usually requires pH adjustment, addition of a chemical precipitant and a flocculant (e.g., polymer). Typically, metals precipitate from the solution as hydroxides, sulfides, or carbonates, while oils will adhere to the coagulant. Depending on the specific gravity of the resulting material, it can be removed as a sludge from the bottom of a separator or skimmed from the surface. The solubilities of the specific contaminants and the required cleanup standards will dictate the process used. In some cases, process design will allow for the generation of sludges that can be sent to recyclers for metal or oil recovery.

In the precipitation process, chemical precipitants, coagulants, and flocculants are used to increase particle size through aggregation. The precipitation process can generate very fine particles that are held in suspension by electrostatic surface charges. These charges cause clouds of counter-ions to form around the particles, giving rise to repulsive forces that prevent aggregation and reduce the effectiveness of subsequent solid-liquid separation processes. Therefore, chemical coagulants are often added to overcome the repulsive forces of the particles. The addition of coagulants is followed by lowsheer mixing in a flocculator to promote contact between the particles, allowing particle growth through the sedimentation phenomenon called flocculant settling. Bench-scale treatability tests should be conducted to determine operating parameters and characteristics (e.g., reagent type and dosage, optimum pH, retention time, flocculent/polymer selection, suspended solids, precipitate settling and filtration rates, and sludge volume and characteristics).

#### **Beneficial Reuse/Reclamation**

Beneficial reuse and reclamation of treated water is an option in lieu of disposal that contributes to the overall conservation of water, and has gained more recognition in recent years. Partially or fully treated water can be reinjected into a deeper aquifer, reinjected into a treatment area to improve capture and control plume migration, sprinkled onto the ground for irrigation or to remove residual contamination, or discharged to lagoons and percolation ponds to replenish aquifers.

Beneficial reuse and reclamation of the treated water has been advocated as part of the sustainable or green remediation concept. Sustainable remediation considers the environmental, social, and economic aspects of potential groundwater conservation and reuse options in remediation projects. Remediation activities that are costly and less efficient can become attractive when considering their positive contribution to the environment. For example, groundwater <u>pump and treat</u> historically is considered a less effective and efficient strategy for groundwater restoration projects because of the difficulty in removing contaminants from the aquifer matrix and the long duration of operation required. However, from a groundwater reuse perspective, groundwater pump-and-treat systems might be viewed differently when the demand for the treated water is high.

In the past several decades, there have been numerous successful beneficial reuse applications ranging from small-scale reuse (e.g., cooling water and dust control) to regional-scale reclamation (e.g., aquifer replenishment and saltwater intrusion prevention projects). One such example is at the former Unidynamics Phoenix, Inc. facility in central Arizona, which produces an aggregate flow of approximately 2,800 gpm from the extraction wells. Approximately 1,600 gpm of treated groundwater is returned to the aquifer via injection wells and the remainder 1,200 gpm is used for dust control, irrigation of local agriculture, a golf course, and a local city park, and precooling of HVAC cooling water by a local school. In another application, extracted groundwater containing chlorinated VOCs is pumped directly into a steel mill's contact cooling water system, where the chlorinated VOCs are volatilized in the steel cooling process. Remediation sites within states having water reuse regulations or guidelines should make reuse or reclamation an option in evaluating remediation strategies.

These applications are subject to state-specific rules as water reuse regulation is generally under the jurisdiction of the states. The regulations developed by states vary, and some states have yet to develop water reuse guidelines or regulations.

### **Development Status and Availability**

The following checklist provides a summary of the development and implementation status of water treatment technologies:

At the laboratory/bench scale and shows promise

In pilot studies

🛛 At full scale

To remediate an entire site (source in vadose zone)

To remediate a source only

As part of a technology train

As the final remedy at multiple sites

To successfully attain cleanup goals in multiple sites

Water treatment technologies are available through the following vendors:

Commercially available nationwide

Commercially available through limited vendors because of licensing or specialized equipment

Research organizations and academia

# Applicability

	Contaminant Class Applicability Rating for Water Treatment										
	(Rating codes: ● Demonstrated Effectiveness, <sup>o</sup> Limited Effectiveness, <sup>O</sup> No Demonstrated Effectiveness,										
Water Treatment Technology	Level of Effectiveness dependent upon specific contaminant and its application/design, I/D Insufficient Data, N/A Not Applicable)										
	Nonhalogenated VOC	Halogenated VOC	Nonhalogenated SVOC	Halogenated SVOC	Fuels	Inorganics	Radionuclides	Munitions	Emerging Contaminants		
					2						
Adsorption/Absorption	Ð	Ð	Ð	D	0	$\bullet$	$\diamond$	0	I/D		
Adsorption by GAC	$\bullet$	$\bullet$	$\bullet$	$\bullet$	$\bullet$	$\diamond$	0	$\diamond$	$\diamond$		
Chemical Oxidation/Reduction	Ð	O	0	O	0	$\diamond$	0	O	I/D		
Advanced Oxidation Processes	$\bullet$	$\bullet$	$\bullet$	$\bullet$	$\bullet$	$\diamond$	$\diamond$	$\bullet$	0		
Filtration (Particulate)	0	0	0	0	0	$\bullet$	\$	0	I/D		
Membrane (Dissolved)	$\bullet$	$\bullet$	$\bullet$	$\bullet$	0	$\diamond$	\$	0	I/D		
Ion Exchange	0	0	0	0	0	$\bullet$	O	0	$\diamond$		
Metal Sequestration	0	0	0	0	0	$\diamond$	0	0	0		
Oil Water Separation	\$	\$	\$	\$	\$	0	0	0	0		
pH Control	0	0	0	0	0	•	0	0	0		

Precipitation/Coagulation/Flocculation

#### Photocatalysis

#### Adsorption and Absorption (non-GAC)

Adsorptive materials can be used to treat most organic contaminants and selected inorganic contaminants from liquid streams. Activated alumina can remove fluoride and heavy metals. The forager sponge is specifically used to remove heavy metals. Lignin clays treat organic, inorganic, and heavy metals contamination within aqueous waste streams. Synthetic resins are better suited for thermally unstable compounds such as explosives than GAC, due to the resins' non-thermal regeneration requirements.

The applicability and effectiveness of adsorptive materials are impacted by several factors. In general, they are not applicable to process water that contains high levels of oily substances, and are less effective for water-soluble compounds and small molecules that do not adsorb well. They are not practical where the content of the absorbable contaminant(s) is so high that frequent replacement of the adsorbent is necessary. Further, if the spent media cannot be regenerated, they may require treatment/disposal as hazardous wastes.

#### Adsorption by GAC

GAC is used to treat hydrocarbons, semi-volatile organic compounds (SVOCs), and explosives, and has limited effectiveness on halogenated VOCs and pesticides. Liquid phase carbon adsorption is effective for removing contaminants at low concentrations (milligrams per liter [mg/L]) from water at nearly any flowrate, and for removing higher concentrations of contaminants from water at low flowrates (typically 2 to 4 liters per minute). GAC can be deployed rapidly, and contaminant removal efficiencies are high.

The applicability and effectiveness of GAC are impacted by several factors. The presence of multiple contaminants can impact process performance. Streams with high suspended solids (> 50 mg/L) and oil and grease (>10 mg/L) may cause fouling of the carbon and may require frequent treatment. In such cases, pretreatment is generally required. The type, pore size, and quality of the carbon, as well as the operating temperature, will impact process performance. Vendor expertise for carbon selection should be consulted. When used for explosives- or metals-contaminated water, the carbon cannot be regenerated. Eventually, all spent carbon needs to be properly disposed.

#### **Chemical Oxidation and Reduction**

Chemical oxidation can treat a wide range of VOCs and SVOCs, control biological growth in treatment units, and convert metals (such as iron and manganese) into forms that are more amenable to precipitation and other physical separation process. Chemical reduction typically is used to remove highly oxidized contaminants (e.g., hexavalent chromium and nitrite), oxygen, or residual oxidants. The rate and extent of degradation of a target contaminant are dictated by the properties of the chemical itself and its susceptibility to degradation as well as pH, temperature, the concentration of oxidant or reductant, and the concentration of other oxidant- or reductant-consuming substances (e.g., natural organic matter, reduced minerals, free radical scavengers, and residual oxidants) in the water stream. ( )

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Dose, contact time, pH, and temperature affect the effectiveness of chemical oxidants or reductants. Enough contact or residence time is needed to allow complete reactions. Hydrogen peroxide and Fenton's reagent oxidation are most effective under very acidic pH (e.g., pH 2 to 4) and become ineffective under moderate to strongly alkaline conditions. Higher pH facilitates ozone decomposition due to increased hydroxyl radical formation. Turbidity, organic matter, color, and inorganics such as iron and manganese increase ozone demand. As temperatures increase, the solubility of ozone in water decreases. Permanganate reactions are effective over a pH range of 3.5 to 12. Higher pH tends to increase the oxidation capabilities of potassium permanganate. Chlorine is more effective as an oxidant and a disinfectant at lower pH as hypochlorous acid is the dominant chlorine species.

#### **Advanced Oxidation Processes**

AOPs are capable of degrading any organic contaminant that is reactive with the generated hydroxyl radicals. A wide range of organic and explosive contaminants are susceptible to destruction by UV oxidation, including petroleum hydrocarbons, chlorinated hydrocarbons, ordnance compounds such as TNT, RDX, and HMX, and 1,4-dioxane. In many cases, chlorinated hydrocarbons that are resistant to biodegradation may be effectively treated by UV oxidation. Typically, easily oxidized organic compounds, such as those with double bonds (e.g., TCE, tetrachloroethene [PCE], and vinyl chloride [VC]), as well as simple aromatic compounds (e.g., toluene, benzene, xylene, and phenol), are rapidly destroyed in UV/oxidation processes. In addition, polyfluoroalkyl substances (PFAS) treatment using advanced oxidation processes is a topic of on-going research that shows promise.

The water being treated must provide for good transmission of UV light (high turbidity causes interference) and should be relatively free of heavy metal ions (less than 10 mg/L) and insoluble oil or grease to minimize the potential for fouling. When UV is used with ozone to treat VOCs such as trichloroethane (TCA), the contaminants may be volatilized (e.g., "stripped") rather than destroyed, which would require <u>vapor treatment</u>. Pretreatment of the water stream may be required to minimize ongoing cleaning and maintenance of the UV reactor and associated components.

Photocatalysis has been applied in the treatment of water containing general contaminants and emerging contaminants. These applications include disinfection of water, self-sterilizing photocatalytic coatings to treat microbial pathogens, oxidation of organic contaminants using magnetic particles coated with titanium dioxide nanoparticles agitated using a magnetic field, decomposition of crude oil with titanium dioxide nanoparticles placed on floating substances, removal and destruction of organic contaminants in groundwater through adsorbents impregnated with photoactive catalysts, and decolorization and desulfuration of reactive dyes. The stability and robustness of these catalysts vary under different environmental conditions and need to be field tested or supported by more research.

#### Filtration (Particulate)

Filtration processes are applied for the removal of particulate and microbial contaminants. With the addition of GAC to filters, biodegradation of certain organic and inorganic contaminants may occur. Biofilters also can be used to

convert nitrate to nitrogen. Parameters used to characterize the process include filtration or filter loading rate, filter run time, and head loss. Factors impacting process performance include temperature, contact time, filter scraping or backwash operations, and water quality parameters such as pH, alkalinity, and turbidity.

MF and UF are frequently used as an alternative to rapid sand filtration in conventional treatment and softening applications. MF can remove silts and sediments, bacteria, and complex metals. In addition to these, UF can remove smaller contaminants such as viruses. MF and UF membranes typically can tolerate a pH range from 2 to 13. Chemical clean-in-place (CIP) is used periodically to control fouling and reduce the increase in transmembrane pressure that occurs as a result.

#### Membrane (Dissolved)

NF membranes are typically used to treat hardness (calcium and magnesium) and various organic compounds (e.g., disinfection byproducts precursors). RO membranes are typically used to control total dissolved solids (TDS) (e.g., seawater and brackish water desalting), and remove ions (e.g., fluoride and chloride removal). Treatment of PFAS currently is a topic of on-going research. ED and EDR can remove any dissolved ionic contaminant, including hardness, but are typically used for TDS reduction and inorganic ion removal. These systems typically require some type of pretreatment dependent on the feed water quality and membrane type.

Standard RO and NF individual membrane elements have recoveries ranging between 80 and 85%. Recovery for seawater desalination is usually in the range of 50%. ED and EDR recoveries are typically 85 and 95%.

#### Ion Exchange

Ion exchange is used to treat inorganics by removing dissolved ionic contaminants such as metals (e.g., arsenic) or anions (e.g., perchlorate, nitrate, ammonia nitrogen, and silicate), and radionuclides from aqueous solutions. It also has been demonstrated and is routinely used to effectively remove perand polyfluoroalkyl substances (PFAS) from aqueous streams. Ion exchange can also be used to soften water by removing calcium, magnesium, and other hardness cations to minimize scaling/fouling potential in a treatment train.

Factors affecting the design and operation of an ion exchange system include the presence of oil and grease, contaminant concentration, exchange capacity of the resin, suspended solids, metals, oxidant content, inorganic ions in groundwater; and pH of the influent water. Specifically, oil and grease may clog the exchange resin, suspended solids content greater than 10 mg/L may cause resin blinding, pH may affect the ion exchange resin selection, and oxidants may damage the ion exchange resin.

#### **Metal Sequestration**

Sequestration can be used to prevent iron, manganese, copper, and other heavy metals to prevent scale in water treatment equipment and associated conveyance piping or process. Since metals tend to precipitate at high pH levels and most of the sequestering products are polyphosphate compounds, the pH of water being treated must be near or below neutral for treatment to be effective. The dosage of the sequestration agent may be calculated based on influent metals concentration and better be determined through bench- or pilot-scale testing to account for the impact of other factors.

#### **Oil Water Separation**

Gravity-based oil/water separators are used primarily to remove free oil, large oil globules (unstable primary dispersions), and oil and/or non-oil-coated solids in suspension. If gravity separation is used in conjunction with coagulation and flocculation, stable emulsions may be broken and separated. Oil-water separators can handle large flowrates, have low power requirements, and need minimum operator attention; however, a large residence time and therefore large equipment are required. Factors affecting oil removal efficiency are flowrate, oil particle size, density of oil, characteristics of wastewater temperature, and separator design.

#### pH Control

pH control can create ideal conditions for metals to precipitate as metal hydroxides. pH control can be used to break oil-water emulsions by acidifying the water to a pH of 3 or lower, allowing time for emulsions to break, running the water through an oil water separator, and adjusting pH upward to meet discharge regulations. pH adjustment is also used to convert and precipitate (hexavalent) chromium. Adjusting pH to between 10 and 11.5 with the addition of a strong oxidizer such as sodium hypochlorite can convert cyanide to cyanate through alkaline chlorination.

#### Precipitation/Coagulation/Flocculation

Precipitation, combined with coagulation/flocculation, is widely used to remove heavy metals as metal hydroxides or sulfides. Coagulation and flocculation also are used to efficiently separate emulsified oil from recovered groundwater as is frequently encountered during <u>multi-phase extraction</u>.

#### **Beneficial Reuse/Reclamation**

Reuse or reclamation of fully or partially treated water from remediation processes can be applied to promote water conservation as well as treat certain contaminants during the process. Beneficial reuse/reclamation has involved a wide range of contaminated water containing petroleum hydrocarbons, chlorinated solvents, polychlorinated biphenyls (PCBs), perchlorate, chromium, and perfluorinated compounds (PFCs). Reuse or reclamation has been implemented in a number of ways for various purposes: recirculation for in situ remediation, treatment and reclamation via storage or percolation ponds, ground sprinkling for irrigation or dust control, reuse for industrial purposes, reinjection for aquifer replenishment or to prevent seawater intrusion, and even reuse as a potable water source.

### Cost

The most critical cost factors are associated with the contaminant type and concentration to be treated and corresponding mass loading rate on the water treatment system, which will dictate the size, number of treatment processes and equipment, and operation and maintenance costs. Oftentimes, for short-

term applications, equipment can be leased and a flexible design approach can be utilized to facilitate replacement of equipment with less expensive equipment as the concentration of contaminants in the water stream decrease over time. For long-term applications, equipment purchases and permanent systems are usually preferred.

Major cost drivers and relative cost impacts are shown in the table below. The table highlights those cost dependencies specific to water treatment technologies, and does not consider the dependencies that are general to most remediation technologies. Click <u>here</u> for a general discussion on costing which includes definitions and repetitive costs for remediation technologies. A project-specific cost estimate can be obtained using an integrated cost-estimating application such as RACER® or consulting with a subject matter expert.

Cost Impact (L, M, H)	Adsorption/ Absorption	Adsorption by GAC	Advanced Oxidation Processes	Chemical Oxidation/ Reduction	Filtration (Particulate)	Membrane (Dissolved)	lron Exchange	detal Sequestratio	Oil Water Separation	pH Control	Precipitation Coagulation/ Flocculation	hotocatalys
Type/ mixture of contaminants 4	н	н	L	н	Μ	М	н	м	М	н	н	M
Contaminant concentration	Н	н	М	н	М	М	н	М	L	н	н	М
Design water stream flowrate	н	н	Н	н	Н	н	н	н	н	н	н	Н
Size of Equipment	н	н	н	Н	н	н	н	Н	Н	н	н	Н
Residence Time	L	L	М	Н	М	М	L	Н	Н	н	Н	М
Utility and chemical costs	L	L	н	н	М	М	L	н	М	L	Н	Н
Waste disposal/ regeneration	н	Н	N/A	N/A	М	М	Н	L	М	L	М	N/A

L — the cost element has a relatively low impact compared to other cost

elements and technologies.

M — the cost element has an average impact compared to other costs elements and technologies.

H — the cost element has a high impact compared to other cost elements and technologies.

NA — not applicable.

## Duration

A water treatment system must operate for the duration of the remedial action that generates the aqueous stream that requires treatment or until COCs within the stream decrease to levels that comply with regulatory requirements or are such that a less aggressive alternative treatment technology can be applied, which can vary greatly, ranging from weeks to years.

Duration of water treatment from process influent to effluent is much shorter. Water treatment systems are designed to provide sufficient residence time to achieve effluent concentration objectives and/or discharge requirements for a given design flowrate and influent COC concentration(s). Several types of treatment operations may be used in series and/or in parallel to achieve the desired effluent concentration. Hence, the total treatment time is the time it takes the water to pass flow through the various treatment operations and be discharged through the effluent, which tends to range from minutes to hours.

### **Implementability Considerations**

The following are general considerations associated with applying water treatment technologies:

- The type and phase(s) of COCs directly affect the selection of water treatment
  processes. Water streams containing NAPL typically require an oil water
  separator as the first treatment step. Dissolved organic contaminants can be
  treated by GAC adsorption, chemical oxidation, or membrane separation.
  Suspended or dissolved metals may require precipitation (through coagulation
  or valent change via oxidation/reduction) or ion exchange to remove from the
  water stream, or metal sequestration to keep in water stream followed by
  filtration. Some recalcitrant organics can be treated with photocatalysis or
  AOPs.
- The COC mass loading rate directly impacts the selection and design of the water treatment system. As such, an accurate estimate of the COC mass loading rate is critical, which typically requires performing a bench and/or pilot study or use of actual data from a similar site application.
- The required size of the treatment equipment is directly related to the expected water flowrate. Higher flowrates in general require a greater treatment area/volume to achieve necessary residence time to ensure desired removal of COCs. COC influent concentrations typically decrease over the duration of the remediation life cycle. If properly accounted for in the upfront planning process, water treatment systems can be transitioned to lower cost options as the COC influent concentrations decrease over time (e.g., transition from initial oil water separation to chemical oxidation to GAC).
- Several types of water treatment systems can be installed in series to remove a wide range of COCs.
- Water treatment units may be installed in series and in parallel to improve treatment efficiency and accommodate high water flow.
- Units may be designed and installed as permanent fixed units for long-term treatment applications or may be installed on a trailer and/or skids for short-term use at multiple sites.

- The water treatment system must be designed to be compatible with the chemical and physical characteristics of the water stream. Water streams containing high levels of ferrous iron may cause equipment fouling and thus the treatment system should be designed to alleviate or remove the impact of fouling. Specialized materials may be required if treating high or low pH process water.
- Beneficial reuse and reclamation may be considered for sites in states having water reuse regulations. Water reuse regulation is generally under the jurisdiction of the states. The regulations developed by states vary, and some states have yet to develop water reuse guidelines or regulations. According to the USEPA (2012), 30 states and one territory have adopted water reuse regulations and 15 states have guidelines or design standards that govern reuse.

### Resources

#### EPA. Drinking Water Treatability Database

This EPA website provides information on various types of treatment processes for a wide range of contaminants.

#### EPA. Guidelines for Water Reuse. EPA/600/R-12/618 (2012) (PDF)

#### (643 pp, 17.4 MB)

This document describes the purpose, planning and management considerations, types of reuse applications, state regulatory programs, regional variations, treatment technologies, and venues of funding.

#### EPA. <u>Oil/Water Separation: State of the Art (1978) (PDF)</u> (106 pp, 5.64 MB)

This document provides a thorough review of the oil/water separation devices and processes. It describes the basic concepts, specific design features, operational conditions, and limitations of each category of the oil/water separation technologies.

#### Sustainable Remediation Forum (SURF). Groundwater Conservation and Reuse at Remediation Sites (January 2013) (PDF). (56 pp, 1.71 MB)

This document is aimed to encourage efforts at water conservation and reuse by providing information and examples to all interested parties involved in cleanups. It reviews the state of the practice, challenges, and several successful applications, and describes the related valuation and quantification approaches.

### Nadagouda, Pillai, McGuinness, Byrne, Falaras, Kontos, Gracia-Pinilla, Mangalaraja, O'Shea, and Dionysiou. Photocatalysis as An Effective Advanced Oxidation Process. Chapter 8, Advanced Oxidation Processes for Water Treatment: Fundamentals and Applications (2017)

This book chapter provides a review of the semiconductor catalyst-based photocatalysis technology and describes the mechanisms, materials, applications, and research needs. The book covers a number of other advanced oxidation technologies including UV/hydrogen peroxide, UV/ozone, photo-Fenton, gamma-ray and electron, ultrasound wave, and sulfate radical ion.

#### USACE. Adsorption Design Guide (2001) (PDF) (99 pp, 683 KB)

This design guide provides practical guidance for the design of liquid and vapor phase devices for the adsorption of organic chemicals.

### Wu and Chang. Decolorization of Reactive Red 2 by advanced oxidation processes: Comparative studies of homogeneous and heterogeneous systems. Journal of Hazardous Materials (2006)

This paper presents the study of dye degradation under several homogeneous and heterogeneous photocatalysis systems, impacts of different factors, and the rate constants for the various systems.

- 1. Often, it is necessary to add acid to the reactor to achieve the necessary pH since in most cases groundwater pH ranges from 6 to 8.  $\stackrel{\frown}{=}$
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- 3.  $\bigcirc$  Including the vapors produced by fuels.
- 4. Including the vapors produced by fuels.  $\underline{\leftarrow}$
- 5. For LNAPL and DNAPL containing the organic contaminant classes.
- 6. For LNAPL and DNAPL containing the organic contaminant classes.
- 7. Assumes contaminants present in water stream are treatable by each respective technology.
- 8. Assumes contaminants present in water stream are treatable by each respective technology.

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**Technology Screening Matrix** 

**Water Treatment Technologies** 

Return to top

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