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S. Sharma¹ · A. Bhattacharya¹ 

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Abstract Water is of fundamental importance for life on earth. The synthesis and structure of cell constituents and transport of nutrients into the cells as well as body metabolism depend on water. The contaminations present in water disturb the spontaneity of the mechanism and result in long/short-term diseases. The probable contaminations and their possible routes are discussed in the present review. Continued research efforts result in some processes/technologies to remove the contaminations from water. The review includes concepts and potentialities of the technologies in a comprehensible form. It also includes some meaningful hybrid technologies and promising awaited technologies in coming years.

Keywords Water · Contaminants · Purification · Hybrid technology

Introduction

Availability of fresh water, the nature's gift controls the major part of the world economy. The adequate supplies of water are necessary for agriculture, human consumption, industry as well as recreation. Ironically, sometimes, natural or added contaminations rob us of the gift and making us confront a lot more challenging world. It is a well-known fact that fresh water is an important necessity for our health. With the advancement of technology and

industrial growth, fresh water resources all over the world are threatened. One-sixth of the world population suffers from the freshwater unavailability situation (Elimelech 2006). It is seen that developed countries suffer most from chemical discharge problems, whereas developing countries from agricultural sources. Contaminated water causes problems to health and leads to waterborne diseases which can be prevented by taking measures even at the household level. Providing safe water for all is a challenging task. Continued research efforts in this area for more than few decades result in many processes/technologies (Shannon et al. 2008).

Water contamination is a common problem to all over the world. These may be geological or anthropogenic (man-made) (Fawell and Nieuwenhuijsen 2003). Higher levels of contaminants in drinking water are seldom to cause acute health effects. Of course it depends on individual susceptibility and mode of contact with the body.

The types and concentrations of natural contaminates depend on the nature of the geological materials through which the groundwater flows and quality of the recharge water. Groundwater moving through sedimentary rocks and soils may pick up a wide range of compounds, such as magnesium, calcium, and chloride, arsenate, fluoride, nitrate, and iron; thus, the effect of these natural contaminations depends on their types and concentrations. The natural occurring elements present at unacceptable levels can contaminate water as well (Liu et al. 2005; Charles et al. 2005; Rukah and Alsokhny 2004; Mulligan et al. 2001; Ghrefat et al. 2014; Meenakshi and Maheshwari 2006).

Other contaminants are man-made by-products of industry, and agriculture, including heavy metals like mercury, copper, chromium, lead, and hazardous chemicals, dyes and compounds like insecticides and fertilizers.

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Improper storing or disposing of household chemicals such as paints, synthetic detergents, solvents, oils, medicines, disinfectants, pool chemicals, pesticides, batteries, gasoline and diesel fuel can lead to ground water contamination (Kass et al. 2005; Anwar 2003) According to UN report 2003 (UN WWAP 2003) every day 2 million tons of sewage, industrial and agricultural waste are discharged into the world's water.

The microbial contaminants include pathogens like bacteria, viruses, and parasites such as microscopic protozoa and worms. These living organisms can be spread by human and animal wastes knowingly or unknowingly.

Some contaminants can be easily identified by assessing color, odor, turbidity and the taste of the water. However, most cannot be easily detected and require testing to reveal whether water is contaminated or not. Thus, the contaminants may result in unappealing taste or odor and staining as well as health effects.

Color of the drinking water is a physical characteristic that cannot be noticed unless it is one of high concentration. For example, if ground water containing a high iron concentration, it gives a reddish appearance; similarly, high tannin concentration makes the water look brown. Generally, it is measured by comparing a water sample to a color standard. One color unit has no effect on the water and usually not detectable while 100 color units could be compared to the color of light tea (Ligor and Buszewski 2006). Odor is also an indicator for the presence of some contamination though odor-free water is not necessarily safe for drinking purpose. Also, some contaminant odors are noticeable even when present in extremely small amounts.

On the other hand, the presence of clays, silts or sand, or organic, algae, and leaf particles results in turbidity. The turbidity may shield bacteria, preventing disinfection chemicals from attacking and destroying the cells. The presence of organic materials in conjunction with chlorine can form trihalomethanes and other potentially harmful chemicals. Generally, surface water sources have higher turbidity compared to groundwater sources. The turbidity of a surface water source can vary greatly from 1 to 200 NTU (NTU: nephelometric turbidity unit). The immunity in turbidity level is different from children to adult people.

Types of contaminants

Basically, the contaminants are four types associated with water pollution-

- Inorganic contaminants,
- Organic contaminants,

- Biological contaminants,
- Radiological contaminants.

Inorganic contaminants

The presence of contaminants can also be measured by its chemical parameters. Hardness of the drinking water is a naturally occurring contaminate, which basically depends on the geographical status. It is caused by significant amounts of calcium or magnesium components; the hardness is classified into carbonate or non-carbonate hardness depending on what molecules are combined with calcium or magnesium. If they are combined with carbonate ions (CO_3^{2-}), the hardness is termed as 'carbonate hardness'; if combined with other ions, it is non-carbonate hardness. Generally, 300–400 mg/L hardness is suitable for drinking purpose. Prolonged exposure to water containing salts (TDS >500 mg/L) can cause kidney stone, etc.

Apart from carbonate/noncarbonated hardness, there are several inorganic substances (viz. fluoride, arsenic, lead, copper, chromium, mercury, antimony, cyanide) that contaminate water resource. They can get into drinking water from natural sources, industrial processes, as well as from plumbing systems (EPA US 2006; Nriagu 1988).

Sources of fluoride may be geological or anthropogenic. Weathering of fluoride-bearing minerals (fluorite, fluor spar, cryolite, fluorapatite, ralstonite and others) on the earth's crust can lead to higher fluoride levels in groundwater. The over exploitation of ground water also aggravates the problem of fluoride concentration in the water even more. Further, the anthropogenic sources of fluorides are certain pharmaceutical products (for treating hyperthyroidism), medicines, tooth pastes, insecticides, disinfectants, preservatives, super phosphate fertilizer, vitamin supplements and others. Their effects are especially harmful to develop children and the elderly people. Fluoride is known to cause dental and skeletal fluorosis. It is also associated with Alzheimer's disease and other forms of dementia (Susheela 1999; Fawell et al. 2006; WHO 2008). Fluoride enters the brain and enables aluminum to cross the blood–brain barrier, resulting in increased risk for these diseases (Ram Gopal and Ghosh 1985). Excessive fluoride (4.0 mg/L by EPA) concentrations have been reported in ground waters of more than 20 developed and developing countries including India where 19 states are facing acute fluorosis problems (Eswar and Devaraj 2011). Arsenic (MCL 0.01 mg/L) (EPA US 2006) enters in drinking water supplies from natural deposits in the earth or from agricultural and industrial practices (Smith et al. 2000). Arsenic contamination is by far the biggest mass poisoning case in the world, especially in India and

Bangladesh (Chatterjee et al. 1995; Khan et al. 2003). Arsenic contamination of drinking water causes a disease called arsenicosis (Chen et al. 1988). Non-cancer effects can include thickening and discoloration of the skin, stomach pain, nausea, vomiting, diarrhea, numbness in hands and feet, partial paralysis, and blindness. Arsenic has been linked to cancer of the skin, bladder, lungs, kidney, nasal passages, liver, and prostate (Yoshida et al. 2004). The toxicity and excretion of arsenic compounds and their metabolites highly depend on the oxidation states [viz. Arsenite (As III) and Arsenate (As V)] and degree of methylation of arsenicals. It is seen that As(III) is ten times more toxic than As(V) (Pontius et al. 1994).

Mercury (MCL 0.002 mg/L) (EPA US 2006) gets into drinking water from agricultural runoff as well as seepage from landfills and some factories. The presence of mercury in water causes impairment of brain functions, neurological disorders, and retardation of growth in children, abortion and disruption of the endocrine system (Clarkson 1992; Counter and Buchanan 2004). *Copper* (MCL 1.3 mg/L) (EPA US 2006) can enter into the water through natural deposits in rock and soil, but more often as a result of corrosion in household plumbing. In short term, exposure leads to mild gastrointestinal distress, but long-term exposure can lead to permanent liver or kidney damage (Semple et al. 1960; Manuel et al. 1998). *Chromium* (MCL 0.1 mg/L) (EPA US 2006) occurs naturally in the ground and is often used in electroplating of metals and leather industries. Generally, it gets into water from runoff from old mining operations and improper waste disposal from these industries. A high level of exposure of chromium causes liver and kidney damage, dermatitis and respiratory problems (Zhang et al. 1997; Ray (Arora) and Ray 2009). *Lead* (MCL 0.015 mg/L) (EPA US 2006) is an increasing problem in cities with older water systems. Water slowly corrodes the lead in municipal water systems which can cause a wide range of developmental difficulties for children and high blood pressure and kidney ailments in older and adults (Needleman et al. 1990). *Antimony* (MCL 0.006 mg/L) (EPA US 2006) occurs naturally in the ground and originates from flame retardant industry. It is also used in ceramics, glass, batteries, fireworks and explosives. It may get into drinking water through natural weathering of rock as well as through industrial and municipal waste disposal or from manufacturing processes. It affects cholesterol, glucose in blood levels (Cooper and Harrison 2009a, b; Public Health Service, US 1992). *Nitrate* (MCL 10 mg/L as Nitrogen) (EPA US 2006) contamination comes through fertilizers. It is found in sewage and wastes from human and/or farm animals and generally gets into drinking water from these activities. Excessive levels of nitrate in drinking water have caused serious illness because of nitrate conversion to nitrite in the body and interferes oxygen transport in the blood. The symptoms include

shortness of breath and blueness of the skin (Gupta et al. 2000). *Asbestos* (MCL 7 million fibers/lit) (EPA US 2006) is a mineral that forms minute fibers in the environment. Asbestos fibers in water have been linked to an increase in the risk of certain cancers and regulated by EPA because of asbestos exposure from water (EPA US 2009a, b; Bull 2007). *Selenium* (MCL 0.05 mg/L) (EPA US 2006) contamination comes through mainly food and soils. It is used in electronics, photocopy operations, manufacture of glass, chemicals, drugs, and as a fungicide and feed additive. Exposure to high levels of selenium over a long period of time has resulted in a number of adverse health effects, including a loss of feeling and control in the arms and legs (Olson 1986; Fan and Kizer 1990). *Barium* (MCL 2 mg/L) (EPA US 2006) occurs naturally in some aquifers that serve as sources of ground water. It generally gets into drinking water after dissolving from naturally occurring minerals in the ground. It may damage heart and cardiovascular system, and is associated with high blood pressure in laboratory animals such as rats exposed to high levels during their lifetimes (Brenniman et al. 1979; Wones et al. 1990). Drinking water that meets the EPA standard is associated with little to none of this risk and is considered safe with respect to Barium. *Beryllium* (MCL 0.004 mg/L) (EPA US 2006) generally gets into water from runoff from mining operations, discharge from processing plants and improper waste disposal. Beryllium compounds have been associated with damage to the bones and lungs and also may increase the risk of cancer in humans who are exposed over long periods of time (Cooper and Harrison 2009a, b). *Cyanide* (MCL 0.2 mg/L) (EPA US 2006) usually gets into water as a result of improper waste disposal. It has been shown to damage the spleen, brain and liver of humans fatally poisoned with cyanide (Ronald 1991).

Organic contaminants

The major anthropogenic sources of organic contamination are pesticides, domestic waste, and industrial wastes, etc. Contamination through organic materials can cause serious health problems like cancers, hormonal disruptions, and nervous system disorder (Ram et al. 1990; Harvey et al. 1984). Trihalomethanes (THMs) are formed when chlorine in the treated drinking water combines with naturally occurring organic matter.

- Pesticides contaminate through agricultural as well as public hygienic sources (Damalas and Eleftherohorinos 2011; Younes and Galal-Gorchev 2000). The adverse environmental effects of pesticides used in agriculture and public health are due to an improper handling and application procedure (WHO 2010). Pesticides are designed to interact with various chemical processes

Table 1 Some of the pesticides with their maximum contamination level (MCL) (Adapted from EPA, US Protection agency)

Pesticides	Nature	Maximum contamination level (MCL), $\mu\text{g/L}$
Carbofuran	Nematicide	40
Dalapon	Herbicide	200
Dibromochloropropane	Nematocide	0.2
Dinoseb	Insecticide/miticide	7
Dioxin	Herbicide	0.0003
Diquat	Herbicide	20
Endothall	Algicide	100
Ethylene dibromide	Insecticide	0.05
Glyphosate	herbicide	700
Methoxychlor	Insecticide	40
Oxamyl	Insecticide	200
Pentachlorophenol	Fungicide	1
Picloram	Herbicide	500
Simazine	Herbicide	4
Toxaphene	Insecticide	3

in the pest's living body chemistry. Unfortunately, doing this, all pesticides may interact with the metabolism of non-targeted living organism. Mostly, pesticides damage the liver and nervous system. Tumor formation in the liver has also been reported (Bolognesi 2003). Environmental agencies have fixed their MCL's (EPA US 2009a, b). Some of the pesticides with their MCLs are in the ensemble (Table 1).

- Volatile organic chemicals (VOCs) include solvents and organic chemicals like toluene benzene, styrene, trichloroethylene (TCE) and vinyl chloride, etc., degreasers, adhesives, gasoline additives, and fuel additives (Wehrmann et al. 1996). These VOCs cause chronic health effects like cancer, central nervous system disorders, liver and kidney damage, reproductive disorders, and birth defects (Brown et al. 1984).
- Dyes constitute one of the largest groups of organic compounds that represent an increasing environmental concern. The release of this contaminated water into the environment is a considerable source of non-esthetic pollution and eutrophication, which can originate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase (Pagga and Bruan 1986; Prevot et al. 2001).
- Apart from the above, compounds present in the water have the potential to cause known or suspected adverse ecological or human health effects. These compounds are termed 'Emerging Organic Contaminants' (Pal et al. 2010, 2014; Stuart et al. 2012; Lapworth et al.

2012). It includes pharmaceuticals (viz. ciprofloxacin, erythromycin, tetracycline, codeine, salbutamol, carbamazepine, paracetamol, ibuprofen, salicylic acid, Tamiflu, chemotherapy drugs such as 5-fluorouracil, ifosfamide) industrial compounds (viz. chlorinated solvents, petroleum hydrocarbons, including the polycyclic aromatic hydrocarbons, the fuel oxygenate methyl tertiary butyl ether, plasticizers/resins bisphenols, adipates and phthalates), personal care products (viz. *N,N* diethyl meta toluamide, alkyl esters of *p*-hydroxy benzoic acid, triclosan), fragrances (viz. tonalide, galaxolide), water treatment by products (viz. trihalomethanes, haloacetic acids, *N*-nitroso dimethyl amine), plasticizers, flame retardants as well as surfactants. Mostly, they are endocrine disruptors, carcinogenic.

- These are commonly derived from a variety of municipal, agriculture and industrial sources and pathways. The pharmaceuticals (viz. antibiotics, analgesic and anti-inflammatory) come from hospital effluents and/or chemical manufactures. There are reports of lowest predicted no-effect concentration (PNEC) values of emerging organic contaminants. Some of them are listed in Table 2 (Pal et al. 2010, 2014).

Biological contaminants

Biological contamination of water is caused by the presence of living organisms, such as algae, bacteria, protozoan or viruses. Each of these can cause distinctive problems in water (Daschner et al. 1996; Ashbolt 2004). Algae are in general single celled and microscopic. These are quite abundant and depend on nutrients (viz. Phosphorus) in water. The nutrients are generally from domestic run-off or industrial pollution. The excess algae growth is not only imparted taste and odor problems in water; it clogs filters, and produces unwanted slime growths on the carriers. Sometimes, they [viz. blue-green algae (*Anabaena*, *Aphanizomenon* and *Microcystis*)] are capable of liberating toxins and they damage the liver (hepatotoxins), nervous system (neurotoxins) and skin (Hitzfeld et al. 2000; Rao et al. 2002).

Bacteria are also microscopic single celled. There are numerous pathogenic bacteria and can be contaminated with water (Inamori and Fujimoto 2009). They can result in typhoid, dysentery, cholera and gastroenteritis. Some non-pathogenic bacteria (viz. sulfur, crenothrix iron bacteria), although not harmful, may cause taste and odor problems (Nwachuku and Gerba 2004; Rusin et al. 1997). Similarly, Protozoans are also single-celled and microscopic organisms. Some protozoans (like *Giardia* and *Cryptosporidium*) are commonly found in rivers, lakes, and streams

Table 2 Lowest predicted no effect concentration (PNEC) values for some of the emerging organic contaminants (Pal et al. 2010, 2014)

Compounds	Lowest PNEC (ng/l)	Compounds	Lowest PNEC (ng/l)
<i>Antibiotics</i>			
Trimethoprim	1000	Bisphenol A (making plastics)	60–150
Ciprofloxacin	20		
Sulfamethoxazole	20,000		
<i>Analgesic and anti-inflammatory</i>			
Naproxen	37,000	PPOS (protective coatings, surfactants)	1100
Ibuprofen	5000		
Ketoprofen	15.6×10^6		
Diclofenac	10,000		
<i>Beta blockers</i>			
Propranolol	500	Fipronil (termiticide)	250
Atenolol	10×10^6		
<i>Blood lipid regulators</i>			
Clofibrilic acid	12000	NP1EO (surfactant)	330
Gemfibrozil	100,000		
Benzafibrate	100,000		
<i>Hormones</i>			
Estriol	0.8	4MBC (sun screen)	560
Estrone	18		
Sucralose (sugar substitute)	93×10^4	DEET (mosquito repellent)	$5-24 \times 10^6$

contaminated with animal feces or which receive wastewater from sewage treatment plants. These may cause diarrhea, stomach cramps, nausea, fatigue, dehydration and headaches. Viruses are the smallest living organisms capable of producing infection and causing diseases. Hepatitis and polio viruses are commonly reported in the contaminated water.

Radiological contaminants

Radiological contaminants are caused by radioactive elements. Sources of radioactive material could be soils or rocks the water moves through or some industrial waste. Erosion of natural deposits of certain minerals (radioactive) may emit radiations (like α , β). Radiological elements (viz. U^{226} , Ra^{226} , Ra^{228} and Rn^{228}) tend to be a greater problem in groundwater than in surface water. All types of radiological contamination increase the risk of cancer (Alireza et al. 2010; Haki et al. 1995). Some of the radioactive contaminants with their MCLs are listed in Table 3.

Solving approaches

The famous saying of Minora Shirota's statement is "Prevent disease rather than treat disease: a healthy intestine leads to a long life, and deliver health benefits to as many people as possible at an affordable price" (Heasman and

Table 3 Radioactive contaminants and their MCLs (adapted by EPA, US)

Contaminants	MCL
Alpha particles	15 (pCi/L)
Beta particles and photon emitters	4 mrems/year
Radium 226 and Radium 228 (combined)	5 pCi/L
Uranium	30 ug/L

Mellentin 2001). This philosophy, elaborated almost half a century ago, is becoming more valid now than ever before. The need of science-based solutions for uncontaminated water provisioning results in several water treatment methods to counter the problem. Of course, the suitable technology is based on raw water characteristics (i.e., the nature and extent of contamination), infrastructure (i.e., power, manpower, availability of chemicals), affordability/cost as well as acceptability. Some of the common water purification methods are sedimentation or settling, boiling/distillation, chemical treatment (precipitation/coagulation/adsorbents), disinfection and filtration. The processes and techniques in mitigating the contaminations are as follows.

Precipitation and coagulation

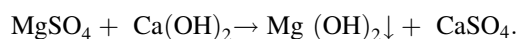
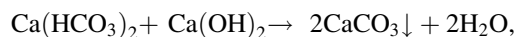
Precipitation is a technique of removing one or more substances from a solution by adding reagents so that insoluble

solids appear. The ‘solubility’ rules the technique, i.e., when the product of ion concentrations (in simple) in the solution over the solubility product of the respective solid, the precipitation occurs. It is one of the simple methods to purify water. The chemicals are added to form particles which settle and remove contaminants from water. The treated water is reused whereas the settled portion is dewatered and disposed of. The technique is used in softening of water as well as to remove impurities like phosphorus, fluoride, arsenic, ferrocyanide and heavy metals, etc. (EPA US 2000; Matlock et al. 2002; Eikebrokk et al. 2006).

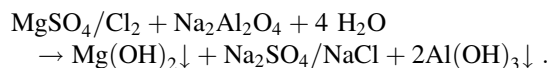
Softening of water

The presence of Ca/Mg in terms of carbonate, bicarbonate, chloride and sulfate results in hardness of water. Addition of proper chemical forms precipitation and makes it soft.

Addition of Ca(OH)₂ forms precipitation with bicarbonate and sulfate in water.

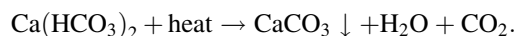


Addition of Na-aluminate forms precipitation of hydroxide with sulfate and chloride in water. Actually, Na-aluminate forms sodium hydroxide with water, and with sulfate/chloride it forms hydroxide.



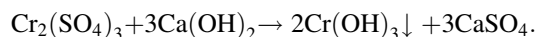
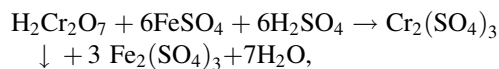
Formation of aluminum hydroxide aids in floc formation, sludge blanket conditioning and silica reduction.

Softening of water is also feasible by simple boiling



Removal of heavy metals

Heavy metals (e.g., Ba, Cd, Pb, Hg, Ni, Cu) typically precipitated from waste water as sulfates, sulfides, hydroxides, and carbonates (Matlock et al. 2002). Metal co-precipitation during flocculation with iron and aluminum salts is also possible for some metals (e.g., As, Cd, Hg, Cr). The following reaction represents as chromium co-precipitation in terms of hydroxides or sulfates



Removal of arsenic

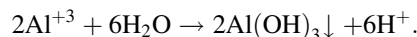
Arsenic removal with coagulants, viz. Alum [Al₂(SO₄)₃·18H₂O] ferric chloride (FeCl₃) and ferric sulfate

[Fe₂(SO₄)₃·7H₂O] is effective (Harper and Kingham 1992; Fields et al. 2000). In these cases, arsenic (V) can be more effectively removed than arsenic (III). The microparticles and negatively charged arsenic ions are attached to the flocs by electrostatic attachment during the process. The possible steps of coagulation and co-precipitation are as follows:

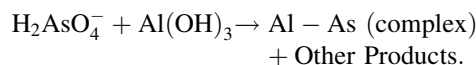
Alum dissolution:



Aluminum precipitation (acidic):



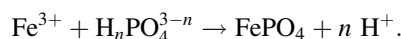
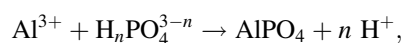
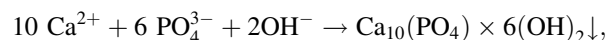
Co-precipitation (non-stoichiometric, non-defined product):



Similar reactions take place in case of ferric chloride and sulfate with the formation of Fe-As complex as an end product which is removed by the process of sedimentation and filtration (Mok and Wai 1994; Hering et al. 1997). The efficient removal depends on pH range.

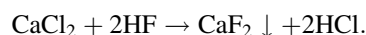
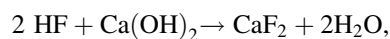
Removal of phosphorus

The removal of phosphates is generally done by coagulant, i.e., by mixing coagulant into waste water (Xie et al. 2005). The most commonly used multivalent metal ions are Ca, Al, and Fe.

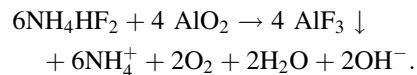


Removal of fluoride

Precipitation of fluoride species into chemically stable form is the most effective option for the removal of fluoride (in terms of Ca, Mg, Al) from effluent streams (Dahi 1997; Lawrence et al. 2005). Among all metal fluorides, CaF₂ is less soluble in water. Consequently, removal of fluoride from the effluents by converting it into CaF₂ has become the most widely used method of treatment. CaCl₂, limes, may be used for this purpose, but CaCl₂ is preferred with respect to lime due to its higher solubility and the lower ratio of additive to effluent.



The reaction of hydrofluoric acid and ammonium fluoride with the aluminum treatment agent is as follows:



Inorganic flocculants have the potential in different separations (Gray et al. 1995; Jiang and Graham 1998), but they are used in very large quantities. These leaves large amounts of sludge and strongly affected by pH changes, whereas polymeric flocculants cause the formation of large cohesive aggregates (flocs) and inert to pH changes. Both natural and synthetic polymers are useful for this purpose. Generally, synthetic polymers (viz. polyacrylamide, polyethylene oxide, poly (diallyl dimethyl ammonium chloride), poly (styrene sulfonic acid) are highly effective flocculants at small dosages and have high tailor ability but poor shear stability, whereas though natural polymers (viz. starch, guar gum, alginate, glycogen, dextran) are biodegradable and effectively shear stable (Brostow et al. 2009).

Removal of dyes

Dyes are non-biodegradable, and precipitation with CaCO_3 can be one of the approaches to remove them from the water (Hoffmann et al. 1995; Reife and Freeman 1996).

As a whole, the precipitation technique has the features Benefits:

- Simple process,
- Effective for the removal of As, Cd, Ba, Cd, Cr, Pb, Hg, Se, Ag, etc.,
- It is also applicable to remove natural organic matter (NOM) or dissolved organic carbon (DOC).

Limitations:

- Requires continuous supply of huge chemicals,
- Handling of by-products,
- Disposal of coagulation/precipitation sludge is a concern.

Distillation

It is the most common separation technique (<http://www.msue.msu.edu>; Veil. 2008). In this separation technique, the mixed components in water are separated by the application of heat. It is based on the differences in boiling points of the individual components. The boiling point characteristics depend on the concentrations of the components present. Thus, the distillation process depends on the vapor pressure characteristics of liquid mixtures. The basic principle described as the input of heat energy raises

vapor pressure. When the vapor pressure reaches its surrounding pressure, the liquid mixture boils and distillation occurs because of the differences of volatility in the mixture.

This process results in a separation between water and inorganic substances, such as lead, calcium, magnesium, etc. are also destroying bacteria. However, organics with boiling points lower than 100 °C cannot be removed efficiently and can actually become concentrated in the product water. Distilled water purification technology was originally developed for industrial purpose. However, it came eventually for home use. Since, this process is not very effective in removing organic chemicals so the carbon filter system must be added to make the water really safe to drink. The carbon filters require regular changing because they can quickly become breeding grounds for bacterial growth.

Although distilled water is safe, it is not healthy as this contains no nutrient minerals, which are essential for the drinking purpose. This type of water purification technology is also very slow. Adding to that, the cost of a carbon filter and the result is an unwieldy system of water purification.

Benefits:

- Removes a broad range of contaminants (toxic chemicals, heavy metals, bacteria, viruses, parasites),
- Continuous,
- Does not rely on physical barriers (filters),
- Does not require additional disinfecting process.

Limitations:

- It consumes an enormous amount of energy both in terms of cooling and heating requirements,
- Some contaminants can be carried into the condensate,
- Requires careful maintenance to ensure purity,
- The process is not very effective which are of lower volatility (viz. organics) compared to water.

Adsorption

In this physical process, dissolved contaminants adhere to the porous surface of the solid particles (Jiuhui 2008). It is the surface phenomena and the outcome of surface energy. With the material, all the bonding requirements of the constituent atoms of the material are filled with other atoms. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and physical attractive force results. It can be physisorption (originates from vanderwaals forces) and chemisorption (originates from co-valent forces).

The adsorbent systems are added directly to the water supply or via mixing basin. Adsorbents combine chemical

and physical processes to remove the compounds that impart color, taste, and odor to water. In principle, all microporous materials can be used as adsorbents. However, those with well controlled and highly microporous are the most preferred (Yang 1997). The porous solids, e.g., activated carbon, silica gels, aluminas, zeolites, etc. contain many cavities or pores with diameters as small as a fraction of a nanometer is useful (Ali and Gupta 2007; Qu 2008).

The isotherms are the quantitative interrelation between the adsorbate and adsorbent. The three most well-known isotherms are Freundlich, Langmuir and Linear. The most commonly used for the water contaminants is Freundlich and it is expressed as:

$$\frac{x}{m} = KC_e^{1/n}.$$

where x is the mass of solute adsorbed, M is the mass of adsorbent, C_e is the equilibrium concentration of solute, and K and n are experimental constants.

Activated carbon

The most commonly used adsorbent is activated carbon—a substance which is quite similar to common charcoal. Actually, the active carbon is much more efficient because of its high porous character. The high porous character is generated by treating carbon to steam and high temperature (1300 °C) with or without oxygen in the presence of inorganic salts (physical method). The carbon may be of petroleum coke, bituminous coal, lignite, wood products, and coconut/peanut shells. At high temperature, parts of carbon are oxidized in CO₂ and steam. The gases are evacuated and micro fractures and pores are generated in the carbon structure. It dramatically increases the carbon surface area, making a useful material for the removal of contaminants (Baudu et al. 1991; Yang and Benton 2003). In some cases, the carbonaceous matter may be treated with a chemical activating agent such as phosphoric acid, zinc chloride and the mixture carbonized at an elevated temperature, followed by the removal of activating agent by water washing (chemical method).

Active carbon uses the physical adsorption process, whereby Vanderwaals attractive forces pull the solute contamination out of the solution and onto its surface. The efficiency of the adsorption depends on the nature of the carbon particle and pore size, surface area, density and hardness as well as the nature of the contaminants (concentration, hydrophobicity, polarity and solubility of the contaminant and contaminant attraction to the carbon surface).

There are two different forms of activated carbon in common use, granular activated carbon (GAC) and powdered activated carbon (PAC). Physically, the two differ as their names suggested by particle size and diameter. The reusability of the carbon is done primarily with the GAC as PAC particles are too small to be reactivated.

Benefits:

- Activated charcoal is effective for trapping carbon-based impurities (volatile organic chemicals), chlorine (including cancer-causing by-product trihalomethanes) as well as colors and odors,
- Very cost effective,
- Long life (high capacity).

Limitations:

- In GAC scheduled filter replacements, it is important to eliminate the possibility of ‘channeling’ which reduces the contact between the contaminant and the carbon. Therefore, it reduces efficiency, and the accumulation of bacteria in the filter,
- Frequent filter changes often required,
- Can generate carbon fines.

Activated alumina

Activated alumina consists mainly of aluminum oxide (Al₂O₃) spherical beads, highly porous and exhibits tremendous surface area. The surface area of activated alumina is in the range 345–415 m²/g. It does not shrink, swell, soften or disintegrate when immersed in water. It can exist in three forms, viz. activated alumina sorbent, activated alumina desiccant and activated alumina catalyst carrier. The granulated alumina has the internal active surface of the alumina.

In this process, contaminated water is passed through a cartridge or canister of activated alumina. The contaminant adsorbs on the alumina (Chen et al. 1987). As the physical adsorption has a particular limit, the cartridge of activated alumina must be replaced periodically.

Benefits:

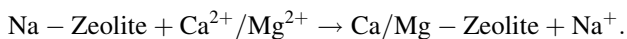
- Tailoring of activated alumina is possible by varying the activation process and dopant variation,
- Effective in removing As⁵⁺, PO₄³⁻, Cl⁻, and F⁻ from water,
- Removal of Se, Sb, Pb and Bi from the water is also possible.

Limitations:

- The method is not very much capable of reducing levels of other contaminants of health concern. It needs another support.

Zeolite

Zeolites are aluminosilicates with an Si/Al ratio between 1 and infinity. It has a tetrahedral network of silicon and oxygen atoms, and some of the silicon atoms are replaced by aluminum to form alumino-silicates. The adsorptive property of zeolite is considered due to the crystalline nature of the materials. The channels in it are of extended honeycomb and cavities. Zeolites have the surface area 1–20 m²/g. Synthetic Zeolites are manufactured by hydrothermal processes in a temperature range of 90–100 °C, an autoclave followed by ion exchange with certain cations (Na⁺, Li⁺, Ca²⁺, K⁺, NH₄⁺) (Rahman et al. 2012). The high cation exchange and molecular sieve properties, such as zeolites, have been widely used as adsorbents. The water softening process is by exchanging Na⁺ with the Ca²⁺/Mg²⁺ in water, as follows:



Natural zeolites in the waste-water treatment are very useful (Margeta et al. 2013; Kalló 2001). Many natural zeolites (e.g., Clinoptilolite, mordenite, phillipsite, chabazite) show selective separation towards NH₄⁺ and also for transition metals (e.g., Cu²⁺, Ag⁺, Zn²⁺, Cd²⁺, and Hg²⁺) (Jafarpour et al. 2010; Karapınar 2009).

Benefits:

- Recharging of zeolite is feasible by exchanging the cations with the initial one and thus reuse is also feasible,
- Removes NH₄⁺ and heavy metal removal of inorganic anions (nitrates, phosphates, arsenates, chromates and fluorides) as well as radionuclides (e.g., 137Cs, 90Sr, 60Co, 45Ca, 51Cr, 111mCd, 110mAg) is also possible,
- Removal of organics and other humic substances (including humic, fulvic acid, and humin) and odor is also possible,
- Microorganisms capturing (the large surface area of the zeolites is accessible for adhering microorganisms. This makes selecting a suitable material for biofilter for removal of pathogenic microorganisms),
- By the zeolites, the permeable reactive barriers (PRB) can be prepared in the waste disposal site, so that contaminations could not spread in the ground water.

Limitations:

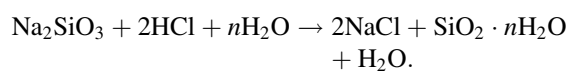
- As zeolites are used as softener in detergent formulations and insoluble, they lead to increase in sewage sludge mass.

Silica gel

Silica gel is an amorphous hard glass-like granules or beaded material made of silicon dioxide (SiO₂). Basically, it is a naturally occurring mineral which is purified and

processed. Silica gel is a high capacity adsorbent with fine pores on the surface and can be used especially as desiccant, moisture-proof, rust inhibitor as well as catalysis (Heckel and Seebach 2000).

Generally, it is formed by two routes: (1) polymerizing silicic acid, and (2) aggregation of particles of colloidal silica. Silicic acid, Si(OH)₄, has a strong tendency to polymerize and form a network of siloxane (Si–O–Si), leaving a minimum number of uncondensed Si–O–H groups. The aggregation is by Van der Waals forces or by cations bridging as coagulants. Commercial silica is prepared through the first route by mixing a sodium silicate solution with a mineral acid, such as sulfuric or hydrochloric acid. The reaction produces a concentrated dispersion of finely divided particles of hydrated SiO₂, known as silica hydrosol or silicic acid:



The hydrosol, on standing, polymerizes into a white jelly-like precipitate, which is silica gel. The resulting gel is washed, dried, and activated. Various silica gels with a wide range of properties, such as surface area, pore volume, and strength, can be made by varying the silica concentration, temperature, pH, and activation temperature (Iler 1979). Two common types of silica gel are known as regular-density and low-density silica gels, although they have the same densities (true and bulk). The regular-density gel has a surface area of 750–850 m²/g and an average pore diameter of 22–26 Å, whereas the respective values for the low density gel are 300–350 m²/g and 100–150 Å.

Because of its large pore volume and mesoporosity, silica gel is used as desiccant. The modified silica gel (modified by the impregnation) with a high-molecular weight quaternary amine (triethyl octadecyl ammonium iodide) has been used for the concentration of heavy metals (Cs, Ag, Hg, Cu, Cd, etc.) for water purification (Tzvetkova and Nickolov 2012; Bowe et al. 2003; Bowe and Martin. 2004).

Benefits:

- Silica gel is non-toxic, non-corrosive material,
- It has high adsorption capacity because of very high surface area and porosity.

Limitations:

- Preparative aspects needed very precise control,
- Modification is needed to remove the contaminants.

Ion exchange

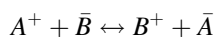
The coulombic attractive force between ions and charged functional groups is more commonly classified as ion exchange. It is a typical reversible chemical reaction where

an ion from a solution is exchanged for a similarly charged ion attached to an immobile solid particle.

The selectivity coefficient controls the preference for ions of particular resins and is expressed as follows:

$$K_{B^+}^{A^+} = \frac{\{\bar{A}\}\{B^+\}}{\{A^+\}\{\bar{B}\}}$$

for the exchange of \bar{A} in solution for B^+ on the resin:



The barred terms indicate location on the resin (solid phase) as opposed to solution phase. The superscript and subscript on the selectivity coefficient indicate the direction of the reaction.

Ion exchange materials are insoluble substances containing loosely held ions, capable of exchanging particular ions within them with ions in a solution that is passed through them. Many natural substances like proteins, cellulose, living cells and soil particles exhibit ion exchange properties, which play an important role in the way the function in nature. Synthetic ion-exchange polymers can be made in two forms, viz. beaded polymer matrix (resins) and membranes.

Ion exchange resins

Ion exchange resins are very small polymer matrix (beads), with a diameter of about 0.6–1.0 mm. The ion exchange resins can be manufactured in one of the two physical structures, gel and porous. The gel resins are crosslinked polymers having no porous structure, while porous resins have considerable external and pore surfaces (microporous, mesoporous and macroporous) where ions can attach. The porous polymer matrices contain invisible water inside the pores of the beads, measured as “humidity” or “moisture content”. The functional groups (ions) can be attached on the polymer matrix which cannot be removed or displaced.

Based on their functional groups attached on polymer matrix, the ion exchange resins are two types: cation and anion exchange resins, which further subdivided into four categories-

- Strongly acidic (typically, sulfonic acid groups, e.g., sodium polystyrene, sulfonate, etc.,
- Strongly basic (quaternary amino groups, for example, trimethylammonium group,
- Weakly acidic (mostly, carboxylic acid groups),
- Weakly basic (primary, secondary, and/or ternary amino groups, e.g., polyethylene amine).

Cation exchange resins (Fig. 1) exchange cations like calcium, magnesium, radium, and anion resins, used to remove anions like nitrate, arsenate, arsenite, or chromate from waste solution/water (Alexandratos 2009; Calmon 1986). Regeneration can be possible using sodium chloride. In case of cation

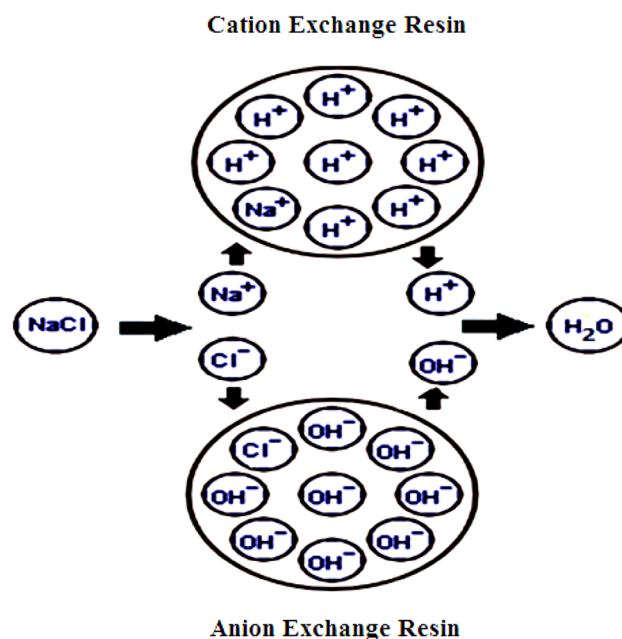


Fig. 1 Schematic diagram regarding the behavior cation exchange and anion exchange resin

resins, sodium ion displaces the cation from the exchange site; whereas in case of anion resins, the chloride ion displaces the anion from the exchange site. Resins can be designed to show a preference for specific ions, so that the process can be easily adapted to a wide range of different contaminants.

The mode of preparation of ion exchange resins is through suspension polymerization technique containing the monomers, cross-linkers and initiators. Various types of polymeric beads like styrene, MMA, MAA, DVB, etc. can be prepared by this technique, varying the ratio of monomers, diluents, the stabilizer, concentration and the agitation rate is dispersed by agitation in a liquid phase, usually water, in which the monomer droplets are polymerized while they are dispersed by continuous agitation also known as pearl polymerization technique (Penlidis et al. 1997).

The most important issue in the practical operation of suspension polymerization is the control of the final particle size distribution. The size of the particles depends on monomer type, monomer purity, interfacial tension, stabilizer concentration, agitation condition in the reactor (degree of agitation) design of reactor/stirrer.

Benefits:

- Simple and low running cost technique,
- Technique is very useful in separating components/contaminations (cations and anions) from dilute solutions/wastes and in water purification, etc.,
- Useful for the recovery of expensive materials from industrial waste (e.g., precious metals),
- Recycling components present in the solutions and/or regenerating chemicals,

- Capability to handle hazardous wastes,
- Simple regeneration process and well-maintained resins last for many years.

Limitations:

- Limitation on the concentration in the effluent to be treated,
- Ion exchange resin-treated water contains sodium, which cannot be recommended for the diet requiring low sodium intake,
- Generation of waste (sodium wastewater) as a result of ion exchange regeneration,
- Ion exchange resins do not remove organic compounds or biological contaminants,
- If resin is not sanitized or regenerated regularly, bacterial colonies proliferate on resin surfaces and can contaminate drinking water.

The ion exchange membranes are discussed in the following part.

Apart from the above, interests are growing to develop different low cost adsorbents. For this purpose, numerous agro-waste biomaterials are found suitable, viz. rice-husk, soyabean hulls, coconut shells, rice straw, sugarcane bagasse, tea leaves, petiolar felt-sheath of palm trees, etc. (Ahluwalia and Goyal 2007; Tee and Khan 1988; Low et al. 1993; Mustafiz et al. 2002). These are useful for removal of heavy metal ions (Pb^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} , etc.) in low concentrations. Biosorption is a rapid phenomenon of passive metal uptake sequestration of non-growing biomass (Beveridge and Doyle 1989). Biomass of *Aspergillusniger*, *Penicillium Chrysogenoum*, *Rhizopusnigricans*, *Ascophyllumnodosum*, *Sargassumnatans*, *Chlorella fusca*, *Oscillatoriaanguistissima*, *Bacillus firmus* and *Streptomyces sp.* has also the potential to sequester metal ions by forming metal complexes from solution and obviates the necessity to maintain special growth-supporting conditions.

Membrane water treatment

Membrane technology is one of the innovative ideas of water treatment. Over here, a semipermeable membrane is used for the removal of water impurities. There are two types of membrane water treatment technologies, namely pressure-driven (e.g., reverse osmosis) and electrically driven (electro-membrane) (Charcosset 2009).

Reverse osmosis

The two processes (viz. osmosis and reverse osmosis) are the regulator of life. Though they are termed as concentration and pressure driven simultaneously, both are controlled by thermodynamic function, i.e., 'chemical potential' of the systems. It is essentially a driving force expressed as a change in the free energy of the system as a result of the change in the composition of the system. Though literally the two signify just the opposite process, thermodynamically they are similar. Under isothermal operating condition, the tendency for material transport is always in the direction of lower chemical potential for both the processes. In osmosis, the flow is occurring solvent to solution side through a semipermeable membrane, whereas in reverse osmosis the flow is a solution for solvent. In both cases, only solvent molecules migrate from one side to another. The schematic diagram of osmosis and reverse osmosis is presented in Fig. 2.

The main two characteristics of a membrane process are flux and rejection. If an RO membrane is considered as permeating water only, the water and solute flux can be written as:

$$J_w = A(\Delta P - \Delta \Pi),$$

$$J_s = B\Delta c_s,$$

where A is the permeability coefficient, and ΔP and $\Delta \Pi$ are the hydraulic pressure and osmotic pressure difference

Fig. 2 Schematic diagram of osmosis and reverse osmosis

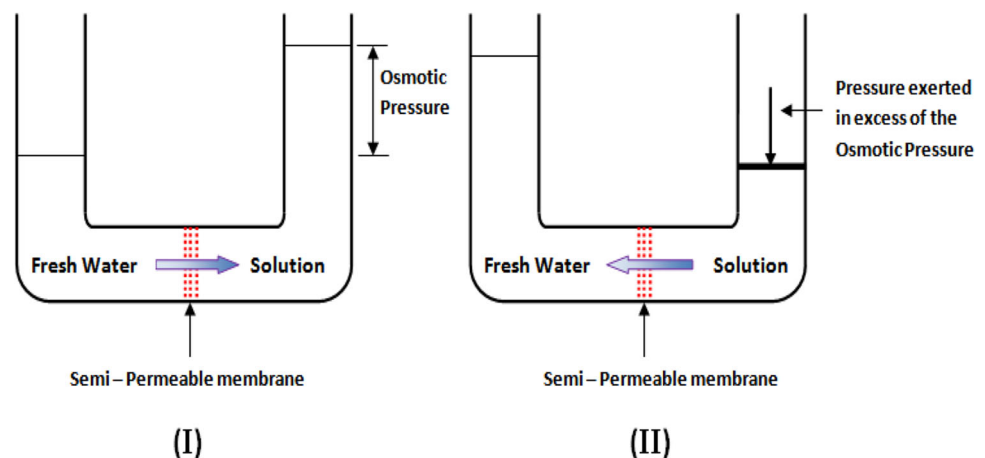
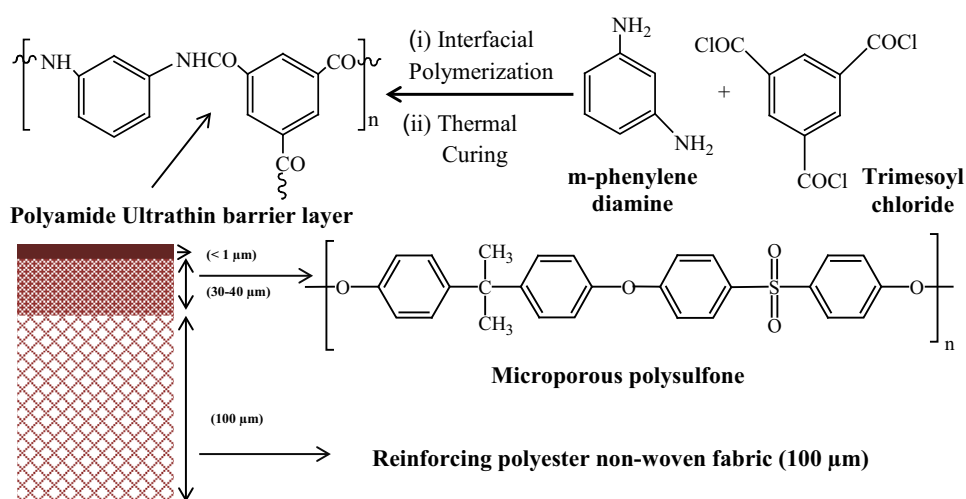


Fig. 3 Schematic diagram of polyamide thin film composite membrane



across the membrane and B is the solute permeability coefficient and ΔC_s is the solute concentration difference across the membrane.

The microfiltration and ultrafiltration membranes have a pore size in the range of >10 and 1–100 nm, respectively, whereas in the case of nanofiltration and reverse osmosis membranes are in the range of ~1 and <1 nm. Size selective separation operates in case of micro and ultrafiltration, whereas the size and charge selective separation operate in the latter two.

The membranes are generally based on natural and synthetic polymers (cellulose acetate, cellulose triacetate, polysulfone, polyamide, etc.). The most popular RO membrane is thin film composite membranes (i.e., polyamide layer on asymmetric polysulfone) (Cadotte and Peterson 1981). The polyamide layer is formed by interfacial polymerization of diamine and acyl halide and shows the charge holding capacity in it (Fig. 3).

Reverse osmosis (RO) is one of the most effective types of water treatment and widely used water purification processes in the world. It is usually used for home water treatment to remove salts (Bhattacharya and Ghosh 2004), chemical toxins (Pawlak et al. 2005), organic contaminants (Bhattacharya et al. 2008), dyes (Nataraj et al. 2009), pesticides (Bhattacharya 2006) and microbes (Park and Hu 2010). In reverse osmosis, the raw water is forced (with pressure) through a dense membrane filter that prevents passing of impurities.

Benefits:

- No phase changes and thus requirement of low energy,
- Eco-friendly as they do not produce or use any harmful chemicals; compactness and space requirements are less compared to distillation, and can be designed according to the requirement,
- Ability to remove almost all kinds of contaminants like Cl^- , NO_3^- , F^- , SO_4^{2-} , Pb^{2+} , Na^+ , K^+ , Mg^{2+} , organics as well as microorganisms,

- No alteration in the taste and smell of water and effective removal of microbes and toxins.

Limitations:

- The purified water obtained after reverse osmosis treatment is devoid of useful minerals,
- Membrane may become clogged after prolonged use and, hence, requires periodical replacement of the membrane.

Electrodialysis membrane treatment

Electrodialysis (ED) is electric potential-driven membrane-based separation process. The basic principle of the membrane separation is similar to ion exchange reactions (Xu 2005; Strathmann 2010a). The charged groups are attached to the polymer backbone of the membrane material and it is obvious that the fixed charge groups partially or completely exclude ions of the same charge from the membrane, i.e., an anionic membrane with fixed positive groups excludes positive ions, but is freely permeable to negatively charged ions whereas cationic membrane with fixed negative groups excludes negative ions but is freely permeable to positively charged ions.

Since the membrane is of ion selective, it separates or rejects opposite charge ions, useful in removal, or separation of electrolytes (Koter and Warszawski 2000; Strathmann 2010b). The schematic diagram is presented in Fig. 4.

The ion transportation depends on the current efficiency in the particular system. Generally, the current efficiencies >80 % are required in commercial stacks to minimize energy operating costs. The low current efficiencies result in water splitting in the dilute or concentrate streams, shunt currents between the electrodes, or back-diffusion of ions from the concentrate to the dilute. The current efficiency is

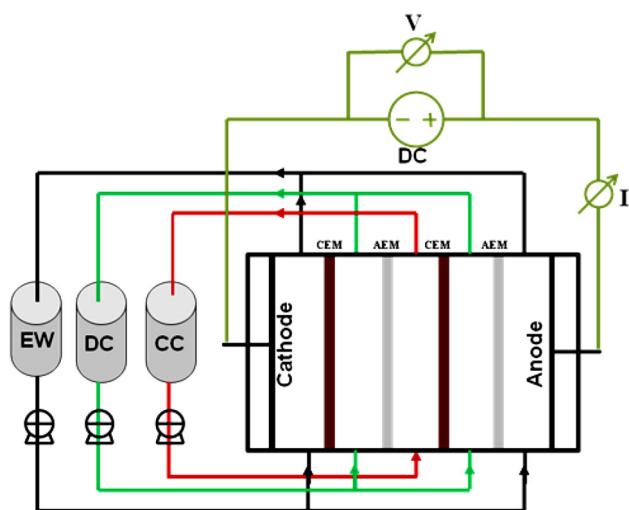


Fig. 4 Schematic diagram of electrodesialysis. *DC* diluted chamber, *EW* electrode wash, *CC* concentrated chamber, *CEM* cation exchange membrane, *AEM* anion exchange membrane

calculated according to the following equation (Shaffer and Mintz 1980).

$$\xi = zFQ_f(C_{\text{inlet}} - C_{\text{outlet}})/NI,$$

where ξ is the current utilization efficiency, z is the charge of the ion, F is the Faraday constant 96485 Amp-s/mol, Q_f is the dilute flow, L/s C_{inlet} is the dilute ED cell inlet concentration, mol/L, C_{outlet} is the ED cell outlet concentration, mol/L, N is the number of cell pairs, and I is the current, Amps.

Apart from their chemical structure (cation and anion), the commercial ion-exchange membranes can be divided, according to their structure and preparation procedure, into two major categories, homogeneous and heterogeneous and depending on the degree of heterogeneity of the ion-exchange membranes, these can be further classified into different types: mono polar (cation/anion) ion-exchange, amphoteric ion-exchange, bipolar ion-exchange, inter-polymer membranes.

The ion-exchange membranes are very similar to normal ion-exchange resins in terms of chemical structure as well as of high selectivity and low resistivity. The difference between membranes and resins arises largely from the mechanical requirement of the membrane process. Thus, it is generally not possible to use sheets of material that have been prepared in the same way as a bead resin. However, the most common solution to this problem is the preparation of membrane with a backing of a stable reinforcing material that gives the necessary strength and dimensional stability. The preparation method of ion-exchange membranes can be summarized in three different steps, viz. Polymerization or polycondensation of monomers; at least one of them must contain a moiety that either is or can be

made anionic or cationic groups, respectively, introduction of anionic or cationic moieties into a preformed solid film such as styrene-DVB-based membrane, and introduction of anionic or cationic moieties into a polymer, such as Poly-sulfone, followed by dissolving the polymer and casting it onto a film.

Benefits:

- Non-pollution, safety and reliability,
- Completely eliminated the chemicals for regeneration,
- Effective for complete removal of dissolved ionic particles (cation and anions), heavy metals, etc.,
- Ability to treat feed water with higher SDI, TOC and silica concentrations.

Limitations:

- Removal of low-molecular weight ionic contaminations,
- Non-charged, higher molecular weight, and less mobile ionic species cannot be significantly removed by the process,
- Large membrane areas are required to satisfy capacity requirements for low concentration (and sparingly conductive) feed solutions.

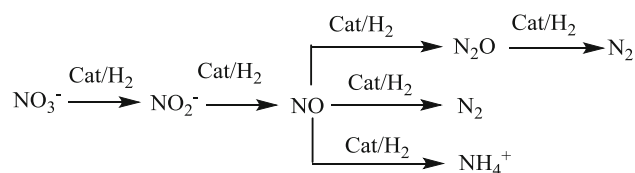
Catalytic processes

Catalytic processes are typically achieved by the following three methods: hydrogenation of nitrate, photocatalytic and electrocatalytic.

Hydrogenation of nitrate

The hydrogenation via catalytic method is one of the promising techniques for removal of nitrate from water. It needs very active catalysts because the reaction is performed preferably at an ambient/low temperature. The reaction scheme shows that nitrate is reduced to the desired products involving NO_2^- , NO , N_2O and N_2 . The undesired byproduct NH_4^+ is also formed by a side reaction due to over hydrogenation (Soares et al. 2010; Mikami et al. 2006; Berndt et al. 2001). Supported bimetallic catalyst (viz. Pd/Cu, Pd/In, and Pd/Sn) has emerged as efficient catalysts for nitrate hydrogenation (Gao et al. 2003; Mikami et al. 2003; Deganello et al. 2000). Apart from Pd, the other metals (e.g., Cu, In, Sn, Co) serve as the role of promoter for the first reduction step to convert NO_3^- into NO_2^- (Soares et al. 2008; Pintar et al. 2004; Arino et al. 2004; Qi et al. 2006). It is seen in the schematic reaction, below that N_2 and ammonium (NH_4^+) are the stable end products of the catalytic reduction process. N_2 is not harmful, but the second one is considered a hazardous aquatic pollutant.

That is why target is to convert NO_3^- into N_2 as an end product.



Benefits:

- The method can be of single operation mode,
- Selectivity of catalyst can counter the formation of ammonia ions,
- Addition of other chemicals can be avoided.

Limitations:

- Increase in pH in the reaction medium forms ammonia in dissolved condition, which is more harmful than nitrate.

Photocatalytic method

The method is based on the acceleration of photodegradation of organic pollutants, pathogens, green algae, and substances in the presence of catalyst (Esplugas et al. 2002; Pera-Titus et al. 2004; Akira et al. 2000; Eggins et al. 1997; Bekbolet et al. 1998; Ibhaddon and Fitzpatrick 2013; Gaya and Abdullah 2008; Chong et al. 2010). In response to UV light, when they excited charge separation followed by scavenging e^- s and holes by surface adsorbed species. The heterogeneous photocatalysts employing semiconductor catalysts (TiO_2 , ZnO , Fe_2O_3 ,) have shown their efficiency in degrading a wide range of pollutants in water. Metal oxides are more suitable, since they are more resistant to poisoning and deactivation.

Upon UV-irradiation, photocatalytic reactions are initiated by the absorption of illumination with photo-energy equal to or greater than the band gap of the semiconductor. It results in electron-hole (e^-/h^+) pairs as shown in Fig. 5. Thus, it participates in the redox reaction with the adsorbed pollutant species in water. Apart from the reaction, the semiconductor also oxidizes water to produce OH^\bullet , a powerful oxidant, which rapidly reacts with the pollutants in the water (Teoh et al. 2012).

To improve the catalytic activity using visible light, various approaches are also developed, viz. addition of dopants, stoichiometry of catalytic metal oxides and mixed metal oxides, particle size and shape. TiO_2 doped with nitrogen showed excellent photo catalytic activities compared to unmodified TiO_2 nanoparticles in both degradation of chemicals and bactericidal reaction (Daneshvar et al. 2007).

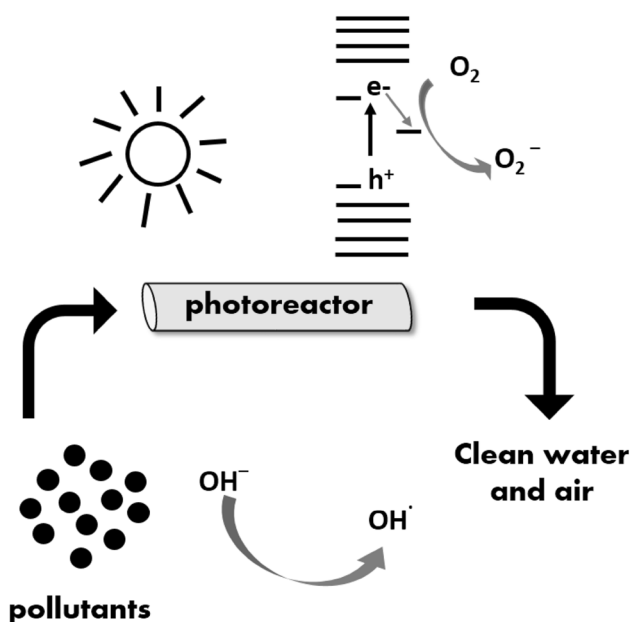


Fig. 5 Schematic diagram of the photocatalytic arrangement

Benefits:

- Reusability of the catalyst as it is unchanged during the process,
- Reactions can occur in ambient condition as well as no consumable chemicals are required,
- Operational process is simple
- It is good enough to treat low concentration of pollutants.

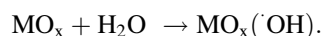
Limitations:

- Post-separation of the semiconductor catalysts after water treatment is important and failing results in catalyst poisoning.
- The catalysts with their fine particle size and large surface area to volume ratio create a strong catalyst agglomeration tendency during the operation.

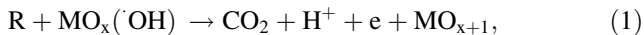
Electrocatalytic oxidation

In the electrocatalysis, the oxidation occurs through surface mediator on the anodic surface. The rate of oxidation depends on temperature, pH and diffusion rate of generating oxidants in indirect electrolysis (Mohana and Balasubramanian 2006). This is somewhat different from electrolysis where direct oxidation of pollutants takes place and rate of oxidation depends on electrode activity, pollutants diffusion rate and current density.

The electrocatalysis through metal oxide (MO_x) electrode can be shown (Comminellis 1994) as follows:



In the presence of organics (R) present in waste water, the physiosorbed active oxygen ($\cdot\text{OH}$) involves in complete combustion of organics (1) and chemisorbed active oxygen in the form of MO_{x+1} (2) does the selective oxidation



The key role in the electrocatalytic process is electrocatalytic material. Ru/Pb/Sn oxide and Pb/PbO₂ coated with Ti is used in the dye oxidation (Mohana and Balasubramanian 2006; Morsia et al. 2011). Pt, TiO₂, IrO₂, PbO₂, several Ti-based alloys and boron-doped diamond (BDD) electrodes are employed for the removal of effluents containing various organics, viz. phenols, pharmaceuticals, alcohols, carboxylic acids, anionic surfactants and pesticides (Comninellis and Nerini 1995; Radovici et al. 2009; Klavarioti et al. 2009; Canizares et al. 2008; Louhichi et al. 2008; Ventura et al. 2002). Pt(acac)₂ onto ruthenium nanoparticles is used for the removal of formic acid (Chen et al. 2009).

Electrocatalytic reduction is largely used for NO₃⁻ removal. In this regard, the development of electrodes (viz. Ti–Rh, Ti/IrO₂–Pt, PPy–Graphite, Carbon cloth–Rh, Pd–Sn activated carbon fiber (Tucker et al. 2004; Li et al. 2010; Zhang et al. 2005; Peel et al. 2003; Wang et al. 2006) is interesting direction.

Benefits:

- High pollutant degradation, easy control and low cost,
- It can be easily controlled by putting on/off the power,
- Environmentally compatible since there is little or no need for additional chemicals,
- It has the potential to eliminate different types of pollutants as well as bulk volume,
- It operates at low temperature and pressure compared to nonelectrochemical methods; thus, the volatilization and discharge of un-reacted wastes can also be avoided.

Limitations:

- High operating cost due to the high energy consumption during operation,
- Electrode fouling may also occur on the surface of the electrodes,
- It needs, conducting nature of the effluent. Sometimes the addition of an electrolyte may be necessary,
- The use of metal ions resulted in an effluent with a higher toxicity than that of the initial effluent. Thus, this approach requires a separation step to recover the metallic species (Martinez-Huitle and Ferro 2006).

Bioremediation

Phytoremediation

It signifies the removal of pollutants from the environment by the use of plants. The technology involves different mechanisms, viz. phytoextraction, rhizofiltration, phytostabilization, phytotransformation/phytodegradation (Rai 2009). Phytoextraction involves metal accumulation into the harvestable parts of the roots and the above ground shoot. Rhizofiltration indicates the absorption, precipitation and concentration of toxic metals from polluted effluents. Phytostabilization is a process in which mobility of heavy metals is reduced through the use of tolerant plants, whereas phytotransformation/phytodegradation is the process in which contaminants can be eliminated via phytodegradation or phytotransformation by plant enzymes or enzyme co-factors.

The history of the particular study, including the uptake of toxic metals Hg, As, and other metals, begins in the 70's (Dolar et al. 1971) and other metals (Stanley 1974). In this regard, macrophytes water hyacinth (*Eichhorniacrassipes*) (Zhu et al. 1999); pennywort (*Hydrocotyle umbellata* L.) (Dierberg et al. 1987); duckweeds (*Lemna minor* L.) (Rai 2007a) and water velvet (*Azollapinnata*) (Rai 2007a, b) are considered the biological filters and play the important role in the maintenance of the aquatic ecosystem. The floating plants *Lemna minor* (Zayed et al. 1998), *Eichhorniacrassipes* (Zhu et al. 1999) and *Pistiastratiotes* and *Salviniaherzogii* (Maine et al. 2001, 2004) show good potential in accumulating the metals directly from industrial effluents.

Benefits:

- Cost effective,
- Eco-friendly.

Limitations:

- Seasonal growth of the plants,
- Biomass disposal.

Vegetated filter strips

The filter strips are meant as land areas of either planted or indigenous vegetation, situated between a potential, pollutant-source area and a surface-water body that receives runoff. Vegetated filter strips (viz. grassed filter strips, filter strips, and grassed filters) are vegetated surfaces that are designed to treat sheet flow from adjacent surfaces (Dillaha et al. 1989; Delgado et al. 1995). The run-off usually carries sediment, organics, plant nutrients and pesticides.

The trapped plant nutrients and pesticides may be easily degraded or transformed by biological and chemical processes. Cole et al. (1997) report the removal of chloropyrifos (62–99 %), dicamba (90–100 %), 2,4D (89–98 %), and mecoprop (89–95 %) using Bermuda grass buffer. On the other hand, atrazine (98 %) and pyrethroid (100 %) removal is possible using vegetated drainage ditch (Moore et al. 2001)

Benefits:

- Trap sediments,
- Capture nutrients both through plant uptake and adsorption of soil particles,
- Promote transformation and degradation of pollutants into less toxic forms,
- Removal of pathogens is possible.

Limitations:

- The design is important,
- Proper vegetation is necessary,

Biologically active carbon filtration

Biologically active carbon is another prospective process with this bioremediation technique. The process utilizes granulated activate carbon (GAC) as its water filtration. The microbial (bacterial) colonization is possible over the GAC media particles form ‘biofilm’ (Scholz and Martin 1997). Actually, it is described as a ‘porous tangled mass of slime matrix (Weber et al. 1978). It consists of microbial cells, either immobilized on the surface of the GAC (substratum) or embedded in an extracellular microbial organic polymer matrix (Ghosh et al. 1999; Lawrence and Tong 2005). Bacteria and fungi cells in the biofilms secrete extracellular polymeric substances to form a cohesive, stable matrix in which cells are held in dense agglomeration (Branda et al. 2005; Lazarova and Manem 1995). The extracellular matrix is composed of polysaccharides, proteins, nucleic acids and lipids (Goodwin and Forster 1985). The activity of the biofilm relates to the physiological modifications associated with the promotion of certain genes (Dagostino et al. 1991), or changes the bacteria cell surrounding to increase the local concentration of nutrients, oxygen and enzymes (Ghosh et al. 1999) or limit the invasion of toxic or inhibiting substances (Blenkinsopp and Costerton 1991).

Most of the dissolved organic chemical removal occurs through physical adsorption in the GAC media. Apart from the adsorption, biodegradation can also operate.

Benefits:

- It can avoid chemical disinfection water treatment processes,

- Because of the microbial biodegradation of organic substrates on the GAC media, the service life can be extended,
- Bacterial regrowth is less possible,
- Eliminates the need for coagulant in source filtration processes (Hillis 2000).

Limitations:

- The control of the growth of the process is necessary.

Magnetic separation

In the magnetic separation process, the high-gradient magnetic separation (HGMS) is a commonly used process (Hoffmann and Franzreb 2004a, b; Ditsch et al. 2005; Okada et al. 2005). In this case, device comprising bed of magnetically susceptible wires placed inside an electromagnet is used. There are various influencing factors, viz. nature of impurities, concentration, size, magnetic susceptibility, spacing design, and intensity of magnetic field and its orientation, magnetic field strength.

Generally, there are three categories of separators based on magnet type, viz. permanent magnet, electromagnet and superconducting magnet. The permanent magnet (ferromagnets of iron-based, nickel, cobalt or rare earth element) is having magnetic fields of less than 1 T, though trend is to improve the magnetic field strength by the development of materials and shape design parameters (Ormerod and Constantinides 1997; Zhu and Halbach 2001; Iwashita et al. 2008). The electromagnetic-based device consists of a solenoid of electrically conducting wires which can generate a magnetic field of 2–4 T within their cavity on passage of electric current (Li et al. 2007) (Timoshenko and Ugarov 1994). The third category of magnetic separators generates the highest intensity magnetic field from 2 to 10 T (Selvaggi et al. 1998; Yan et al. 1996).

The magnetically assisted water purification can be primarily classified into the following type depending on the difference in adoption of physical processes, viz. direct purification, seeding and separation by magnetic flocculant, and magnetic sorbent application in organic and inorganic contaminants including radionuclides. In the direct purification technique, there is no carrier magnetic component utilized for the separation. The basic properties of ions or solid response to the magnetic field are utilized for purification. In this method, the anti-scaling technique is most commonly practiced. In the area of anti-scale magnetic treatment, the most common constituents of scale are CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and silica, BaSO_4 , SrSO_4 , $\text{Ca}_3(\text{PO}_4)_2$ and ferric and aluminum hydroxides (Busch and Busch 1997; Gabrielli et al. 2001; Fathia et al. 2006; Jianxin et al.

2007). In the magnetic flocculant separation, coagulant cation [viz. Fe(III)] forms an insoluble precipitate under applied magnetic field. It is an effective means of lowering significantly both the oil and suspended solids of water effluent streams (Kakihara et al. 2004; Nishijima and Takeda 2007). Ions (polymerise as polyhydroxycomplexes, or nitroso-hydroxy, or hydroxy-carbonato or halogenohydroxy-carbonato complexes), which are difficult to coagulate magnetic sorbents, are utilized for waste water purification.

Benefits:

- Useful for the separation of pollutants,
- Magnetic pre-treatment improvises purification RO membrane filters,
- Calcium carbonate scale formation in heat exchanger can be reduced,
- Promotes the homogeneous precipitation of calcium carbonate scales.

Limitations:

- Not fully sufficient.

Disinfection

The disinfection methods are classified as physical and chemical methods. In physical treatment UV, solar radiation, and ultrasound are included, whereas chlorine, iodine, ozone are included in chemical treatment (Kerwick et al. 2005).

The features of the treatments are described in the following:

By ultraviolet radiation:

In the ultraviolet treatment, the water to be treated passes through germicidal ultraviolet (UV) light configured inside a low-pressure lamp. As the water passes the ultraviolet purifier, the biological contaminants are exposed to UV light, which damages the genetic components of the microbes. The microbes are killed this way using ultraviolet water treatment (Hijnen et al. 2006; Bergmann et al. 2002). They are the pioneers of using UV in water purifiers. A major drawback of this water treatment type is that it is ineffective in removal of dissolved chemicals and other particulate matter.

Benefits:

- Ability to destroy or make inactive many pathogenic microorganisms,
- It has no effect on minerals in water,
- Ability to degrade some organic contaminants,

- No additional toxic and nontoxic chemicals are introduced.

Limitations:

- Not suitable for water with high levels of suspended solids, turbidity, color or soluble organic matter,
- Without electricity, it could not operate.

It is employed by solar radiation also. It is very useful to inactivate pathogens, especially diarrhea. The contaminated water is to fill into transparent plastic bottles and expose to the full sunlight for 6 h. The UV-A radiation (wavelength 320–400 nm) of the sunlight destroys the pathogen.

Benefits:

- Easy to use as well as inexpensive,
- Good bacterial and viral disinfection,
- No toxic chemicals except plastic bottles,
- Does not require constant attention to use,
- No effect for minerals in water.

Limitations:

- Dependent on climatic condition,
- Toxicity can come from poor quality of plastic bottles,
- Need turbidity of 30NTU or less,
- Less effective against bacterial spores and cysts stage of some parasites.

By ultrasound

Ultrasound is the cyclic sound pressure with a frequency greater than the upper limit of human hearing. The ultrasound is used in many different fields by penetrating the medium, measuring the reflection signature or supplying focussed energy. The mechanical vibration of the waves can be caused to damage cellular structures of bacteria. Thus, it can be useful to disinfect water. However, the regrowth of the microorganisms is also possible. Thus, combination of this and chemical disinfectant is the best technique.

Benefits:

- Easy to use,
- Does not require constant attention.

Limitations:

- Regrowth of microorganism is also feasible,
- Not fully self-sufficient.

By ozone

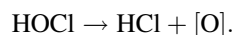
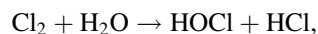
Ozone, O₃ is an unstable form of oxygen and protective layer of UV-radiation. But in drinking water, it makes an

effective disinfectant (VonGunten 2003a, b). It readily gives up oxygen and thus a powerful oxidizing agent. Ozone is made by passing oxygen through UV-light or a 'cold' electrical discharge. The very high oxidation potential of ozone is easy enough to insert oxygen into the bonds of organic compounds to form aldehydes and ketones. It is effective for killing the biological contaminants (viz. pathogens) than that of chemical disinfection method like chlorination. Actually, the ozone oxidizes the organics in bacterial membrane, which weakens the cell wall and leads to cellular rupture. This exposes the organism to the external environment, which causes almost immediate death of the cell. Ozone also improves the clarity (clarifying iron, sulfur and manganese). The soluble Fe(II) and Mn(II) which are not filtered in the normal condition transformed to insoluble Fe(III) and Mn(VII) with ozone treatment and, thus, filtration is possible. It also reduces odor problems and concentrations of sulfur and other dissolved chemicals. The main advantage of ozone is that it leaves no disinfectant residual in the water. To use ozone as disinfectant, it is generated and immediately applied on site. The limitations of using ozone as disinfectant are a significant air pollutant, explosive, and an irritant to skin, eyes, respiratory tract and mucous membrane. It can produce carcinogens if little bromine is there in the water.

By chlorine

The most common strong oxidant in the form of chlorine and its compounds, viz. chloramine or chlorine oxide are used in disinfection technique. Chlorine is well to do against bacteria and protozoa that form cysts (viz. *Giardia lamblia* and *Cryptosporidium*) (Gala-Gorchev 1996); Melvin et al. 1967). Handling of chlorine gas is dangerous, thus the use of sodium and calcium hypochlorite is the trend. It releases free chlorine in water. Electrolytic method is another mode to get chlorine solution. The free chlorine is released when dissolved in water. The limitation of using chlorine that reacts with natural organic compounds in the water forms potentially harmful chemical by-products, such as trihalomethanes and haloacetic acids. They are shown to cause cancer (Univ. Florida Report 1998). The maximum allowable annual average level of trihalomethane and haloacetic acids is 80 and 60 µg/L, respectively. They tend to increase with pH, temperature, time and the level of organics in water. One way to decrease the level of trihalomethane and haloacetic acids is to reduce the organics (EPA, US 2012). Thus, it is preferable to use after the removal of organic compounds from water. EPA has suggested 'enhanced coagulation' (i.e., the process by increasing the feed rate of coagulants, adding better coagulants, possibly ferric coagulants) process to remove the organics for controlling

trihalomethane and trihaloacetic acids. The advantage of using chloramine is that it will not form THMs or haloacetic acids, but it results in nitrification, as ammonia is a nutrient for bacterial growth, with nitrates being generated as by-products



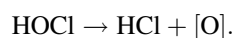
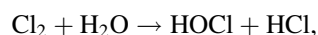
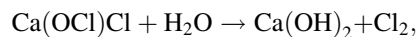
Benefits:

- Simple method,
- Availability of inexpensive chemicals/cheaply available,

Limitations:

- Excess of chlorine produces characteristic unpleasant taste and odor and irritating effect on mucous membrane.

However, the usual practice is bleaching powder in place of chlorine. The mechanistic process is as follows:



Bleaching powder should be used only in calculating amount because excess of it will give a bad taste and disagreeable odor, while the lesser amount of it will not sterilize the water completely (Snoeyink and Jenkins 1980).

Benefits:

- Simple method,
- Availability of inexpensive chemicals.

Limitations:

- It requires continuous supply of the chemicals and trained personal so that the chlorine is at effective levels.

By iodine

Similar to chlorine, it is also a good oxidizing agent. It is effective against many varieties of pathogenic organisms including spores, cysts, viruses, etc. in a short time (Punayani et al. 2006). Compounds-based formulations (organic iodide compounds: bisglycine hydroiodide, potassium tetraglycine triiodide, etc., iodophores: combination of iodine and solubilizing compounds, i.e., non-ionic surfactants, iodine incorporated resins, cross-linked copolymer of styrene and divinylbenzene with I_3^- , iodine with polyvinyl pyrrolidone) are there to regulate the release of iodine.

The mechanistic way of inhibition of protein function is forming *N*-iodo compounds, i.e., reacting with basic –NH functions of amino acids and nucleotides. Thus, important positions for H-bonds are blocked, resulting in a lethal change in protein structure. The –SH groups in the cytoplasm are oxidised. Thus, the ability to make disulphide bonds in protein formation is lost. The addition of olefinic double bonds of unsaturated fatty acids may also be the reason to decrease the fluidity of cell membranes.

Benefits:

- Effective against many varieties of pathogenic organisms including spores, cysts, viruses, etc. in a short time,
- Eliminates the chances of disease caused due to deficiency of iodine,
- Ammonia and other nitrogenous substance have no pronounced effect on the efficiency.

Limitations:

- Higher concentrations are required compared to chlorine,
- Costly than chlorine per unit of germicidal effectiveness,
- Taste and slight color produced can affect palatability and esthetic quality.

By hydrogen peroxide

Though it is known for high oxidative and biocidal efficiency, the use in drinking water disinfection is not available, but coupled with ozone, UV-radiation it can be used (Andreozzi et al. 1999). The disinfection mechanism is based on the decomposition of peroxide, i.e., the release of free oxygen radicals. The free radicals have both oxidizing and disinfecting abilities.

Contrary to other chemical substances, it does not produce residues or gases. The limitations of peroxide are: it can irritate the eyes, skin, and lung. Skin exposure causes painful blisters, burns and skin whitening.

Apart from the above, recent trend is there to employ Ag, Au, Cu, Zn, titanium nanoparticles supported in solid matrix. Due to the bactericidal effect, the water passed in the matrix will be free from bacterial contamination (Li et al. 2008; Savage and Diallo 2005).

Hybrid technologies

In true sense, no technologies independently counter all the problems. The development of technology is a dynamic process that moves forward slowly and recommendations are made based on the best science available at that time. However, with new research and new results, the flaws of existing technologies may be removed. That is why the

concept of the combinations of technologies or in other sense hybrid technologies has come. Scientists and technologists have orchestrated according to the requirement. Let us discuss with the synergistic RO technology first. In the RO technology, feed pretreatment is vital for RO to avoid problems, i.e., fouling, damaging the membranes. Conventional pretreatment steps include chemicals addition, i.e., acid, coagulant/flocculant, disinfection. Coagulation and flocculation (coagulants–flocculants) are dealt in water treatment process. Chlorine treatment is treated as disinfection process and commonly employed. But chlorination shortens the stability of the membrane and, thus, dechlorination treatment (viz. sodium bi sulfite) is required. In media filtration, water is treated by passing through granular media like pumice, anthracite, gravels, etc. that can be used in combination. Cartridge filter (made up of papers, woven wire, cloth) is used as the last pretreatment step to retain particles in the size range 1–10 μ m. To check the quality, ‘Silt Intensity Index’ or SDI parameter is important. Actually, SDI considers the ratio of two flow measurements, one at the beginning, and the other at the end by passing feed water through a 0.45 μ m filter paper in dead end mode at constant pressure (Saha and Bhattacharya 2010).

Similarly, the pretreatment step coagulation is coupled with ion exchange treatment of water. The coupled electrodeionization technology based on electro dialysis and ion exchange results in a process which effectively deionizes water, while the ion exchange membranes are continuously regenerated by the electric current in the unit. This electrochemical regeneration replaces the chemical regeneration of conventional ion exchange systems. Recently, hybrid technologies like ED-RO or ED-RO and distillation have been developed for the water purification and these processes offer many advantages over the traditional technologies (Saha and Bhattacharya 2010; Makwana et al. 2010). The ED-RO technologies desalinate the brackish water with high recoveries along with zero discharge and reduced energy consumption. ED-RO is a high recovery system since RO concentrates can be recycled through the ED system to reduce the feed flow rate, pre-treatment cost and the reduced amount of effluent. Thus, coupling of the technologies/processes offers a solution to an increasing important issue in water treatment as well as for water conservation. To get better results, UV is typically used as a final purification stage in terms of removing contaminants bacteria and viruses.

Awaited/coming technologies

The torch of the scientific quest along with the traditional technologies has now been handed over to the nanotechnologists of the twenty-first century, to whom a major challenge is to transform this into the field. Nanotechnology

refers to technologies involving particles on the approximate size scale of a few to hundreds of nanometers in diameter. The elevated surface area to mass ratio, a common characteristic of nanoparticles, makes it promising. In terms of applicability, three approaches are there, viz. individual nanoparticles (Watlington 2005), binding the nanoparticles to a powder/granule form and nanoparticles onto membranes/polymers. As individual zero valent iron particles (Can-Bao and Zhang 1997), palladium-coated iron particles and palladium-coated gold nanoparticles (Michael et al. 2005) are very promising in terms of permeable reactive barriers and photocatalysts. The nanoscopic materials such as carbon nanotubes and alumina fibers embedded in zeolite filtration membranes (Valli et al. 2010), TiO₂/Al₂O₃ membranes (Zhang et al. 2006), carbon nanotubes, wrapped around a carbon block filter structure (Cooper et al. 2007) have the capacity to remove the impurities from water. Nanoreactive membranes are able to decompose pollutants such as 4-nitrophenol (Dotzauer et al. 2006) and bind metal ions (Hollman and Bhattacharya 2004) in water solution. Polysulfone membranes impregnated with silver nanoparticles are found to be effective in bacteria and virus removal (Zodrow et al. 2009). Superchlorination is another advanced technique to get clean and disinfected water. It signifies that extra dose of chlorine oxidize organics kill and remove algae and pathogens from the water within the short-contact time. HOCl is the active chemical that provides sanitation as well as shows reactivity towards organic pollutants. When there is sufficient HOCl, the pollutants are easily oxidized. But in case of low level of HOCl compared to organic pollutants combined chlorine is formed. These combined chlorine compounds can be oxidized by increasing the level of HOCl level in water. The point at which all the organic impurities are oxidized is called the break point (Bahadori et al. 2013). To avoid the flaws (viz. corrosion, bleaching of hair and skin, foul smelling), sometimes superchlorination followed by dechlorination is necessary before the use of water. Superchlorination is practiced after the sunset as there are no possibilities to react with UV-rays from the sun.

Conclusions

The world is facing turbulent water future. With the growing economy and rising population, the theme of all nations is 'Save water'. Quantity and quality of water should be given equal importance. Awareness related to 'water conservation' and 'safe drinking water' is extremely important, and should be given a good thought to the people.

The technological solution depends on raw water characteristics, affordability and acceptability and level of application. Of course, sustainability depends on an awareness of the related issues. Since there are limitations

in every individual treatment technologies and, thus, hybrid technologies are always beneficial; however, availability, selection, optimization, etc. are important for the best performances of the system. Lastly, it must be mentioned through the gambling of research that the future of the water treatment technology is highly prosperous and hope 1 day we will fulfill the demand 'fresh water for everyone'.

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