Metal Decontamination: Techniques Used So Far

The constantly increasing degree of industrialization and rising standards of living are strongly impacting on the use of available water sources. Controlling heavy metal discharges and removing toxic heavy metals from aqueous solutions have become a challenge for the twenty-first century. The commonly used procedures for removing metal ions from aqueous streams include distillation, ion exchange, reverse osmosis, electrodialysis, precipitation, coagulation, flocculation, and nanofiltration. The basic principle, procedural details, and commercially available instrumentation based on the above phenomenon are described in brief below.

Distillation

Distillation is probably the oldest method of water purification. Water is first heated to boiling. The water vapor rises to a condenser where cooling lowers the temperature so the vapor is condensed, collected, and stored. It removes a broad range of contaminants.

Evaporation

Evaporation is the most common and cost-effective technique for recovery of heavy metals. Evaporation can provide total as well as partial recovery of metals. The application of atmosphere evaporation is used on a wide variety of process effluents from industries.

Chemical Precipitation

Chemical treatment process prior to biological process is widely applicable in the treatment of raw wastewaters. Moreover, various existing conventional primary wastewater plants are shifting toward chemically enhanced treatment to improve

S. Srivastava, P. Goyal, *Novel Biomaterials*, Environmental Science and Engineering,
DOI 10.1007/978-3-642-11329-1_3,

the quality of the treated effluent and reduce cost. Chemical precipitation is incorporated by raising the pH of wastewater by addition of alkaline chemicals, viz., lime, limestone, caustic soda, soda, ash, and magnesium hydroxide; at alkaline pH most heavy metal sizes range between 0.1 and 100 μm precipitated as metal hydroxides or metal carbonates and separated by gravity clarification or field separation methods.

Flocculation and Coagulation

Flocculation is a process that clarifies the water. Clarification is done by causing a precipitate to form in the water which can be removed using simple physical methods. For water treatment plants using surface water as the source water, coagulation–flocculation is the most commonly used physicochemical process for particle removal and is an essential pretreatment process for sedimentation and filtration (Fig. 1). The three main types of chemical coagulants are (i) inorganic electrolyte, e.g., alum, lime, ferric chloride, anhydrous sulfate; (ii) organic polymers; and (iii) synthetic polyelectrolytes with anionic and cationic functional groups which are often used for precipitation. On addition of coagulant, flocculation occurs and the size of the particle in floc increases by aggregation and settles at a faster rate. Soluble impurities in water can also be partially removed by coagulation. Because the complete removal of impurities requires the separation of aggregates from water treatments, colloidal systems of extremely slow settling velocity are viewed as stabilized systems. The coagulation process in water treatment includes three sequential steps (Fig. 2).

Fig. 1 Coagulation

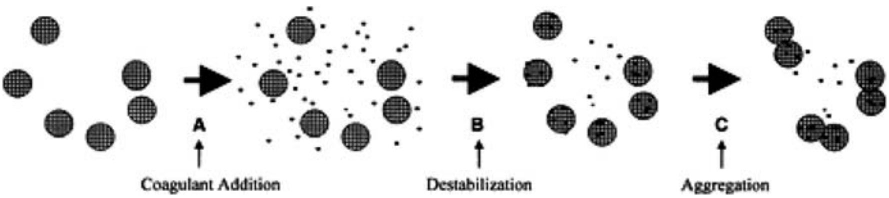

Fig. 2 Schematic illustration of coagulation–flocculation: (**a**) addition of coagulant, (**b**) destabilization of particles, (**c**) aggregation of destabilized particles

Electrocoagulation

Electrocoagulation is based on the formation of the coagulant as the sacrificial anode corrodes due to an applied current while the simultaneous evolution of hydrogen at the cathode allows the pollutant removal by floatation. Chemical reaction occurring in the electrocoagulation process shows that the main reaction occurs at the electrodes which are as follows:

$$\mathrm{Al} \leftrightarrow \mathrm{Al}^{+3} + 3\mathrm{e}^-$$
$$2\mathrm{H_2O} + 3\mathrm{e}^- \leftrightarrow 3/2\,\mathrm{H_2} + 3\,\mathrm{OH}^-$$

In addition, Al^{+3} and OH^- ions generated at electrode surfaces react in the bulk media wastewater to form aluminum hydroxide [$\mathrm{Al(OH)_3}$] flocs which act as adsorbents for metal ions and eliminate them from the wastewater. The hydroxyl ions which are produced at the cathode increase the pH in the electrolyte bulk liquid and may include co-precipitation of metals in the form of their corresponding hydroxides (Fig. 3). This acts synergistically to remove pollutants from wastewater.

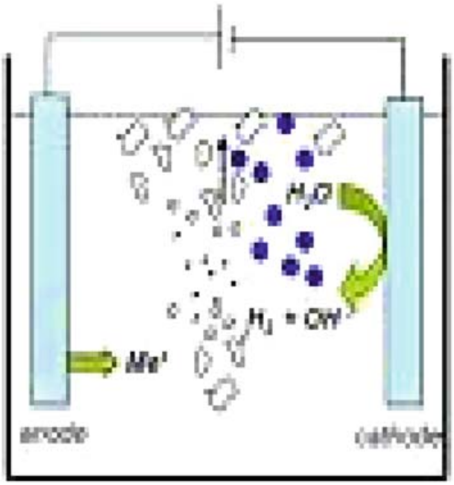

Fig. 3 Electrocoagulation

The efficiency of electrocoagulation is dependent on pH, current density, and metal ion concentration.

Ion Exchange

Ion exchange processes in water treatment have been used primarily for softening. Some of them are used to deionize, disinfect, or scavenge macromolecules from water. Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, soil humus, and synthetically produced organic resins. The synthetic organic resins are frequently used today because their characteristics can be tailored to specific applications.

Ion exchange is an exchange of *ions* between two *electrolytes* or between an electrolyte *solution* and a *complex* (Fig. 4). In most cases the term is used to denote the processes of purification, separation, decontamination of aqueous and other ion-containing solutions with solid *polymeric* or *mineralic* ion exchangers. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in mixed beds that contain a mixture of anion and cation exchange resins or passing the treated solution through several different ion exchange materials.

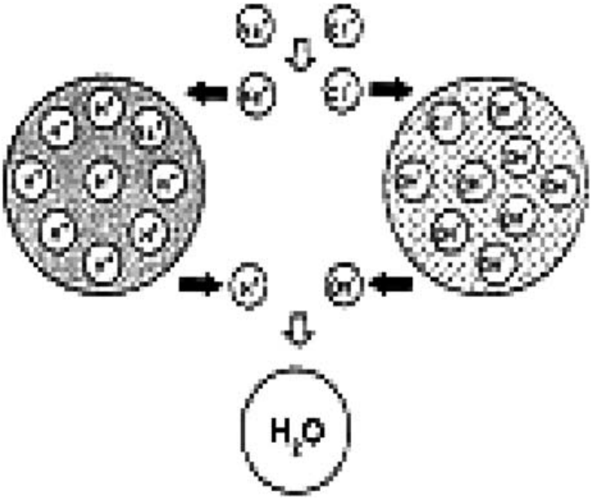

Fig. 4 Ion exchange process

Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure.

The commercially available resins used in ion exchange technology for wastewater treatment are listed in Table 1.

Table 1 List of commercially available ion exchange resins

Commercially available ion exchange resins	Activity	Company
Cesium ion exchange resin (CPU)	For liquid tank waste removal	Northwest Laboratories, UK
Resorcinol-formaldehyde ion exchange resin (ReFlX)	For radioactive waste removal	AlChem Laboratories, USA
Macroporous resin (A62MP)	For nitrate removal	Nytrox systems, UK

Membrane Process

A membrane is best defined as a material through which one type of substance can pass more readily than others.

Ultrafiltration

Ultrafiltration (UF) is a type of *membrane filtration* in which hydrostatic pressure forces a liquid against a *semi-permeable membrane*. Suspended solids and solutes of high molecular weight are retained while water and low molecular weight solutes pass through the membrane (Fig. 5). This *separation process* is used in industry and research for purifying and concentrating macromolecular (10^3–10^6 Da) solutions, especially protein solutions. Ultrafiltration is not fundamentally different from *reverse osmosis*, *microfiltration*, or *nanofiltration*, except in terms of the size of the molecules it retains.

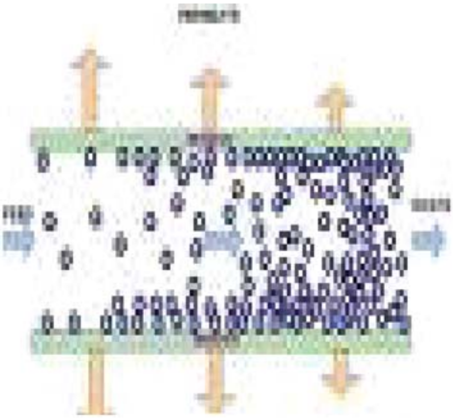

Fig. 5 Ultrafiltration

The UF process is applicable for particles in the molecular range of 0.1–0.01 μm. Ultrafiltration (UF) is a pressure-driven, membrane filtration process that is used to separate and concentrate macromolecules and colloids from wastewater. A fluid is placed under pressure on one side of a perforated membrane of a measured pore size. All materials smaller than the measured pore size pass through the membrane, leaving large contaminants concentrated on the feed side of the membrane. UF is used as a pretreatment step to reverse osmosis (RO) or as a stand-alone process. The UF process cannot separate constituents from water as effectively as RO. However, the two technologies can be used in tandem, with UF removing most of the relatively large constituents of a process stream before RO application selectively removes water from the remaining mixture.

Reverse Osmosis

Reverse osmosis (RO) fills a unique position in the area of water and wastewater treatment. Reverse osmosis (RO) is the most economical method of removing 90–99% of all contaminants. The pore structure of RO membranes is much tighter than UF membranes. RO membranes are capable of rejecting practically all particles, bacteria, and organics of molecular weight >300 Da.

Natural osmosis occurs when solutions with two different concentrations are separated by a semi-permeable membrane (Fig. 6). In water purification systems,

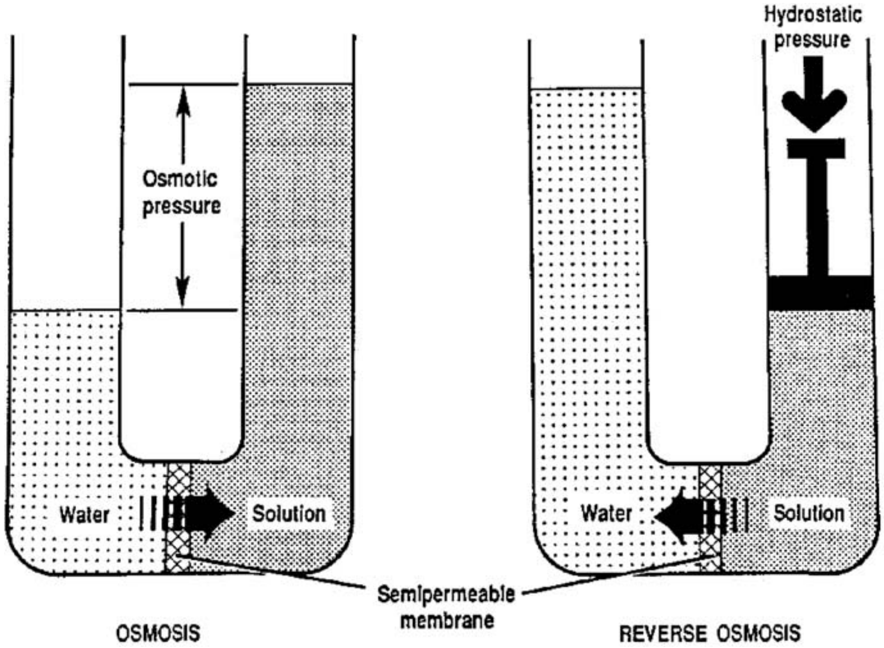

Fig. 6 Reverse osmosis

hydraulic pressure is applied to the concentrated solution to counteract the osmotic pressure. Pure water is driven from the concentrated solution and collected downstream of the membrane. Because RO membranes are very restrictive, they yield very slow flow rates. RO also involves an ionic exclusion process. Only solvent is allowed to pass through the semi-permeable RO membrane, while virtually all ions and dissolved molecules are retained (including salts and sugars). The semi-permeable membrane rejects salts (ions) by a charge phenomena action: the greater the charge, the greater the rejection. Therefore, the membrane rejects nearly all (>99%) strongly ionized polyvalent ions but only 95% of the weakly ionized monovalent ions like sodium (Table 2).

Table 2 List of commercially available reverse osmosis membranes

Commercially available reverse osmosis membranes	Activity company	Reverse osmosis membranes
Cellulose acetate membranes	For salt removal	Biosource Inc., Worcester, UK
Cellulose triacetate membranes	For bacterial removal	Miox Corp., Albuquerque
Thin film composite membranes	For silica removal	Miox Corp., Albuquerque

Electrodialysis

Electrodialysis (ED) is used to transport *salt ions* from one *solution* through *ion-exchange membranes* to another solution under the influence of an applied *electric potential* difference. The membranes are cation or anion selective, which basically means that either positive ions or negative ions will flow through. Cation-selective membranes are polyelectrolytes with negatively charged matter, which reject negatively charged ions and allow positively charged ions to flow through. This is done in a configuration called an electrodialysis cell. The cell consists of a feed (dilute) compartment and a concentrate (brine) compartment formed by an *anion* exchange membrane and a *cation* exchange membrane placed between two *electrodes* (Fig. 7). In almost all practical electrodialysis processes, multiple electrodialysis cells are arranged into a configuration called an electrodialysis stack, with alternating anion and cation exchange membranes forming the multiple electrodialysis cells. Inside an electrodialysis unit, the solutions are separated by alternately arranged anion exchange membranes, permeable only for anions, and cation exchange membranes, permeable only for cations. By this, two kinds of compartments are formed, distinguishing in the membrane type facing the cathode's direction. Applying a current, cations within the dilute move toward the cathode passing the cation exchange membrane facing this side and anions move toward the anode passing the anion exchange membrane. A further transport of these ions, now being in a chamber of the concentrate, is stopped by the respective next membrane. Electrodialysis processes are unique compared to *distillation* techniques and other membrane-based processes in that dissolved species are moved away from the feed stream rather than the reverse.

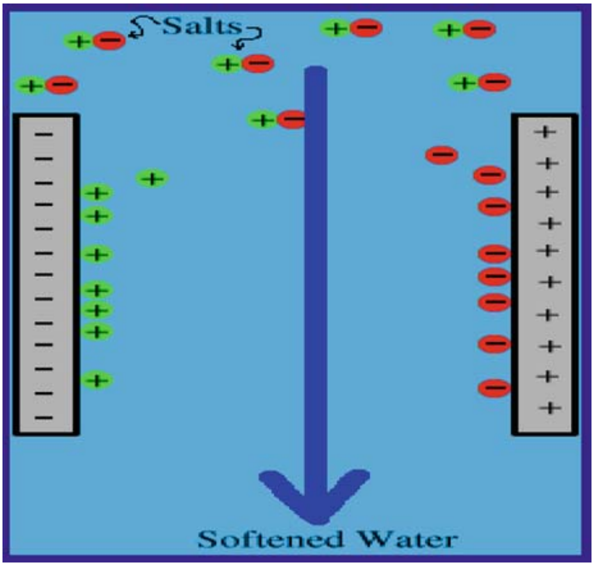

Fig. 7 Electrodialysis

Because the quantity of dissolved species in the feed stream is far less than that of the fluid, electrodialysis offers the practical advantage of much higher feed recovery in many applications.

Nanofiltration

Nanofiltration is a relatively recent membrane *filtration* process used most often with low *total dissolved solids* water such as *surface water* and fresh *groundwater*, with the purpose of softening (*polyvalent cation* removal) and removal of disinfection by-product precursors such as natural *organic* matter and synthetic organic matter. Nanofiltration is also becoming more widely used in *food processing* applications such as *dairy* for simultaneous concentration and partial (*monovalent ion*) demineralization.

Nanofiltration is a pressure-driven separation process. The filtration process takes place on a selective separation layer formed by an organic semi-permeable membrane. The driving force of the separation process is the pressure difference between the feed (retentate) and the filtrate (permeate) side at the separation layer of the membrane. However, because of its selectivity, one or several components of a dissolved mixture are retained by the membrane despite the driving force, while water and substances with a molecular weight <200 Da are able to permeate the semipermeable separation layer. Because nanofiltration membranes also have selectivity for the charge of the dissolved components, monovalent ions will pass the membrane and divalent and multivalent ions will be rejected.

A nanofiltration filter has a pore size around 0.001 μm. Nanofiltration removes most organic molecules, nearly all viruses, most of the natural organic matter, and a range of salts. Nanofiltration removes divalent ions, which make water hard, so nanofiltration is often used to soften hard water. Heavy metal separation by nanofiltration takes place through combination of charge rejection, solubility diffusion, and sieving. Copper and cadmium were reported to be removed successfully from industrial wastewater by nanofiltration technology. Efficient removal of about 90% and 82–97% of Cu^{+2} and Cd^{+2}, respectively, was observed from wastewater with initial concentration ranging between 25 and 2,000 mg/L (Fig. 8).

Fig. 8 Nanofiltration