

Lecture 12

Adsorption, Ion Exchange, and Chromatography

Adsorption, ion exchange, and chromatography are sorption operations, in which certain components of a fluid phase, called solutes, are selectively transferred to insoluble, rigid particles suspended in a vessel or packed in a column. Sorption, which is a general term introduced by J.W. McBain, includes selective transfer to the surface and/or into the bulk of a solid or liquid. Thus, absorption of gas species into a liquid and penetration of fluid species into a nonporous membrane are also sorption operations. In a general sorption process, the sorbed solutes are referred to as sorbate, and the sorbing agent is the sorbent.

In an adsorption process, molecules, as shown in Figure 1, or atoms or ions, in a gas or liquid diffuse to the surface of a solid, where they bond with the solid surface or are held there by weak intermolecular forces. The adsorbed solutes are referred to as adsorbate, whereas the solid material is the adsorbent. To achieve a very large surface area for adsorption per unit volume, highly porous solid particles with small-diameter interconnected pores are used, with the bulk of the adsorption occurring within the pores.

In an ion-exchange process, as shown in Figure 1b, ions of positive charge (cations) or negative charge (anions) in a liquid solution, usually aqueous, replace dissimilar and displaceable ions of the same charge contained in a solid ion exchange⁶ which also contains immobile, insoluble, and permanently bound co-ions of the opposite charge. Thus, ion exchange can be cation or anion exchange. Water softening by ion exchange involves a cation exchanger, in which the following reaction occurs to replace calcium ions with sodium ions. The exchange of ions is reversible and does not cause any permanent change to the structure of the solid ion exchanger. Thus, it can be used and reused unless fouled by organic compounds in the liquid feeds that attach to exchange sites on and within the ion exchanger. The ion-exchange concept can be extended to the removal of essentially all inorganic salts from water by a two-step process called demineralization or deionization. In the first step, a cation resin exchanges hydrogen ions for cations such as calcium, magnesium, and sodium.

In the second step, an anion resin exchanges hydroxyl ions for strongly and weakly ionized anions such as sulfate, nitrate, chloride, and bicarbonate. The hydrogen and hydroxyl ions that enter the water combine to form water. Regeneration of the cation and anion resins is usually accomplished with sulfuric acid and sodium hydroxide, respectively.

In chromatography, the sorbent may be a solid adsorbent, an insoluble, nonvolatile, liquid absorbent contained in the pores of a granular solid support, or an ion exchanger. In either case, the solutes to be separated move through the chromatographic separator, with an inert, eluting fluid, at different rates because of repeated sorption, desorption cycles.

During adsorption and ion exchange, the solid separating agent becomes saturated or nearly saturated with the molecules, atoms, or ions transferred from the

fluid phase. To recover the sorbed substances and allow the adsorbent to be reused, it is regenerated by desorbing the sorbed substances. Accordingly, these two separation operations are carried out in a cyclic manner. In chromatography, regeneration occurs continuously, but at changing locations in the separator.

Adsorption processes may be classified as purification or bulk separation, depending on the concentration in the feed fluid of the components to be adsorbed. Although there is no sharp dividing concentration, Keller has suggested 10 wt%. Early applications of adsorption involved only purification. For example, adsorption with charred wood to improve the taste of water has been known for centuries. The decolorization of liquid solutions by adsorption with bone char and other materials has been practiced for at least five centuries. Adsorption of gases by a solid (charcoal) was first described by C.W. Scheele in 1773. Commercial applications of bulk separation by gas adsorption began in the early 1920s, but did not escalate until the 1960s, following the inventions by Milton of synthetic molecular-sieve zeolites, which provide high adsorptive selectivity, and by Skarstrom [3] of the pressure-swing cycle, which made possible the efficient operation of a fixed-bed, cyclic, gas adsorption process. The commercial-scale bulk separation of liquid mixtures also began in the 1960s, following the invention by Broughton and Gerhold of the simulated moving bed for adsorptive separation.

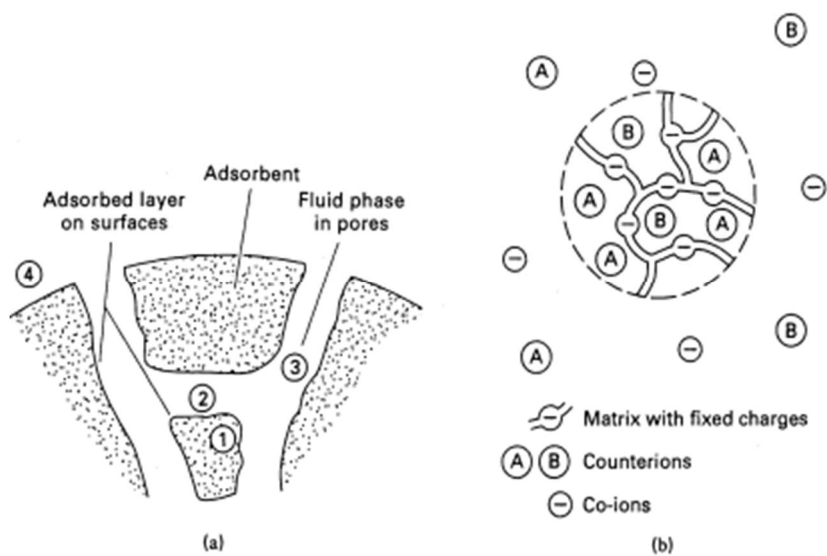


Figure 1 – Sorption operations with solid-particle sorbents: a – adsorption; b – ion exchange

The use of ion exchange dates back to at least the time of Moses, who, while leading his followers out of Egypt into the wilderness, sweetened the bitter waters of Marah with a tree. In ancient Greece, Aristotle observed that the salt content of water is reduced when it percolates through certain sands. Systematic studies of ion exchange were published in 1850 by both Thompson and Way, who experimented with cation exchange in soils before the discovery of the existence of ions.

The first major application of ion exchange, which occurred about 100 years ago, was for water treatment to remove the ions responsible for water hardness, such as calcium. Initially, the ion exchanger was a porous, natural, mineral zeolite

containing silica. In 1935, synthetic, insoluble, polymeric-resin ion exchangers were introduced. Today they are dominant for water-softening and deionizing applications, but natural and synthetic zeolites still find some use.

Since the invention of chromatography by M.S. Tswett, a Russian botanist, in 1903, it has found widespread use as an analytical and preparative laboratory technique. Tswett separated a mixture of structurally similar yellow and green chloroplast pigments in leaf extracts by dissolving the extracts in carbon disulfide and passing the solution through a column packed with chalk particles. The pigments were separated by color. Hence, the name chromatography was coined by Tswett in 1906 from the Greek words *chroma*, meaning color, and *graphe*, meaning writing. Chromatography has revolutionized the laboratory chemical analysis of liquid and, particularly, gas mixtures. The large-scale, commercial applications described by Bonmati et al. and Bernard et al., however, did not begin until the 1980s.