

CHAPTER 1

ADSORPTION FROM SOLUTION

Adsorption from solution is a phenomenon that is applicable to many important processes. These include chromatography, heterogeneous catalysis, the dyeing of textiles, and the removal of impurities from wastewater and effluents. Adsorbents investigated in this regard, i.e. for wastewater and effluent treatment, include naturally occurring materials such as zeolites, chitosan, clays and various oxides; industrial by-products such as fly ash, iron (III) hydroxide, waste slurry, lignin, blast-furnace slag and sawdust; as well as a variety of miscellaneous adsorbents. Research efforts have focussed almost entirely on the removal of heavy metals, due to their well-known toxicity.

1.1. Literature review

Commercial activated carbon (CAC) is the most widely used adsorbent in wastewater applications. The large number of pores produced within the particles during activation and the extremely large specific surface area (on the order of $1000 \text{ m}^2/\text{g}$) makes CAC a very efficient adsorbent. However, CAC is expensive, and this fact has led to on-going research into the feasibility of using lower-cost adsorbents as alternatives to CAC.

Several workers have investigated the removal of heavy metals from aqueous solution by granular activated carbon (GAC). Netzer and Hughes (1984) reported that GAC removed 99 % Co and 93 % Cu, respectively, from 10 ppm solutions at pH 4.0. An adsorption capacity of 30 mg Pb²⁺/g GAC was reported by Reed and Arunachalam (1994), who also showed that the portion of Pb²⁺ not removed represented the amount that was complexed with by the EDTA added to improve the removal performance of the adsorbent. The adsorption capacity value of 145 mg Cr⁶⁺/g GAC type Filtrasorb 400 at pH 3.0 reported by Sharma and Forster (1996) is several orders of magnitude higher than the value of only 0.18 Cr⁶⁺/g GAC reported by Han et al. (2000) in a comparative study.

Leyva-Ramos et al (1997) reported an adsorption capacity value of 8 mg Cd²⁺/g GAC at pH 8.0. They also made the observation that the adsorption capacity decreased with increasing temperature, indicating that the adsorption process was exothermic. It has also been reported (Aggarwal et al, 1999) that chemical modification of the surface of GAC with nitric acid led to a three-fold increase in the adsorption capacity for Cr³⁺ to 30 mg Cr³⁺/g GAC. This can be ascribed to the larger negative charge on the surface of the oxidised GAC compared to the GAC as received.

Other types of CAC have also been investigated. Using clothe activated carbon (ACC), adsorption capacities of 65, 2.0 and 3.8 mg/g ACC were reported (Babi et

al, 2002) for Hg^{2+} , Zn^{2+} and Cd^{2+} respectively. The removal of Hg^{2+} using powder activated carbon (PAC) was studied by Huang and Blankkenschap (1984). They reported 99-100 % removal of 0.2 mM Hg^{2+} in the pH range 4.0-5.0. Oxidative treatment of fibrous activated carbon (ACF) with nitric acid was reported (Rangel-Mendez and Streat, 2002) to result in a marked increase Cd^{2+} in removal. An adsorption capacity of 146 mg Cd^{2+} /g ACF was obtained in the pH range 5.0-6.0.

In addition to removing heavy metals, CAC has also been used widely for deodorising wastewater by removing colour- and odour- producing refractory organic materials (Smethurst, 1979).

Zeolites occur as crystalline aluminosilicates consisting of a framework of tetrahedral molecules interlinked by shared oxygen atoms. The unique capability of zeolites to preferentially exchange constituent cations such as Al^{3+} , K^+ and Na^+ for heavy metal ions makes them good candidates for research and application in wastewater treatment. The family of zeolites consist of a wide variety of species, with clinoptilolite and chabazite being the two commonest types.

Malliou et al (1992) reported adsorption capacities of 1.4 mg Pb^{2+} and 1.2 mg Cd^{2+} /g clinoptilolite. It was further observed (Malliou et al, 1994) that higher temperatures favoured metal uptake. This can be attributed to activation of the metal ions, which enhances adsorption at the coordination site of zeolites.

Chabazite was found to be superior to clinoptilolite with respect to the removal of Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} and Co^{2+} from effluents (Ouki and Kavanagh, 1997). This was attributed to the fact that the former zeolite has a higher Al substitution of Si than the latter, providing a negative framework more favourable for cation exchange. Several workers (Ouki et al, 1993; Semmens and Martin, 1988; Curkovic et al, 1997) have reported that pre-treatment of zeolites influences the cation exchange capacity (CEC). For example, treating chabazite (and clinoptilolite) with NaOH solution was reported by Ouki et al (1993) to result in CECs in excess of 100 mg/g for Pb^{2+} and Cd^{2+} ; 137 mg Cd^{2+} and 175 mg Pb^{2+} /g chabazite (and 70 mg Cd^{2+} and 62 mg Pb^{2+} /g clinoptilolite).

For column operation, effluent flow rate has been found to be an important parameter influencing the CEC of zeolites. In a study using an Italian zeolite containing chabazite and phillipsite a CEC of 7.10 mg Cr^{3+} /g was obtained at a flow rate of 1.83 ml/min (Pansini et al, 1991). A similar study using a flow rate of 15 ml/min yielded a CEC of only 0.25 mg Cr^{3+} /g (Ibrahim et al, 2002). This observation can be attributed to the fact that at a lower flow rate there is a greater chance for physicochemical interactions to occur between the zeolite and the target heavy metal species.

Chitosan is produced by alkaline *N*-deacetylation of chitin, a natural biopolymer similar to cellulose in molecular structure and widely found in the exoskeleton of

crustaceans and shellfish. The large number of surface hydroxyl and primary amino groups, coupled with the flexible structure of the polymer chain, make chitosan a good candidate for the adsorption of metal ions.

The removal of heavy metals by chitosan has been investigated by several workers. McKay et al (1989) reported adsorption capacities of 75, 164, 222 and 815 mg/g for Zn^{2+} , Ni^{2+} , Cu^{2+} and Hg^{2+} , respectively. Another study (Huang et al, 1996) found adsorption capacities of 16.8, 8.5, 2.4, 16.4 and 51.6 mg/g for Cu^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+} and Hg^{2+} , respectively.

The effect of chitosan particle size on removal efficiency can be seen by comparing the results obtained by Annachhatre et al (1996) and Wan-Nga and Isa (1998). The former reported an adsorption capacity of 13 mg Cu^{2+} /g using 50 mesh chitosan, compared to the 4.7 mg Cu^{2+} /g obtained in the latter study, which used 200 mesh chitosan under similar conditions.

Chemical modification of chitosan has been reported to enhance its removal efficiency for metal ions. For example, Guibal et al (1994) obtained a high adsorption capacity of 450 mg V^{5+} /g using the oxo-2-glutaric acid derivative of chitosan. They also reported an optimum pH of 3.0 for vanadium (V) removal and fitted the experimental adsorption data to the Freundlich isotherm. Nga et al (2002) reported adsorption capacities of 45.9, 62.5 and 59.7 mg Cu^{2+} /g for chitosan cross

linked with ethylene glycol diglycidyl ether (EGDA), epichlorohydrin (EC), and glutaraldehyde (GD), respectively, at a pH of 6.0. Although it improves the stability of chitosan, cross linking was reported (Schmuhl et al, 2001) to reduce the capacity of the adsorbent for metal ion removal.

The essential constituents of clay are kaolinite and other hydrous aluminous minerals like smectites (e.g. montmorillonite, wollastonite and bentonite), micas and fine particles (less than 2 μm diameter). An obvious attraction of clays for adsorption studies is its relatively low cost and easy local availability.

Srivastava et al (1989) compared the removal of cadmium and lead by kaolinite and montmorillonite. They obtained adsorption capacities of 0.72 mg Cd^{2+}/g and 0.68 mg Pb^{2+}/g on montmorillonite and 0.32 mg Cd^{2+}/g and 0.12 mg Pb^{2+}/g on kaolinite. They also observed that the uptake of metal ions is improved in the presence of anionic surfactants and attenuated in the presence of cationic surfactants. Montmorillonite was reported (Undaybeytia et al, 1996) to adsorb Zn^{2+} more efficiently than Cd^{2+} . This was ascribed to the fact that Zn^{2+} has a higher ionic potential than Cd^{2+} . Panday et al (1986) studied the removal of Cu^{2+} using homogeneous mixtures of adsorbents such as wollastonite/China clay, wollastonite/fly ash and China clay/fly ash. The wollastonite/fly ash mixture yielded the maximum adsorption capacity, 1.18 mg Cu^{2+}/g .

Chantawong et al (2001) reported adsorption capacities of 4.3 and 1.4 mg Pb²⁺/g, respectively, for kaolinite and illite from Thailand. They observed that an increase in pH improved the efficiency of lead uptake, and that co-ions such as Cd²⁺, Cu²⁺ and Zn²⁺ reduce Pb²⁺ adsorption because they bind strongly with organic matter present in clay. Both the Langmuir and Freundlich isotherms were used to model the experimental adsorption data. China clay and wollastonite were used to evaluate the effect of temperature on lead removal (Yadava et al, 1991). The adsorption capacity was found to decrease with increasing temperature (e.g. 1.68 and 1.10 mg Pb²⁺/g wollastonite at 20 and 40°C, respectively); negative ΔH values were obtained, indicating an exothermic adsorption process. This happens to be opposite to the observation made by Khan et al (1995), who found that the sorption of Cr⁶⁺ on the clay mineral bentonite is favoured at higher temperatures (0.33 and 0.57 mg Cr⁶⁺/g at 20 and 40°C, respectively). Bentonite has also been used to remove radioactive waste (Pusche, 1992).

Several natural oxides have been investigated for their ability to remove heavy metals from aqueous waste. Srivastava et al (1996) reported adsorption capacities of 31 mg Cd²⁺/g and 33 mg Pb²⁺/g for aluminium oxide, and 72 mg Cd²⁺/g and 230 mg Pb²⁺/g for goethite (a ferric oxide). Iron oxide coated with sand was used to develop a unit that can be used domestically to remove over 80 % of the As³⁺ and As⁵⁺ from ground water (1.0 ppm arsenic), regardless of the chemical origin of the arsenic (Joshi and Chaudhuri, 1996). Manganese oxide has also been used to

remove arsenic compounds from ground water (Chakaravarty et al, 2002). Bailey et al (1992) successfully removed 99 % of 0.038 mM Cr^{6+} from aqueous solution using iron oxide coated with sand.

Several solid waste materials generated as by-products in a variety of industrial processes have been investigated for potential use as adsorbents; finding new applications for a particular by-product adds economic value to the process involved in its generation.

Iron (III) hydroxide and waste slurry are both by-products generated in the fertilizer industry. Namasivayam and Ranganathan (1992) reported an adsorption capacity of 0.47 mg Cr^{6+} /g iron (III) hydroxide at pH 5.6. Very high adsorption capacities of 1030 mg Pb^{2+} /g, 560 mg Hg^{2+} and 640 mg Cr^{6+} /g were reported for waste slurry (Srivastava et al, 1989). Lignin, a by-product of paper manufacturing, reportedly (Srivastava et al, 1994) has outstanding adsorption capacities for Pb^{2+} (1865mg/g) and Zn^{2+} (95 mg/g). They found that the high adsorption capacity can be ascribed to the presence of polyhydric phenol groups on the surface of lignin, and that the efficiency of metal ion removal improved with increasing temperature. An adsorption capacity of 13.8 mg Cu^{2+} /g was reported (Ajmal et al, 1998) for sawdust, a by-product of the saw milling of timber.

Fly ash, a by-product of the combustion of coal to produce electrical power, has been investigated by many workers in this regard. It has been used to adsorb heavy metals such as Cr^{6+} (Dasmahapatra et al, 1996), Cu^{2+} , Pb^{2+} and Cd^{2+} (Apaka et al, 1998) and Hg^{2+} (Sen and De, 1987). Panday et al (1984) found that using fly ash in a 1:1 homogeneous mixture with wollastonite improved its removal efficiency for hexavalent chromium. They achieved an adsorption capacity of 2.92 mg Cr^{6+} /g mixed adsorbent at pH 2.0, and modelled the experimental adsorption data on the Langmuir isotherm. Sen and Arnab (1987) reported an adsorption capacity of 2.82 mg Hg^{2+} /g fly ash in the pH range 3.5-4.5. They found the Freundlich isotherm to be the appropriate isotherm for modelling the experimental adsorption data. Slag, which is a by-product of the manufacture of iron and steel in a blast furnace, has been investigated for its adsorptive capability. Srivastava et al (1997) reported adsorption capacities of 40 mg Pb^{2+} /g and 7.5 mg Cr^{6+} /g for slag.

Table 1.1 is a summary of the highest adsorption capacities (for heavy metals) reported in the publications that have been cited in this review. The values reflect the effectiveness of the different types of adsorbents for removing various heavy metals from aqueous solution.

As can be seen from the entries in the Table, a number of alternative adsorbents match and even surpass CAC with regard to their ability to remove toxic heavy metals from aqueous solution. Zeolites, chitosan, waste slurry and lignin exhibit

outstanding adsorption capacities. Zeolites can remove Pb^{2+} over 5 times better than CAC. Chitosan is superior to the other adsorbents for the removal of Hg^{2+} , Ni^{2+} and Cu^{2+} . Waste slurry has very high adsorption capacities for Pb^{2+} , Cr^{6+} and Hg^{2+} , and lignin has the highest reported adsorption capacities for Pb^{2+} and Zn^{2+} .

Table 1.1. Summary of cost and adsorption capacities for various adsorbents.

Material	Typical cost ^a (US \$/kg)	Adsorption capacity (mg/g)						
		Pb^{2+}	Cr^{6+}	Cd^{2+}	Hg^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}
CAC	20	30	145	146	65	2		
Zeolites	0.12	175	3.6	137		5.5	4.5	5.1
Chitosan	16	16.4	50	8.5	815	75	164	222
Clays	0.04-0.12	4.3	0.6	11.4		4.5		1.2
Natural oxides	0.05	230		72				
Fly ash	<i>N.O.</i>		2.9		2.8			
Slag	38/t	40	7.5					
Iron (III) oxide	<i>N.O.</i>		0.5					
Waste slurry	<i>N.O.</i>	1030	640		560			
Lignin	0.06	1865				95		
Sawdust	<i>N.O.</i>							13.8

^aSource: Virta, R., USGS Mineral Information, US Geological Survey Mineral Commodity Summary, 2002.

N.O.: Not obtained

The actual cost of a “low-cost” material is an important consideration in choosing it as a candidate adsorbent for research and/or application. It is hardly surprising that zeolites have received a lot of attention, considering that their adsorption capacities compare favourably to those of CACs but cost 20 times cheaper.

Although chitosan has high adsorption capacities for most heavy metals, it is not really a low-cost material considering that it costs nearly as much as CACs. Lignin appears to offer the best value for money for Pb^{2+} and Zn^{2+} . Although the adsorption capacities of clays appear to be modest, their low cost increases their attraction. It must be emphasised that in certain circumstances local availability is a consideration that might supersede cost.

Both fly ash and slag have also been used to remove chemical species other than heavy metals from aqueous solution. Akgerman and Zardkoohi (1996) obtained adsorption capacities of 67, 20 and 22 mg/g fly ash for phenol, chlorophenol and 2,4-dichlorophenol, respectively. Fly ash has been used for removing radionuclides (Aptak et al, 1996), colour (Gupta et al, 1998), and F^{-} (Piekos and Paslawska, 1999) and from aqueous solution.

The use of slag for the removal of nutrients such as phosphates from aqueous solution has also been studied. Johansson and Gustafsson (2000) concluded that Ca-P precipitation (probably as the hydroxyapatite) was the major phosphate removal mechanism. This conclusion was reached on the basis that with adsorption it is difficult to explain the observation they made, that there was a concomitant decrease in the concentration of dissolved Ca when increasing concentrations of PO_4^{3-} solution were added to the slag. This is not consistent with the findings of either Yamada et al (1986) or Sakadevan and Bavor (1998). Both

studies concluded that adsorption was the dominant mechanism for phosphate sorption by slag. The latter study fitted the experimental data to the Langmuir adsorption isotherm and used it to calculate an adsorption capacity of 44.2 mg P/g slag.

It must be pointed out that Johansson and Gustafsson (2000) did not report any adsorption data, whilst the other 2 studies (Yamada et al,1986; Sakadevan and Bavor, 1998) did not explicitly consider the possible contribution of Ca-P precipitation.

1.2. Fundamental chemistry

Various models may be used to describe adsorption at the solid-solution interface, depending on whether the adsorbate is present in a diluted or concentrated solution, and on the nature of the adsorbate (non-electrolyte or electrolyte) and adsorbent (non-porous particle, ion-exchanger or zeolite). The picture that is most amenable to simple analysis (Adamson, 1990) is that of a monolayer of adsorbate molecules on the adsorbate surface, with solute-solid interactions decaying very rapidly with distance.

1.2.1. Adsorption isotherms

The moles of solute adsorbed per gram of adsorbent, n_2^s , is generally a function of the equilibrium solute concentration, C_2 , and temperature, T , for a given system, i.e.,

$$n_2^s = f(C_2, T) \quad (1.1)$$

The adsorption is a function of concentration at a given temperature, i.e.,

$$n_2^s = f_T(C_2) \quad (1.2)$$

Various functional forms for f , or adsorption isotherms, have been proposed.

1.2.1.1. The Langmuir and Freundlich isotherms

The functions proposed by Langmuir (1918) and Freundlich (1926) are the two most commonly employed isotherms. Although originally proposed for the adsorption of gaseous molecules, the Langmuir and Freundlich isotherms may be adapted to adsorption from solution as shown below in equations (1.3) and (1.4), respectively (Adamson, 1990):

$$(1/x) = (1/[x_m K])(1/c) + (1/x_m) \quad (1.3)$$

$$\log x = \log K + (1/n) \log c \quad (1.4)$$

where x is the mass of solute adsorbed per mass of adsorbent, x_m is the limiting mass of solute that can be taken up per mass of adsorbent, K , n are constants, and c is the concentration of the solute in the solution that is in equilibrium with the adsorbent.

1.2.1.2. The Frumkin isotherm

The basis of the Langmuir isotherm is that the energy of an adsorbed particle is the same at any site on the adsorbent surface, and is independent of the presence or absence of neighbouring adsorbed molecules. This is referred to as ideal adsorption. Non-ideal systems are commonly fitted to the Freundlich isotherm, where the amount adsorbed keeps increasing as the concentration of the solute increases. However, the Freundlich isotherm, although recognising surface heterogeneity, does not account for appreciable surface repulsion (Hayward and Trapnell, 1964).

An isotherm that explicitly accounts for the existence of finite lateral interactions among adsorbate molecules is one suggested by the Russian electrochemist Frumkin (1925). The general expression of the Frumkin isotherm is (Bockris and Khan, 1993):

$$\beta x = [\Phi/(1-\Phi)] \cdot \exp -2\alpha\Phi \quad (1.6)$$

where $\Phi = M/M_{ads}$, M is the mass of solute adsorbed at equilibrium when the molar fraction in the solution is x , M_{ads} is the maximum mass of solute adsorbed at equilibrium, and β is a constant that describes the adsorption equilibrium ($\beta = \exp(-\Delta G_{ads}^0/RT)$, where ΔG_{ads}^0 represents the standard free energy of adsorption). The term α is the lateral interaction coefficient. In terms of molar concentration, equation (1.6) may be rewritten in logarithm form (Brina and De Battisti, 1987) as:

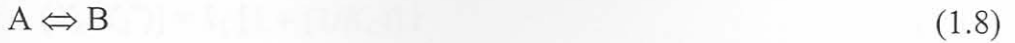
$$v = \log (\beta/55.55) + 2\alpha\Phi/2.303 \quad (1.7)$$

where $v = \log [\Phi/(1-\Phi)c]$, and c is the concentration of the solute that is in equilibrium with the adsorbent.

1.2.2. Adsorption kinetics

The kinetics and the equilibria of adsorption are the two important physicochemical factors for the evaluation of the adsorption process. For adsorption equilibria parameter evaluation, the experimental data is fitted to the appropriate adsorption isotherm. Adsorption kinetics describes the solute uptake rate from solution, and is an important contributory factor to the efficiency of adsorption.

The adsorption of solute from solution can be considered as a reversible reaction with equilibrium being established between the liquid phase (A) and the solid phase (B), i.e.,



Assuming a first order reversible kinetics model, Bhattacharya and Venkobachar (1984) expressed the rate equation as:

$$\begin{aligned} dC_B/dt &= -dC_A/dt = C_A^0(dX_A/dt) = k_1C_A - k_2C_B \\ &= k_1(C_A^0 - C_A^0X_A) - k_2(C_B^0 + C_A^0X_A) \end{aligned} \quad (1.9)$$

where C_A and C_B are the concentrations of solute in solution and on the adsorbent, respectively, at time t , C_A^0 and C_B^0 are the initial concentrations of solute in solution and on adsorbent, respectively, X_A is the fractional conversion of solute at any time t , and k_1 and k_2 are the first order adsorption and desorption rate constants, respectively.

At equilibrium conditions ($dC_B/dt = dC_A/dt = 0$) the rate equation in terms of equilibrium conversion is:

$$dX_A/dt = (k_1 + k_2)(X_A^e - X_A) \quad (1.10)$$

where X_A^e is the fractional conversion of solute at equilibrium. Integration of equation 1.10 gives:

$$-\ln [1 - (X_A/X_A^e)] = k_1 [1 + (1/K_C)] t \quad (1.11)$$

where $K_C (= k_1/k_2)$ is the equilibrium constant. Equation 1.11 can be rewritten in a different form as:

$$\ln [1 - U(t)] = -k' t \quad (1.12)$$

where $k' (= k_1 + k_2)$ is the overall rate constant, and $U(t) (=X_A/X_A^e)$ is the fractional attainment of equilibrium.

The overall rate constant k' (= the slope of the straight-line portion of the plot according to equation 1.12) can be correlated to diffusion coefficients as (Helfferich, 1962):

$$t_{1/2} = 0.03 r^2/D \quad (1.13)$$

$$t_{1/2} = 0.23 r^2 \delta C/(C^*D^*) \quad (1.14)$$

where $t_{1/2}$ is the time at which $X/X_e = 1/2$ (given by $(\ln 2)/k'$), r is the mean radius of adsorbent particles (assuming spherical geometry), D and D^* are the pore and film diffusion coefficients, respectively, C/C^* is the equilibrium loading of the adsorbent, and δ is the film thickness.

1.2.3. Estimation of adsorption capacity: Breakthrough curves

When a solution containing an adsorbate is passed through a fixed bed of a suitable adsorbent, the concentration of adsorbate in the effluent remains negligibly small until breakthrough occurs. Plotting effluent concentration versus effluent volume yields the breakthrough curve, as shown in Figure 1.1. *Breakthrough* is the term used to describe that point in the experiment (represented by V_E) after which there is a rapid, continuous increase in effluent concentration until the bed is exhausted.

For a fixed-bed unit operating at a steady liquor flow rate, and for which a symmetrical breakthrough *S*-curve has been obtained experimentally, the height of the mass transfer zone, h_Z , and the specific dynamic adsorption capacity, C_T , are given, respectively, by the relations (Michaels, 1952):

$$h_Z = h_T [V_Z / (V_T - 0.5 V_Z)] \quad (1.15)$$

$$C_T = \int_0^{V_T} (X_0 - X) dV/m \quad (1.16)$$

where h_T is the bed height, V_T is the volume of effluent collected upon exhaustion of the bed, V_E is the volume of effluent collected up to breakthrough, $V_Z = V_T - V_E$, X_0 is the influent concentration, X is the effluent concentration, V is the effluent volume, and m is the mass of adsorbent.

Several workers (Kocirik et. al., 1982; Ko et. al., 2000; Chern and Chien, 2002) have used breakthrough curves to study and evaluate the sorption of various adsorbates on various adsorbents.

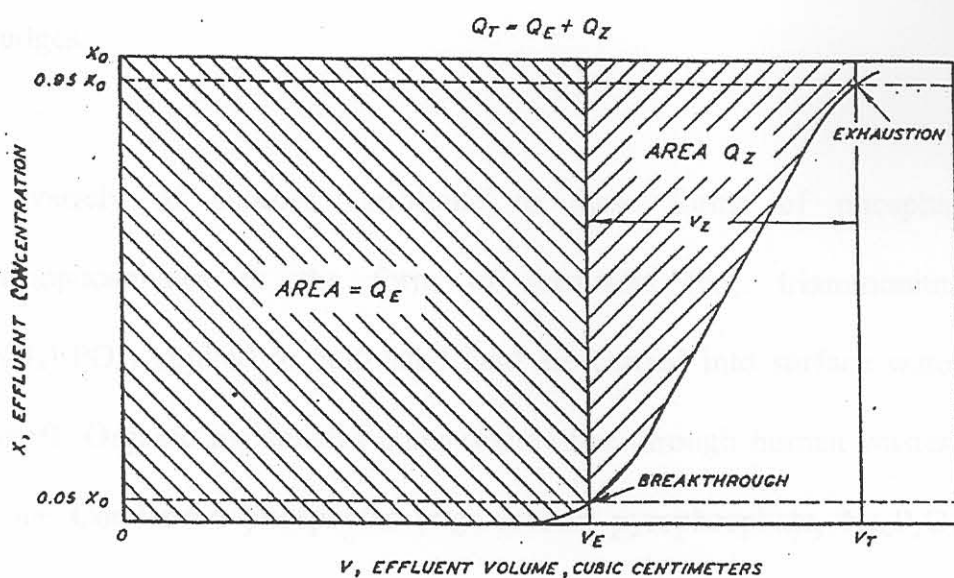


Figure 1.1. Idealised breakthrough curve for a fixed bed column (Michaels, 1952).

1.3. Phosphates in water

1.3.1. Forms and sources of phosphorus in water

Phosphorus occurs in natural waters and wastewater almost invariably as various forms of phosphates (Arnold, 1985). These are orthophosphates (PO_4^{3-} , HPO_4^{2-} , and PO_4^-), condensed phosphates (pyro-, meta-, and other polyphosphates, e.g. $\text{P}_2\text{O}_7^{4-}$, $\text{P}_3\text{O}_{10}^{5-}$, and $\text{P}_3\text{O}_9^{3-}$), and organically bound organic phosphates. They occur in solution, in particles, in aquatic organisms, in bottom sediments, and in biological sludges.

A variety of sources contribute to these forms of phosphate in water. Orthophosphates in the form of fertilisers (e.g. triammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$) applied to cultivated land are carried into surface waters with storm runoff. Organic phosphates enter wastewater through human wastes, primarily as urine. Condensed phosphates (e.g. sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$ and sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$) are used in the synthesis of commercial detergent formulations because they form soluble complexes with Ca^{2+} and Mg^{2+} ions in tap water, preventing the deposition of scum in the washing. These phosphates subsequently pass into the water used for laundering and cleaning (Sundstrom and Klei, 1979). Phosphates (e.g. Na_3PO_4) are also used extensively in the treatment of

boiler waters to remove hardness by precipitating Ca^{2+} and Mg^{2+} ions as the phosphates, preventing the formation of boiler scale, which can lead to the blocking of pipes.

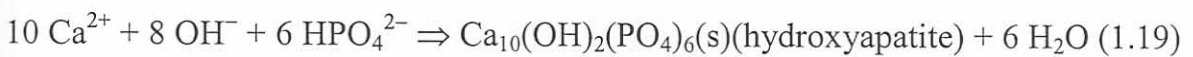
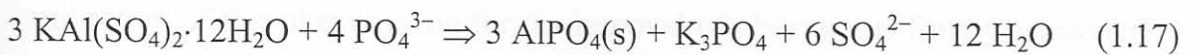
1.3.2. Large-scale removal of phosphorus from wastewater and effluents

Eutrophication, the gradual increase in the levels of phosphorus, nitrogen, and other plant nutrients in an ageing aquatic ecosystem such as a lake, leads to an explosion in algae growth, which eventually results in a lack of light penetration and oxygen absorption that is necessary for underwater life (Britannica, 1989). Cultural or anthropogenic eutrophication, resulting from runoff containing excessive amounts of nutrients in the form of sewage, detergents, and fertilisers, is a well-known environmental concern. It is known that phosphorous is usually the limiting nutrient for the onset of eutrophication (Droste, 1997); therefore, the control of phosphorus concentrations in effluents is especially important.

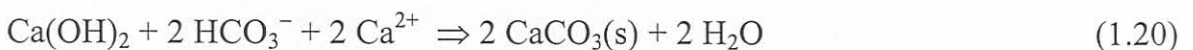
Total phosphorus concentrations in raw wastewater are typically in the range of 4-10 mg/L, which must be reduced to 1 mg/L or less in order to meet environmental requirements (Eckenfelder, 1980). The majority of phosphorus compounds in wastewater are soluble, mostly orthophosphates (micro-organisms present in sewers slowly convert condensed phosphates into orthophosphates). They are not, therefore, adequately removed by plain sedimentation. Chemical precipitation and

microbiological treatment, usually in conjunction with each other, are the two commonly used processes for the large-scale removal of phosphate from wastewater.

Chemical agents used to precipitate phosphorus are compounds of calcium, iron, or aluminium, these being metals that form sparingly soluble salts with dissolved forms of phosphate. Examples of such coagulants are alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), FeCl_3 , and lime, and the complex reactions involved may be simplified as (Droste, 1997):



Apatites are highly insoluble, which makes lime the most efficient agent for phosphate precipitation. However, a high pH (ca 10) is required for apatite formation, and Ca^{2+} tends to consume additional lime and then precipitate as CaCO_3 in the presence of carbonate alkalinity:



This means that very high doses of lime are required (Droste, 1997), which makes the process rather costly. The precipitates are subsequently physically removed by sedimentation, and the lime sludge produced may be dewatered and discarded or recalcined in a furnace to recover part of the lime.

When sludge containing certain microorganisms (e.g. *Acinetobacter*) is subjected to anaerobic conditions, phosphorus is released to solution; when the sludge is subsequently mixed with wastewater and then subjected to aerobic conditions, an immediate accumulation of phosphorus by the activated sludge occurs. Several workers (Bouck, 1978; Bark et. al., 1992; Rasmussen et. al., 1994) have studied the utilisation of this phenomenon for the removal of phosphorus from wastewater, and the process is used on a large scale.