Adsorption Design for Wastewater Treatment

ADSORPTION DESIGN for WASTEWATER TREATMENT

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Preface

Adsorption is a very important method for removing contaminants, particularly organic contaminants, from wastewater streams. The usual adsorbent is activated carbon. The process is often carried out in a batch mode, by adding powdered activated carbon to a vessel containing the contaminated water, stirring the mixture for a sufficient time, then letting the carbon settle, and drawing off the cleansed water. Just as often, the process is carried out by feeding the water continuously to a packed bed of granular activated carbon. The carbon gradually becomes exhausted (i.e., its capacity to adsorb the contaminant is used up), proceeding from the inlet end to the outlet end, until there occurs "breakthrough" of the contaminant in the effluent. When the outlet concentration reaches some predetermined level, the unit is shut down, the carbon is dumped, and fresh carbon is added.

Activated carbon is also used extensively for adsorbing contaminants from drinking water sources (usually rivers, lakes, or reservoirs). However, drinking water sources differ significantly from wastewaters in two important ways: (1) the contaminant levels in most drinking water sources are quite low as compared with contaminant levels in wastewaters derived from industrial-type activities and (2) drinking waters are also commonly treated by several other methods, such as coagulation/flocculation, sedimentation, filtration, and chlorination, whereas wastewaters often require only treatment by adsorption. Since this book focuses only on adsorption, and not on other treatment methods, and because the examples presented involve quite significant contaminant levels, the book therefore pertains mainly to wastewaters, not drinking waters. Notwithstanding this, it should be stated that the adsorption design methods used for wastewaters are equally valid for drinking waters.

The "designs" we are concerned with in this book are those pertaining to a mixed contacting vessel in a batch operation and the fixed-bed column of granular carbon in a continuous-flow operation. That is, we are not concerned with ancillary equipment, such as pumps, mixing motors/propellers, piping, storage vessels, etc., that make up the rest of these overall systems. In other words, we will only size the equipment which contains the activated carbon.

Designing a batch adsorption vessel amounts to determining how much carbon needs to be added to the water (e.g., in milligrams of carbon per liter of solution), and deciding whether to break the process into more than one stage of treatment. Designing a fixed-bed adsorber amounts to determining the diameter and depth of the granular carbon bed required to give the desired service time until the breakthrough concentration occurs in the effluent.

This book has been written for students and practicing engineers who wish to learn how to design batch adsorption units and fixed-bed adsorbers without having to delve into long, detailed, and largely theoretical treatises on adsorption. The design methods are presented mainly in Chapters 6 and 8. Chapters 1 through 5 contain material which lays the groundwork for an intelligent understanding of the physical and chemical processes taking place in such systems. These chapters describe the production and important properties of activated carbons, the fundamental nature of adsorption, ways of determining adsorption equilibria experimentally and fitting the data to equations, and the basic mechanisms involved in adsorption kinetics. These chapters, along with Chapter 6, are sufficient for designing batch contactors. For designing fixed-bed adsorbers, we give an introductory survey of various mathematical descriptions of fixed-bed behavior in Chapter 7. These descriptions are generally too detailed for practical application, or require knowing parameters which are difficult to determine. Thus, the simpler and more tractable design methods which are usually used in practice are presented in detail in Chapter 8.

As mentioned earlier, this book should be of value to practicing engineers. Academically, this book will be of use to those students in civil, chemical, and environmental engineering, at junior/senior undergraduate levels and graduate student levels, who wish to learn about adsorption.

This book differs significantly from other books on adsorption. First, this book has been limited in scope to adsorption design methods, plus just enough background material to permit the reader to understand the fundamentals of what goes on in adsorption systems.

Second, and most important, the central chapters on equilibria, kinetics, and design methods (Chapters 4, 5, 6, and 8) are presented in textbook style, with many illustrative examples, and a wide variety of homework problems. Some of the background chapters (e.g., Chapters 2 and 7) also have example and homework problems.

Thus, the book is not meant to be an extensive treatise on adsorption. For an excellent, more exhaustive, and more fundamental treatment of adsorption, the reader may wish to consult the monograph *Principles of Adsorption and Adsorption Processes*, by Ruthven.[1] Other monographs on adsorption include *Adsorption Calculations and Modeling*, by Tien;[2] *Adsorption Engineering*, by Suzuki;[3] and *Adsorption Technology for Air and Water Pollution Control*, by Noll, Gounaris, and Hou.[4] These monographs present much of the same type of material on batch kinetics given in Chapter 5, and many of the theoretical descriptions of fixed-bed behavior given in Chapter 7. However, the treatments of these topics are generally quite mathematical and detailed, with no examples. None of these four monographs cover any of the batch and fixed-bed design methods presented in Chapters 6 and 8 of the present work. Finally, being monographs, they contain no homework problems.

Another monograph on adsorption is *The Little Adsorption Book*, by Basmadjian.[5] This short but excellent book is subtitled "A Practical Guide for Engineers and Scientists," and indeed it contains many practical examples.

However, the book deals primarily with gas and vapor adsorption, chromatography, and non-isothermal operations (desorption, purging, regeneration). There is little overlap with the present book.

In many ways, the book which comes closest to the present one is *Adsorption Processes for Water Treatment*, by Faust and Aly.[6] This excellent work contains much of the same background material as the present book, and also discusses the design methods described in Chapters 6 and 8. However, this book includes a wide variety of additional topics, such as inorganic compound adsorption, combined biological/carbon treatment processes, a variety of case studies, and the use of resins as adsorbents. Thus, the book does not lend itself to a limited treatment of adsorption. Additionally, though containing some detailed example problems, the book has no homework problems.

This is a good place to state that bacterial degradation of adsorbed solutes can often be significant in fixed-bed operations; however, in order to keep the present treatment down to a moderate length, we will not consider this removal mechanism in this text. The Tien and Faust/Aly books just mentioned offer excellent treatments of this subject.

Beyond the books just discussed, there are volumes which are compilations of papers presented at research conferences. These are, of course, not textbooks, but they are a valuable source of much information on adsorption, particularly on practical applications. These books include (1) *Activated Carbon Adsorption of Organics from the Aqueous Phase* (two volumes), edited by Suffet and McGuire;[7] (2) *Treatment of Water by Granular Activated Carbon*, edited by McGuire and Suffet;[8] and (3) *Application of Adsorption to Wastewater Treatment*, edited by Eckenfelder.[9] There are also five conference proceedings volumes to date which have come out of a series of international conferences on the *Fundamentals of Adsorption*, held for 6 days in May every 3 years since 1983. The conference locations, conference years, and proceedings editors are

- First: Klais, Bavaria, West Germany, 1983, Myers and Belfort.[10]
- Second: Santa Barbara, CA, 1986, Liapis.[11]
- Third: Sonthofen, East Germany (formerly), 1989, Mersmann and Scholl.[12]
- Fourth: Kyoto, Japan, 1992, Suzuki.[13]
- Fifth: Pacific Grove, CA, 1995, LeVan.[14]

May 24 to 29, 1998 are the dates of the Sixth conference, in Gien, France.

Additionally, there are many volumes of the "handbook" type, containing a series of chapters written by different authors. These also are very valuable sources of information on practical applications of adsorption. Some of these are (1) *Carbon Adsorption Handbook*, edited by Cheremisinoff and Ellerbusch;[15] (2) *Activated Carbon Adsorption for Wastewater Treatment*, edited by Perrich;[16] (3) *Use of Adsorbents for the Removal of Pollutants from Wastewaters*, edited by McKay;[17] and (4) *Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application*, edited by Slejko.[18] Most of the material in these four books is general and descriptive; however, the Perrich and McKay volumes do contain brief treatments of batch and fixed-bed design methods, but without concrete examples. Indeed, in all of these four books, there are few example problems and, of course, no homework problems.

Let us now mention some books which, on the surface, may appear to relate significantly to the topic of adsorption, but which, in fact, do so in only a limited way. The first are the fairly large number of books dealing with general physicochemical and biological methods of water and wastewater treatment. These books contain rather limited treatments of adsorption, generally one to two chapters, and only a few homework problems relating to adsorption (on the order of 6 to 12 total). They are simply too brief to be used as adsorption texts, unless this level of brevity is, in fact, desired. However, their limited material on adsorption may nevertheless be of some interest to the reader. Examples of such books are (1) *Wastewater Treatment*, by Sundstrom and Klei;[19] (2) *Water and Wastewater Treatment*, by Humenick;[20] and (3) *Process Chemistry for Water and Wastewater Treatment*, by Benefield, Judkins, and Weand.[21]

Then there are a number of "environmental engineering" books. These are similar to "water and wastewater" books in that they cover a wide range of topics. However, since their coverage goes far beyond water pollution, and includes air pollution, solid waste disposal, etc., the coverage of adsorption is usually extremely brief, often amounting to only one to two pages. As examples of these, three titles will be mentioned: (1) *Introduction to Environmental Engineering*, 2nd edition, by Davis and Cornwell;[22] (2) *Environmental Engineering*, 3rd edition, by Vesilind, Peirce, and Weiner;[23] and (3) *Environmental Systems Engineering*, by Rich.[24]

Thus, we have tried to explain what this book is, and what it is not. In summary, it is a textbook or short reference work on adsorber design, with sufficient background material to acquaint the reader with fundamental relevant knowledge of adsorption.

The author has used this text in manuscript form several times for a 4-week treatment of adsorption in a first-year graduate course populated with civil, chemical, and environmental engineering students. The book can be covered completely in this 4-week period. All of Chapters 1 through 3 can be covered in one class session. Chapters 4, 5, and 6, each with assigned homework, should require only two class periods each. And, although Chapter 7 is rather detailed, for the purposes of the book it also can be covered in two sessions. This leaves a full three classes for Chapter 8. This type of schedule has worked well for the writer.

A Discussion of Units Used in This Text

Adsorption books which deal both with fundamentals and with practical applications typically use a rather wide mixture of units. The units are neither strictly SI (kg, m, s), nor English Engineering (lb mass, ft, s). In the SI system, units with prefixes such as "k" (kilo, 10^3), "m" (milli, 10^{-3}), "c" (centi, 10^{-2}), and "μ" (micro, 10^{-6}) are common, e.g., cm, mg. The mass unit of "mol" or mole (by which we usually mean a gram-mole) is frequently employed. Many units derived from the basic SI units are used, such as m^3 and the liter (l, 1×10^{-3} m^3).

In the English Engineering system, time units in seconds, minutes, hours, and days are all commonplace. Also, the derived volume unit of ft^3 and the related unit of gallons (gal) are also used routinely.

Typical units for common quantities are:

- Weights: kg, g, mg, μg, mol, mmol, μmol, lb
- Volumes: m^3, l, ml, ft^3 gal
- Concentrations of a substance adsorbed on a solid: mg/g, g/g, mmol/g, lb/lb
- Concentrations of a substance in a liquid: g/l, mg/l, μg/l, mol/l, mmol/l, μmol/l, ppm, lb/ft^3, lb/gal
- Flow rates: l/min, m^3/min, ft^3/s, ft^3/h, gpm (gal/min), gal/d, etc.
- Temperatures: K, °C, °F

For example, when dealing with adsorption equilibria (Chapter 4) one often relates the amount of a solute A adsorbed on activated carbon, in mg A/g carbon, to the residual concentration of A in the surrounding liquid, in mg A/L of solution. And yet, in designing fixed-bed adsorbers (see Chapter 8), while the concentrations in the liquid stream are usually also given in mg/l or ppm, the total flow rate to the adsorber is often cited in terms of gallons/day, and the "hydraulic loading" (flow rate per unit empty-bed cross-sectional area) usually is gpm/ft^2 (i.e., gallons per minute per square foot). The "carbon usage rate" is usually determined in lb/1000 gal, that is, pounds of carbon per 1000 gallons of feed treated (in SI units, one would use kg/m^3). Thus, just in this one chapter (Chapter 8), a wide range of units is involved.

When considering the kinetics of mass transfer of a solute to the surface of a carbon particle, and its rate of diffusion inside the particle, as we do in Chapter 5, the "mass transfer coefficient" values are typically given in cm/s and the "diffusion coefficient" values are usually cited in cm^2/s. Hence, for these topics, the most common system is not true SI, but the closely related "cgs" (cm-g-s) system.

The main reason for the mixture of SI and English units is that the fundamental scientific aspects of adsorption (kinetics, equilibria) have been studied by academics, who prefer to use SI and SI-derived units, while design and operational aspects of adsorption have been the province of municipal, industrial, and consulting personnel, who favor traditional English Engineering units.

In this book, the units which are used are those which have been used in previous books and articles for the topic being considered. We will not engage in the practice of giving the magnitude and units for a quantity in one system, with the magnitude and units in the other system in parentheses. As pointed out below, the conversion from one system to another is really quite simple.

This book could have been written totally in SI units, as many current undergraduate textbooks have been. While this might be laudatory in terms of trying to "force" readers to convert uniformly to SI, the reality of life is that English units are still deeply embedded in practice. Graduating engineers must work in the real world, and thus must be comfortable in both systems, at least for the immediate future.

Being versatile in both systems is really rather easy. If one is familiar with the meaning of prefixes (c, m, k, μ) and knows a few simple equivalences, such as 1 ft = 0.3048 m, 1 ft³ = 7.48 gal, and 1 lb = 453.6 g, little more is really needed. For example, to convert a flow rate from 20,000 gal/day into m³/s, one need only write

$$\frac{20{,}000\ \text{gal}}{\text{day}}\ \frac{\text{day}}{24\ \text{h}}\ \frac{\text{h}}{3600\ \text{s}}\ \frac{\text{ft}^3}{7.48\ \text{gal}}\left(\frac{0.3048\ \text{m}}{\text{ft}}\right)^3 = 0.000876\,\frac{\text{m}^3}{\text{s}}$$

Or, rather than "stringing together" all of these simple conversion factors, one can use some of the conversion factors given below for reference. By using these, the conversion just illustrated is simplified to

$$\frac{20{,}000\ \text{gal}}{\text{day}}\ \frac{\text{day}}{86{,}400\ \text{s}}\ \frac{0.003786\ \text{m}^3}{\text{gal}} = 0.000876\,\frac{\text{m}^3}{\text{s}}$$

Some Useful Equivalences and Conversion Factors

Equivalences within Each System

1 m³ = 1000 l
1 ft³ = 7.48 gal
1 day = 1440 min = 86,400 s
K = °C + 273.15

Conversion Factors: English to SI

1 ft = 0.3048 m
1 ft³ = 0.02832 m³ = 28.32 l
1 gal = 0.003786 m³ = 3.786 l
1 lb = 453.6 g = 0.4536 kg
1 lb/ft³ = 16.02 kg/m³
1 gpm/ft² = 0.1337 ft³/ft²-min or ft/min = 0.0408 m³/m²-min or m/min = 58.68 m/day

Conversion factors: SI to English

1 m = 3.281 ft
1 m^3 = 35.31 ft^3 = 264.2 gal
1 l = 0.0353 ft^3 = 0.2462 gal
1 kg = 2.205 lb
1 kg/m^3 = 0.0624 lb/ft^3

Acknowledgment

A significant portion of the material on pages 10–23 (Chapter 2) and on pages 29–36 (Chapter 3) appeared previously in my book *Activated Charcoal in Medical Applications*, Marcel Dekker, New York, 1995. It is used here with the kind permission of Marcel Dekker, Inc.

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Contents

1

Adsorption for Wastewater Treatment

Many wastewaters contain significant levels of organic contaminants which are toxic or otherwise undesirable because they create odor, bad taste, unsightly color, foaming, etc. These substances are often resistant to degradation by biological methods, and are not removed effectively by conventional physicochemical treatment methods, such as coagulation/flocculation, sedimentation, filtration, and ozonation.

Because activated carbon has a strong affinity for binding organic substances, even at low concentrations, it has become the premier method for treating organic-laden wastewaters. It also is widely used for purifying drinking water from sources containing relatively small but offensive levels of organic contaminants.

Activated carbons, both powdered and granular, are made from a wide variety of carbonaceous starting materials: coals (anthracite, bituminous, lignite), wood, peat, coconut shells, etc. They are manufactured in such a way that they have a tremendous network of pores inside, and the total surface area inside such carbons is typically 500 to 1500 m^2/g, a huge amount. It is this extensive surface on which adsorption of organics can occur. Adsorption amounts up to as high as 0.30 g organic/g carbon are not unusual. Experimental activated carbons have been made with over 3000 m^2/g surface area which are capable of adsorbing more than their own weight of organic substances!

The use of activated carbon in a wastewater treatment facility can involve either granular or powdered carbon. If the carbon is used in granular form, it is placed inside a cylindrical steel vessel with screens in the bottom and top to confine the carbon in the form of a packed bed. More than one vessel may be used, with the vessels being connected either in series or in parallel. The water usually flows downward in each column, either pressure driven (with a pump) or gravity driven. Most real feed streams contain suspended solids, which are largely filtered out as the feed passes through the carbon bed. Therefore, the bed must be periodically backwashed (with as much as 50% expansion of the bed), to flush out these solids. Alternatively, a pressure-driven