# **Publications on Adsorption Science and Technology**

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**Abstract.** A key word search of Chemical Abstracts Registry and Derwent Patent Index on various topics of Adsorption Science and Technology between 1970–2000 reveals an immense volume of patents and publications in this area. A detailed breakdown of this search is provided.

**Keywords:** literature, patent, adsorption science and technology, bibliography

Adsorption science and technology has been a subject of considerable interest during the last forty years among many academic and industrial scientists and engineers around the world. This is evident from the extraordinarily large number of technical publications on various aspects of this subject in the scientific and patent literature. Some of the key driving forces behind this phenomenal interest in adsorption are given below:

- (a) Adsorption technology has found numerous practical applications for separation and purification of gaseous and liquid mixtures in the chemical, petrochemical, biological, pharmaceutical, environmental and electronic industries. Some of the key application areas are listed in Table 1. The application portfolio continues to grow.
- (b) Numerous micro-mesophorous, crystalline, and amorphous families of adsorbents like zeolites, activated carbons, silica and alumina gels, ion-exchange resins, polymeric sorbents, etc. having a large spectrum of surface chemistry and pore structures are synthesized for carrying out the desired separations. Physico-chemical characterization of these materials as well as synthesis of novel or modified materials are ongoing efforts.
- (c) A large variety of generic process concepts like temperature swing adsorption (TSA) for trace impurity removal from gas and liquid mixtures, pressure swing adsorption (PSA) for bulk gas separation, high pressure liquid chromatography and simulated

- moving bed (SMB) adsorption for bulk liquid separation, etc. have been commercialized to serve the market needs. The optimal marriage between the adsorbent and the process introduces immense scope for new innovations.
- (d) Experimental and theoretical studies of multicomponent adsorption equilibria, kinetics, and heats, which form the core fundamental variables for design of adsorptive processes, continue to be very active and challenging research fields due to the complex nature of fluid-solid adsorption on heterogeneous porous solids of practical interest. Understanding adsorption at the molecular level is a relatively newer research direction in this area.
- (e) Extensive efforts are made for developing fast, efficient and accurate methods of solving mathematical models for adsorptive process design using the above described fundamental properties.
- (f) Development of adsorption process hardware, machinery and control systems continue to improve the economics and enlarge the scale of application of this technology.
- (g) Novel concepts like adsorbent membranes for gas separation, gas and liquid phase sorption-reaction for simultaneous generation and separation of desired products, gas storage and energy production using adsorbents, etc. are emerging frontiers for this technology.

Publications on adsorption science and technology cover all of the above areas and much more. The

Table 1. Key commercial applications of adsorption technology.

# Gas separation

- Gas drying
- Trace impurity removal
- Air separation
- Carbon dioxide-methane separation
- Carbon monoxide-hydrogen separation
- Solvent vapour recovery

# Liquid separation

- Liquid drying
- Trace impurity removal
- Xylene, cresol, cymene isomer separation

#### Environmental separation

- Municipal and industrial waste treatment
- VOC removal

Bioseparation and pharmaceutical separation

- Recovery of antibiotics
- Purification and recovery of enzymes
- Purification of proteins

#### Electronic gas purification

- $\bullet$  Production of ultra high purity  $N_2,$  Ar, He,  $H_2,\,O_2$
- Purification of fluorinated gases NF3, C2F6, CF4, SiF4
- Purification of hydrides NH<sub>3</sub>, PH<sub>3</sub>, ASH<sub>3</sub>, SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub>

- Hydrogen and carbon dioxide recovery from steam methane reformer off-gas
- Hydrogen recovery from refinery off-gases
- · Alcohol dehydration
- Production of ammonia-synthesis gas
- Normal-iso paraffin separation
- Ozone enrichment
- Fatty chemical separation
- Olefin-paraffin separation
- Fructose and glucose separation
- Breaking azeotropes
- Carbohydrate separation
- Ground and surface water treatment
- Air pollution control
- Removal of micro-organisms
- Recovery of vitamins
- Separation of enantiomers of racemic compounds
- Home medical oxygen production

purpose of this article is to provide an idea of the size of this vast literature through key word searches (Title and Index only) in the Chemical Abstracts Registry (CAR) and the Derwent Patent Index (DPI). All searches were conducted between the years of 1970 and 2000 (May).

Table 2 summarizes the CAR search results using general key words like adsorption, chemisorption,

Table 2. Title and index terms in chemical abstracts literature citations (1970–2000) (General topics).

Terms	Total entries	Languages (%)								
		English	Russian	German	French	Chinese	Japanese	Others		
Adsorption	134,300	66.1	17.7	3.0	1.6	3.8	4.2	3.6		
Chemisorption	20,390	76.2	15.6	1.7	1.6	1.9	1.3	1.7		
Ion exchange	38,517	56.0	22.6	4.1	1.8	4.4	4.9	6.2		
Chromatography	230,130	69.6	7.9	4.6	1.7	5.5	5.4	5.3		
Adsorbent	16,074	51.1	26.2	3.7	1.0	5.1	7.1	5.8		
Gas adsorption	8,473	61.2	18.9	5.2	1.8	3.6	5.0	4.3		
Liquid adsorption	4,835	68.1	17.7	2.6	1.6	3.3	3.4	3.3		
Bio sorption	878	83.1	5.8	1.8	0.6	3.8	1.6	3.3		

Table 3. Title and index terms in chemical abstracts literature citations (1970–2000) (Specific application topics).

	Total entries	Languages (%)							
Terms		English	Russian	German	French	Chinese	Japanese	Others	
Gas separation by adsorption	722	51.1	22.9	9.4	1.0	3.7	6.6	5.3	
Liquid separation by adsorption	444	64.6	16.2	2.9	0.7	5.6	5.0	5.0	
Bio separation by adsorption	8	75.0	_	_	_	25.0	_	_	
Air pollution and adsorption	701	72.2	4.4	7.0	1.3	2.0	8.1	5.0	
Waste water treatment and adsorption	1,324	52.0	13.5	7.5	1.7	4.0	16.2	5.1	
Gas drying by adsorption	508	_	_	_	_	_	_	_	
Liquid drying by adsorption	51	_	_	_	-	_	_	_	

Table 4. Title and index terms in chemical abstracts literature citations (1970–2000) (Specific science and technology topics).

	Total entries	Languages (%)							
Terms		English	Russian	German	French	Chinese	Japanese	Others	
Adsorption equilibria	2,741	66.5	17.9	3.3	1.0	2.8	4.2	4.3	
Adsorption kinetics	13,826	71.4	17.9	2.2	1.4	2.8	1.4	2.9	
Adsorption heat	9,554	63.1	22.1	3.2	2.8	2.3	2.7	3.8	
Pressure and vacuum swing adsorption	871	68.1	1.6	5.1	0.6	6.0	12.1	6.5	
Temperature swing adsorption	72	83.3	_	2.8	1.4	4.2	6.9	1.4	
Simulated moving bed adsorption	14	85.7	-	-	-	-	14.3	-	

ion-exchange, chromatography and adsorbent. The total number of entries in each area is overwhelming. Chromatography appears to be the most popular topic of work. The number of entries for gas, liquid, and bio adsorption as key words indicate that much more work has been done on gas adsorption than liquid adsorption, while bio sorption is a relatively newer area.

Table 3 lists the results of CAR search for several application topics in the areas of gas, liquid and biological separations. It again shows that there are more publications on gas separation than liquid separation, and those for bio separation are only emerging. The list also shows that considerable effort is made in using adsorption for control of air and water pollution. Gas drying by adsorption appears to be a more popular subject than liquid drying by adsorption.

Table 4 gives the number of citations in CAR for several specific scientific topics like adsorption equilibria, kinetics, and heats. It appears that all of these core areas have received significant attention in the published literature. Table 4 also shows the number of publications on specific adsorptive processes (TSA, PSA and SMB) for gas and liquid separation. Publications on PSA dominate the literature.

The reason for such a large volume of articles on adsorptive processes is that they have become the state of the art technologies for many industrial applications. For example, TSA is the process of choice for most trace impurity removal needs from gases and liquids; PSA is the preferred technology for (a) many small to large scale gas drying operations (product dew point  $\sim$  -40°C, (b) small to large scale production of high purity (99.99+%) hydrogen from many hydrogen containing gas sources (e.g., steam-methane reformer or refinery off gases), (c) production of small to medium scale oxygen (90–95% purity) and nitrogen (98+% purity) enriched gas from ambient air; SMB is frequently chosen for small to large scale separation of liquid mixtures which are difficult to separate by distillation alone (e.g. olefins from paraffins, isomer mixtures, mixtures of carbohydrates, mixtures of enantiomers).

The application size range of these technologies are immense. For example, oxygen-PSA sizes may range between 0.012–100 TPD, hydrogen-PSA sizes can be between 1.0–100.0 MMSCFD, SMB processes are designed to process 100–100,000 TPY of bulk chemicals and 10–50 TPY of enantiomers. Clearly,

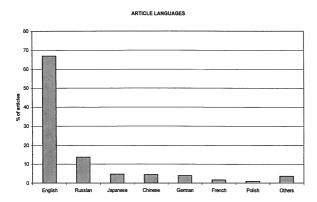


Figure 1. Adsorption literature breakdown by languages.

the commercial interests in these areas are very large, which explains the high volumes of scientific and engineering publications on these subjects.

Tables 2–4 also give breakdowns (percentage of total) of the languages used in these publications. English is the most frequently used language for all topics. Figure 1 shows a bar chart summary of the languages used by all of the entries presented in these tables. It shows that Russian language is a distant second ( $\sim$ 14%) to English ( $\sim$ 67%). Japanese ( $\sim$ 4.7%), Chinese ( $\sim$ 4.4%), German ( $\sim$ 3.9%), French ( $\sim$ 1.7%) and Polish ( $\sim$ 1.0%) are the other languages which contributed to 1% or more of these publications.

Figure 2 shows a year-by-year tally of U.S. Patents issued between 1980 and 2000 (May) on five different topics related to adsorptive gas and liquid separations. They were obtained from the DPI using the key words given in the figure. A very impressive number of patents has been granted by the U.S. Patent Office on all of these subjects. However, gas separation by adsorption dominates the field. The figure also demonstrates that there is a steady average growth in the number of patents issued per year over the last twenty years in all areas except bioseparation. The data in Fig. 2 provide good examples of commercial interests in practical applications of adsorption technology for gas and liquid separations.

Figure 3 shows the number of U.S. Patents issued every year between 1980 and 2000 (May) on three specific applications of PSA technology, viz. air separation, hydrogen production, and gas drying. A total of 608 patents were issued in these areas. About 65% of these patents deal with air separation by adsorption and about 30% are on hydrogen production by adsorption. The assignorships of these patents are distributed among 159 corporations around the world. The corporations holding major fractions of these PSA patent portfo-

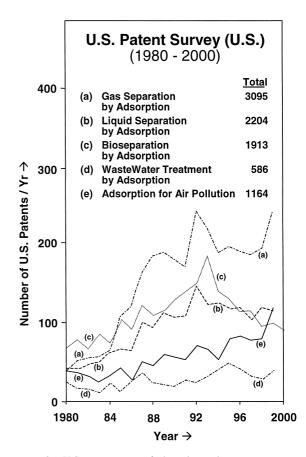


Figure 2. U.S. patent survey of adsorption topics.

lios include British Oxygen Corporation of the U.K. (17.6%); Air Products and Chemicals (11.6%), Praxair (6.6%), Union Carbide Corporation (7.7%) and UOP Corporation (5.0%) of the U.S.A.; and Air Liquid Corporation (6.2%) of France. Other notable corporations who have been active in this area include Linde AG, Bayer AG and Bergwerksverband GMBH of Germany; Seitetsu Kagaku Corporation, Sumitomo Seika Chemicals, and Kuraray Chemicals of Japan; Imperial Chemical Industry of the U.K.; Pall Corporation, Green and Kellog, Airsep Corporation, Nitrotec Corporation and Litton Systems of the U.S.A. This clearly demonstrates the commercial interest and the high level of activity in the development of the PSA technology around the world. Figure 3 also shows that there is a steady average growth for patent activity in the air separation and hydrogen production areas while that for gas drying appears to have leveled off.

A large number of monographs have also been published covering many different aspects of adsorption science and technology. A selected list of book titles

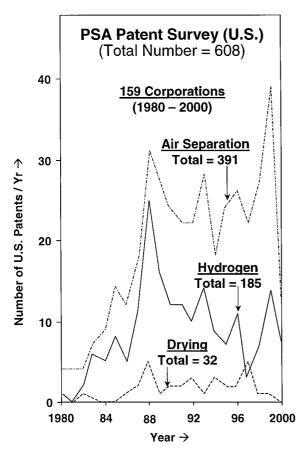


Figure 3. U.S. patent survey of pressure swing adsorption applications.

and book chapters dealing with physical chemistry, engineering science, and materials of adsorption is given in the appendix. Books dealing exclusively with ion exchange and chromatography are not included in this list. Most of these books emphasize the author's areas of expertise and some of them provide up-to-date reviews of the subject matter at the time of their publication.

Other important literature on the topics of adsorption include (a) the journal entitled "Adsorption" which is the flagship publication (since 1995 by Kluwer Academic Publishers in the Netherlands) of the International Adsorption Society founded in 1989, and (b) the journal entitled "Adsorption Science and Technology" published by Multi-Science Publishing Company in the United Kingdom since 1984. In addition, the proceedings of many periodic international conferences, which exclusively deal with the subject of adsorption, provide information on the current state of research and devel-

opment in this area. Two notable conferences are the annual meetings of the American Institute of Chemical Engineers and the triennial conferences on Fundamentals of Adsorption (since 1983).

Despite such a voluminous history of publication in this area, the complex but fascinating field of adsorption will provide many new challenges and opportunities to scientists and engineers for many years to come. So expect many more publications in the future.

# Appendix: Selected List of Books and Book Chapters on Adsorption Science and Technology

Physical Chemistry

- "Physical Adsorption of Gases," D. M. Young and A. D. Crowell, Butterworths, London (1962).
- "Chemisorption," D. O. Hayward and B. M. W. Trapnell, Butterworths, London (1964).
- "On Physical Adsorption," S. Ross and J. P. Olivier, Interscience Publishers, New York (1964).
- "Adsorption from Solutions of Non-electrolytes," J. J. Kipling, Academic Press, London (1965).
- "Surface Tension and Adsorption," R. Defay, I. Prigogine, A. Bellemans and D. H. Everett, John Wiley, New York (1966).
- "Introduction to Powder Surface Area," S. Lowell, John Wiley, New York (1979).
- "Physical Chemistry of Surfaces," A. W. Adamson, John Wiley, New York (1982).
- "Adsorption, Surface Area and Porosity," S. J. Gregg and K. S. W. Sing, Academic Press, London (1982).
- "Adsorption and the Gibbs Surface Excess," D. K. Chattoraj and K. S. Birdi, Plenum Press, New York (1984).
- "Physical Adsorption on Heterogeneous Solids," M. Jaronicc and R. Madey, Elsevier, New York (1988).
- "Adsorption of Gases on Heterogeneous Surfaces," W. Rudzinski and D. H. Everett, Academic Press, London (1992).
- "Diffusion in Zeolites and Other Porous Solids," J. Kärger and D. M. Ruthven, John Wiley, New York (1992).
- "Physical Adsorption: Forces and Phenomenon," L. W. Bruch, M. W. Cole and E. Zaremba, Clarendon Press, Oxford (1997).
- "Adsorption Analysis: Equilibria and Kinetics," D. D. Do, Imperial College Press, London (1998).
- "Adsorption by Powders and Porous Solids,"

F. Rouquerol, J. Rouquerol and K. S. W. Sing, Academic Press, London (1999).

#### **Engineering Science**

- "Principle of Adsorption and Adsorption Processes," D. M. Ruthven, John Wiley, New York (1984).
- "Adsorption Technology," F. L. Slejko (ed), Marcel Dekker, New York (1985).
- "Gas Separation by Adsorption Processes," R. T. Yang, Butterworths, London (1987).
- "Adsorption Data Handbook," D. P. Valenzuela and A. L. Myers, Prentice Hall, Englewood Cliffs, New Jersey (1989).
- "Adsorption Engineering," M. Suzuki, Kodansha, Tokyo (1990).
- "Pressure Swing Adsorption," D. M. Ruthven, S. Farooq and K. S. Knaebel, VCH Publishers, New York (1994).
- "The Little Adsorption Book," D. Basmadjian, CRC Press, Boca Raton, Florida (1997).
- "Adsorption Technology and Design," B. Crittenden and W. J. Thomas, Butterworth-Heinemann, Oxford (1998).
- "Adsorption Design for Wastewater Treatment, D. O. Cooney, Lewis Publishers, Boca Raton, Florida (1999).

#### Adsorbents

- "Zeolites and Clay Minerals as Sorbents and Molecular Sieves," R. M. Barrer, Academic Press, London (1978).
- "Carbon Adsorption Handbook," P. N. Chermisinoff and F. Ellerbusch (eds), Ann Arbor Science Publishers, Ann Arbor, Michigan (1978).
- "Activated Carbon—A Fascinating Material," A. Capelle and F. de Vooys, Norit, Amersfoort (1983).
- "Zeolite Molecular Sieves," D. W. Breck, R. E. Krieger, Publisher, Malabar, Florida (1984).
- "Active Carbon," H. Jankowska, A. Swiatkowski and J. Choma, Ellis Harwood, New York (1991).
- "Handbook of Molecular Sieves," R. Szostak, Van Nostrand Reinhold, New York (1992).

# Chapters in Books

"Introduction to Statistical Thermodyamics," T. L. Hill, Chapters 7 and 15, Addison-Wesley, London (1960).

- "Adsorption and Ion Exchange," T. Vermeulen, G. Klein and N. K. Hiester in "Chemical Engineers Handbook," R. H. Perry and C. H. Chilton (ed), Chapter 16, McGraw-Hill, New York (1973).
- "Gas Dehydration and Purification," A. L. Kohl and F. C. Riesenfield in "Gas Purification," Chapter 12, Gulf Publishing, Houston (1979).
- "Gas Phase Adsorption," J. L. Kovach in "Handbook of Separation Techniques For Chemical Engineers," P. A. Schweitzer (ed), McGraw-Hill, New York (1979).
- "Adsorption," G. E. Keller, R. A. Anderson and C. M. Yon in "Handbook of Separation Process Technology," R. W. Rousseau (ed), Chapter 12, John Wiley, New York (1987).
- "Adsorption," D. M. Ruthven, "Encyclopedia of Physical Science and Technology," R. A. Meyers (ed), Vol. 1, pp. 238–260, Academic Press, London (1987).
- "Adsorption Science and Technology," A. E. Rodrigues, M. D. Levan and D. Tondeur (eds), Nato ASI Series, Kluwer, Boston (1989).
- "Adsorption," S. Sircar in "The Engineering Handbook," R. C. Dorf (ed), Chapter 59, CRC Press, Boca Raton, Florida (1996).
- "Activated Alumina," A. Pearson, in "Kirk Othmer Encyclopedia of Separation Technology," Vol. 1, pp. 60–72, John Wiley, New York (1997).
- "Activated Carbon" F. S. Baker, C. E. Miller, A. J. Repic and E. D. Tolles, in "Kirk Othmer Encyclopedia of Separation Technology," Vol. 1, pp. 72–93, John Wiley, New York (1997).
- "Adsorption," J. L. Humphrey and G. E. Keller in "Separation Process Technology," Chapter 4, McGraw-Hill, New York (1997).
- "Adsorption," D. M. Ruthven in "Kirk Othmer Encyclopedia of Separation Technology," Vol 1, pp. 94–129, John Wiley, New York (1997).
- "Adsorption," B. E. Bent in "McGraw-Hill Encyclopedia of Science and Technology," Vol. 1, pp. 155–158, McGraw-Hill, New York (1997).
- "Adsorption Gas Separation," J. D. Sherman, C. M. Yon, in "Kirk Othmer Encyclopedia of Separation Technology," Vol. 1, pp. 129–172, John Wiley, New York (1997).
- "Adsorption Liquid Separation," S. A. Gembicki, A. R. Oroskar and J. A. Johnson, in "Kirk Othmer Encyclopedia of Separation Technology," Vol. 1, pp. 172–199, John Wiley, New York (1997).

- "Adsorption Operations," A. L. Myers and S. Sircar, in "McGraw-Hill Encyclopedia of Science and Technology," Vol. 1, pp. 158–161, McGraw-hill, New York (1997).
- "Physical Adsorption: Experiment, Theory and Applications," J. Fraissard and C. Conner (ed). Nato ASI Series, Kluwer, Boston (1997).
- "Adsorption, Ion Exchange and Chromatography," J. D. Seader and E. J. Henley in "Separation Process Principles," Chapter 15, pp. 778–879, John Wiley, New York (1998).
- "Surfaces of Nanoparticles and Porous Materials," J. A. Schwarz and C. I. Contescu (eds), Marcel Dekker, New York (1999).