

Adsorption and Adsorptive Separations: A Review and Bibliographical Update (1994)

MARTYN S. RAY

*School of Chemical Engineering, Curtin University of Technology, GPO Box U1987, Perth 6001,
Western Australia*

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Abstract. This paper provides a review of the 1994 journal literature and complete bibliography concerned with adsorptive separations. The references are taken from the 45 most important chemical engineering journals. This paper provides an update to the literature as provided in previous bibliographic papers (Ray 1990; 1991; 1995). References for membranes and membrane-type separations (for 1992–1993) were the subject of a separate bibliographic paper (Ray 1994), due to the number of papers now published on this topic each year. A review and bibliography paper covering 1994 for membranes has been submitted for publication. Bibliographic papers covering traditional unit operations (Ray 1992; 1993; 1994; 1994) and supercritical extraction (Ray 1994) have been published. A bibliography of the chemical engineering journal literature from 1967–1988 has been published by the author (Ray 1990), and can provide access to a wider range of topics. A complete bibliographic listing of the chemical engineering journal literature from 1989 to 1994 (with subsequent six-monthly updates) is available on a CD-ROM database (Published by Royal Melbourne Institute of Technology) and full details can be obtained from the author.

Keywords: applications, bibliography, processes

The papers reviewed here have been divided into the following subject groups:

- 1.1. Theory
- 1.2. Design Data
- 1.3. Adsorbents
- 1.4. PSA and Cyclic Systems, and Applications
- 1.5. Liquid-Phase Adsorption
- 1.6. Ion Exchange, Chromatography, etc.

Some articles which were not reviewed are also included to provide a complete bibliography.

1.1. Theory

Akman, U. and Sunol, A.K., Equilibrium theory for exsorption: A gas-liquid-adsorbent mass-transfer operation, *Chem. Eng. Sci.*, 49(21), 3555–3563

(1994). An equilibrium theory for three-phase (gas-liquid-adsorbent) mass-transfer has been established based on the distributed-parameter models of the system.

Anand, N., Manoja, B.G.R., and Gupta, A.K., Kinetics of adsorption on biporous solids, for a system with rectangular equilibrium, reanalysed, *Chem. Eng. Sci.*, 49(19), 3277–3290 (1994). Mass transfer equations were solved numerically using a finite-difference technique. There are three distinct adsorption regions: (a) outer shell of completely (or almost) saturated microspheres; (b) adsorption shell of microspheres where adsorption is taking place at a given moment; (c) core of microspheres yet to be exposed to the adsorbate. Defined a dimensionless parameter; the rate of adsorption may be much higher than that predicted by the shrinking core model.

- Annesini, M.C., Giona, M., and Gironi, F., Continuous model for complex mixture adsorption, *Ind. Eng. Chem. Res.*, 33(11), 2764–2770 (1994).
- Bakaev, V.A. and Steele, W.A., The characteristic curve in physical adsorption, *Adsorpt. Sci. Technol.*, 10, 123–136 (1994). Traces the concept of the characteristic curve in physical adsorption and the rule of its temperature invariance, also the theory of volume filling of micropores, and the theory of adsorption on heterogeneous surfaces.
- Carrott, P.J.M., On the Dubinin-Serpinski equation, *Adsorpt. Sci. Technol.*, 10, 63–74 (1994). This simple model accounts for many of the principal factors involved in the formation of an adsorbed water phase on carbon surfaces. The limited results suggest that the D-S equation may be able to describe the characterisation of both the functionality and microstructure of carbon adsorbents.
- Chen, A. and Hirtzel, C.S., Monte Carlo simulation of multicomponent system by Marco State Markov Chain Model (MSMCM), *Sep. Technol.*, 4(3), 167–173 (1994). The MSMCM model is used in developing parallel Monte Carlo simulation schemes to dramatically reduce computer simulation time. It is used here to study the adsorption of a mixture of oxygen and nitrogen in zeolite 5A.
- Croft, D.T. and Levan, M.D., Periodic states of adsorption cycles. I. Direct determination and stability, *Chem. Eng. Sci.*, 49(11), 1821–1829 (1994). Method is compared to a literature PSA model and shows that for the constrained case, the first and only periodic state found satisfies a design specification.
- Croft, D.T. and Levan, M.D., Periodic states of adsorption cycles. II. Solution spaces and multiplicity, *Chem. Eng. Sci.*, 49(11), 1831–1841 (1994). The method allows location of both stable and unstable periodic states and determines the manner in which a cycle loses stability. Compared to literature models of PSA and TSA, mapping the solution spaces showed different types of multiplicity all of which have constraints such as a control scheme in the model.
- Dunne, J. and Myers, A.L., Adsorption of gas mixtures in micropores: Effect of difference in size of adsorbate molecules, *Chem. Eng. Sci.*, 49(17), 2941–2951 (1994). Adsorbed solutions of molecules of unequal size (CCl_2F_2 and CO_2 on activated carbon) show negative deviation from ideal mixing, and the size effect was studied by molecular simulation. The partial exclusion effect of the larger molecule is calculated from the cavity radius and the molecular diameters of the adsorbates.
- Filippov, L.K., Multicomponent non-isothermal adsorption dynamics, *Chem. Eng. Commun.*, 127, 75–107 (1994). Major review of the theoretical models for non-isothermal kinetics and dynamics of multicomponent adsorption. Model classifications are included, and model equations accounting for all major qualitative physicochemical features of heat and mass transfer through interfaces and in the intergranular space of porous media. A very useful summary paper.
- Filippov, L.K., Coherent and incoherent frontal patterns of multicomponent adsorption dynamics for variable linear fluid velocity in the fixed bed. I. Frontal patterns for linear adsorption isotherms, *Chem. Eng. Sci.*, 49(20), 3499–3509 (1994). The influence of the dispersive factors (kinetics and longitudinal dispersion) on the nature of the concentration distributions is considered. For different nonequilibrium theoretical models, a simple formula to calculate the mass transfer zone is derived for the coherent constant patterns. It is shown that the dispersive factors can convert coherent patterns into incoherent ones.
- Filippov, L.K., Study of adsorption of polymers on particulate surfaces by impregnation, *Chem. Eng. Commun.*, 129, 1–18 (1994).
- Gomes, V.G. and Fuller, O.M., Fixed-bed adsorber dynamics in binary physisorption-diffusion, *Can. J. Chem. Eng.*, 72(4), 622–630 (1994). Reactions carried out at close to the equilibrium vapour pressure of the participating species involve physisorption on the catalyst surface, e.g. propene metathesis over rhenium oxide/gamma-alumina catalyst at room temperature. The model equations were solved by orthogonal collocation within the method of lines.
- Harriott, G.M., Memory-integral mass-transfer models for adsorption process simulation (errata), *AIChE J.*, 40(6), 956 (1994).
- Hassan, M.M., Rahman, A.K.M.S., and Loughlin, K.F., Numerical simulation of unsteady continuous countercurrent adsorption system with nonlinear adsorption isotherm, *Sep. Technol.*, 4(1), 15–26 (1994). Theoretical dispersed plug-flow model including a mass transfer resistance represented by a linear driving force approximation for unsteady-state continuous countercurrent adsorption systems with nonlinear equilibrium isotherms. Shows that optimal choice of bed length, feed and eluent flow

- rates, and switch times must be adapted as nonlinearity changes. Results lie between the 'pore diffusion' and 'equilibrium' models.
- Hu, X., Do, D.D., and Rao, G.N., Experimental concentration dependence of surface diffusivity of hydrocarbons in activated carbon, *Chem. Eng. Sci.*, 49(13), 2145–2152 (1994). A differential adsorption bed is operated so that the adsorbed concentration is nearly constant during the adsorption process, and surface diffusivity is determined using a pore and surface diffusion model. A much stronger concentration dependence of surface diffusivity was observed than is predicted by the Darken equation.
- Jin, X., Talbot, J., and Wang, N.H.L., Analysis of steric hindrance effects on adsorption kinetics and equilibria, *AIChE J.*, 40(10), 1685–1696 (1994). Extension of the random adsorption concept for irreversible adsorption was used to analyze reversible adsorption on a continuous surface and a random site surface. Simulation results show that the model can correlate experimental data, and predict the physical significance of the adsorption parameters such as the maximum adsorption capacity.
- Jordi, R.G. and Do, D.D., Analysis of the frequency response method applied to non-isothermal sorption studies, *Chem. Eng. Sci.*, 49(7), 957–979 (1994). Finite rates of heat transfer from the gas phase to the environment, and from the sorbent particle to the gas phase, are shown to influence significantly the in-phase and out-of-phase components of the gas pressure response.
- Kaminsky, R.D. and Monson, P.A., A simple mean field theory of adsorption in disordered porous materials, *Chem. Eng. Sci.*, 49(17), 2967–2977 (1994). Theory applies to fluids in heterogeneous solids (e.g. silica gel) based on a molecular model which treats the solid as a matrix of particles with a predefined structure. It was compared to experimental results for single and binary adsorption of argon-methane and ethane-methane mixtures.
- Mazzotti, M., Storti, G., and Morbidelli, M., Robust design of countercurrent adsorption separation processes: 2. Multicomponent systems, *AIChE J.*, 40(11), 1825–1842 (1994). Developed a procedure for optimal and robust design using equilibrium theory, where adsorption equilibria are described through the constant selectivity stoichiometric model, neglecting mass-transfer resistances and axial dispersion. An approximate shortcut method predicts explicit and reliable relationships for estimating the boundaries of the exact region where complete separation occurs. Can also analyze the role of the desorbent in determining the separation performance.
- Mazzotti, M., Storti, G., and Morbidelli, M., Shock layer analysis in multicomponent chromatography and countercurrent adsorption, *Chem. Eng. Sci.*, 49(9), 1337–1355 (1994). Theory presented for fixed-bed and countercurrent columns with Langmuir-type adsorption isotherms. Two models were developed to describe adsorption-diffusion processes in solid particles, namely the solid diffusion model and pore diffusion model. Theory agrees well with numerical results except when strong interactions occur between neighboring shocks.
- Mendes, A.M.M., Costa, C.A.V., and Rodrigues, A.E., Linear driving force approximation for diffusion in spherical adsorbents with binary non-linear adsorption, *Gas Sep. Purif.*, 8(4), 229–236 (1994). Applies to cyclic steady-state for pore diffusion in the presence of binary Langmuirian adsorption under a periodic boundary condition in composition, total pressure, or both. Uses two parameters, one for each solute, calculated for a square wave with the same period and a second pair of parameters that correct the approximation for the phase lags. Error is less than 5% for equilibrium, diffusion and frequency conditions in the range of most practical systems. Can also be used for homogeneous diffusion.
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- Rao, G.N., Hu, X., and Do, D.D., Multicomponent sorption of hydrocarbons in activated carbon: Simultaneous desorption and displacement, *Gas Sep. Purif.*, 8(2), 67–76 (1994). Comparison of experimental data for ethane-propane with a macropore, surface and micropore diffusion (MSMD) model, using the ideal adsorbed solution theory (IAST) with the Unilan isotherm equation.
- Rozwadowski, M., Wloch, J., Kornatowski, J., and Erdmann, K., Equation of the sorption isotherm on zeolite Y including heterogeneity of the sorbent: A novel modification, *Adsorpt. Sci. Technol.*, 10,

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- Serpinski, V.V. and Jakubov, T.S., Dubinin-Radushkevich equation as the equation for the excess adsorption isotherm, *Adsorpt. Sci. Technol.*, 10, 85–92 (1994). The D-R equation describes the experimental excess adsorption isotherm excellently over a very wide range of gas equilibrium pressures. An algorithm allows conversion of measurable values of excess adsorption to absolute values.
- Shah, D.B., A course on the fundamentals of adsorption, *Chem. Eng. Educ.*, 28(4), 250–253 (1994). Details of a graduate course in adsorption, dealing mainly with molecular sieves.
- Shen, C.M. and Worek, W.M., Cosorption characteristics of solid adsorbents, *Int. J. Heat Mass Transfer*, 37(14), 2123–2129 (1994). The cosorption isothermal dynamic behaviors on activated carbon (AC), silica gel (SG), and molecular sieve (ZMS) were simulated. The simultaneous presence of water vapor and CO₂ in process air decreases the adsorption capacities on these adsorbents. The roll-over effect, which occurs when the outlet concentration is higher than the inlet concentration, appears in the breakthrough curves of CO₂. This effect is due to faster diffusion and a lower affinity of CO₂ than water vapor for the adsorbents. This effect is more pronounced for the cosorption process on ZMS than on AC or SG.
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- Stoeckli, F., Dubinin's theory for the volume filling of micropores: An historical approach, *Adsorpt. Sci. Technol.*, 10, 3–16 (1994). New approach includes the enthalpy of immersion into water, a thermodynamic consequence of Dubinin's theory. The adsorption of water by microporous carbons (corresponding to a type V isotherm) can also be described by the equation of Dubinin and Astakhov.
- Sun, L.M., Meunier, F., Grenier, P. and Ruthven, D.M., Frequency response for nonisothermal adsorption in biporous pellets, *Chem. Eng. Sci.*, 49(3), 373–381 (1994). Theoretical analysis including heat and mass transfer resistances in both micropores and macropores.
- Tan, H.K.S., Analysis of cyclic fixed bed sorption processes for second-order irreversible kinetics, *Chem. Eng. Sci.*, 49(8), 1277–1285 (1994). Process performance is shown to depend upon four cyclic design parameters, and sorption effectiveness is independent of the direction of regeneration.
- Tolmachev, A.M., The characteristic curve method in adsorption, *Adsorpt. Sci. Technol.*, 10, 155–164 (1994). The method enables a priori calculations of adsorption equilibria on microporous adsorbents in single and multicomponent systems over a wide range of temperature and equilibrium phase compositions. Requires only very limited 'basic' experimental information.
- Van Tassel, P.R., Davis, H.T. and McCormick, A.V., New lattice model for adsorption of small molecules in zeolite micropores, *AIChE J.*, 40(6), 925–934 (1994). Adsorption assumed to occur onto a 3-D polyhedral lattice, and both the energy and entropy of the lattice sites are accounted for in a statistical mechanics approach. Energetic interactions and entropic interactions are taken into account. The model was applied to xenon and methane adsorbed in idealized zeolite NaA, and it quantitatively predicted the simulated isotherm over the entire pressure range.
- Van Tassel, P.R., Somers, S.A., Davis, H.T., and McCormick, A.V., Lattice model and simulation of dynamics of adsorbate motion in zeolites, *Chem. Eng. Sci.*, 49(17), 2979–2989 (1994). Examines the effect of the structure and energetics of the adsorption site lattice on the mobility of small molecules in cage-like micropores using Monte Carlo lattice dynamics simulations. Also compared to molecular dynamics simulations for methane adsorbed in zeolite-A showing qualitative agreement between the two approaches.
- Vega, L.F., Panagiotopoulos, A.Z., and Gubbins, K.E., Chemical potentials and adsorption isotherms of polymers confined between parallel plates, *Chem. Eng. Sci.*, 49(17), 2921–2929 (1994). Results of Monte Carlo simulations of chains confined in a very narrow slit, in the limit of strongly attractive walls. A strong bridging effect is observed due to this strong attraction.
- von Gemmingen, U., A new approach to adsorption isotherms (corrigendum), *Gas Sep. Purif.*, 8(4), 272 (1994).
- Vortmeyer, D., Giese, M., and Lingg, G., Extension of the van Deemter equation to nonlinear isotherms of the Langmuir type, *Chem. Eng. Sci.*, 49(16), 2593–

- 2598 (1994). The van Deemter equation included a generalized dispersion term which includes the simulation of zone spreading by mass transfer. This paper shows that equivalence between one- and two-phase models is also obtained for nonlinear Langmuir isotherms, if linear driving force conditions prevail and intraparticle diffusion is rate controlling.
- Wei, J., Nonlinear phenomena in zeolite diffusion and reaction, *Ind. Eng. Chem. Res.*, 33(10), 2467–2472 (1994).
- Yao, C. and Tien, C., Approximate solution of intraparticle diffusion equations and their application to continuous-flow stirred tank and fixed-bed adsorption calculations, *Sep. Technol.*, 4(2), 67–80 (1994). Application of two approximate uptake rate expressions (for batch calculations) for spherical adsorbent pellets in continuous-flow stirred tank and fixed-bed adsorption processes. Both expressions provide improvement over the conventional linear driving force model, and the accuracy depends upon the type of driving force for interphase mass transfer that is present in a particular situation.
- Zhou, C., Hall, F., and Gasem, K.A.M., Predicting gas adsorption using two-dimensional equations of state, *Ind. Eng. Chem. Res.*, 33(5), 1280–1289 (1994).
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- Afzal, A., Khan, M., and Ahmad, H., Kinetics of the sorption of organic vapours in chromatographic silica gel, *Adsorpt. Sci. Technol.*, 11(2), 113–122 (1994). Adsorption of ethyl methyl ketone, methyl acetate, methyl alcohol, diethyl ether, acetone, and acetaldehyde between 273–297 K and a vacuum of 10^{-4} to 10^{-5} Torr.
- Aguayo, A.T., Gayubo, A.G., Erena, J., Olazar, M., Arandes, J.M., and Bilbao, J., Isotherms of chemical adsorption of bases on solid catalysts for acidity measurement, *J. Chem. Technol. Biotechnol.*, 60(2), 141–146 (1994). Measurement of adsorption equilibrium constants of the bases and the total mass of base adsorbed at 200°C are proposed as reproducible indices of average acidity strength and of total acidity of the solid, respectively. The bases (ammonia, *n*-butylamine, tert-butylamine, pyridine) adsorbed from the gas phase onto solid acidic catalysts (silica-alumina and zeolite catalysts and a silica gel).
- Anthony, R.G., Dosch, R.G., and Philip, C.V., Use of silicotitanates for removing cesium and strontium from defense waste, *Ind. Eng. Chem. Res.*, 33(11), 2702–2705 (1994).
- Biernat, J.F., Konieczka, P., and Izatt, R.M., Complexing and chelating agents immobilized on silica gel and related material and their application for sorption of inorganic species, *Sep. Purif. Methods*, 23(2), 77–120 (1994).
- Butani, M.M. and Kumari, R., Surface and charge characteristics of the oxide/solution interface towards chromium(VI) sorption, *Adsorpt. Sci. Technol.*, 11(3), 145–154 (1994).
- Cal, M.P., Larson, S.M., and Rood, M.J., Experimental and modeled results describing the adsorption of acetone and benzene onto activated carbon fibers, *Environ. Prog.*, 13(1), 26–30 (1994). Experimental data and model results show that activated carbon fibres have potential as an adsorbent for removing low concentrations of VOCs from indoor air.
- Calleja, G., Jimenez, A., Pau, J., Dominguez, L., and Perez, P., Multicomponent adsorption equilibrium of ethylene, propane, propylene and carbon dioxide on 13X-zeolite, *Gas Sep. Purif.*, 8(4), 247–256 (1994). Experimental adsorption isotherms for binary, ternary and quaternary mixtures at 293 K; data were fitted to three theoretical models.
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- Choudhary, V.R., Mayadevi, S., and Kamble, K.R., Adsorption of oxygen and nitrogen on AlPO₄(4)-5 and SaPO-5 at moderate pressures using a novel adsorption/desorption method, *Ind. Eng. Chem. Res.*, 33(5), 1319–1323 (1994).
- Do, H.D. and Do, D.D., Structural heterogeneity in the equilibrium data for hydrocarbons and carbon oxides on activated carbons, *Gas Sep. Purif.*, 8(2), 77–93 (1994). Comparison of experimental data to a theory developed to investigate the structural heterogeneity

- (characterized by micropore size distribution) in the adsorption equilibria for gas-solid systems.
- El-Shoubary, Y., Woodmansee, D.E., and Shilling, N.Z., Sorption and desorption of contaminants from different host matrices, *Environ. Prog.*, 13(1), 37–44 (1994). Using air and nitrogen atmospheres to determine the effect of surface area on contaminant sorption and desorption for sand, oil and sand, and PCB mixtures. As surface area increases, the contaminant concentration increases. For desorption, the onset temperature decreases as the surface area increases. However, this phenomenon was reversed when the surface area included pore structure.
- Fitch, F.R., Bulow, M., and LaCava, A.I., Investigation of the mechanism for the separation of nitrogen-oxygen mixtures on carbon molecular sieves, *Gas Sep. Purif.*, 8(1), 45–51 (1994). Experimental data suggests the existence of a surface barrier in the pore mouths of slit-like micropores for the samples. This conclusion is supported by canonical and Monte Carlo simulations.
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- Golden, T.C. and Sircar, S., Equilibrium and kinetics of adsorption of freon-12 at infinite dilution, *AIChE J.*, 40(6), 935–943 (1994). Coadsorption of the bulk carrier gas can severely reduce the equilibrium adsorption capacity and adsorptive mass-transfer coefficient of strongly adsorbed Freon-12. The mass transfer was dominated by surface diffusion into the pores of the activated carbon.
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- Hu, X. and Do, D.D., Effect of energy distribution shape on the sorption equilibrium and dynamics of sulphur dioxide in activated carbon, *Chem. Eng. Sci.*, 49(6), 919–923 (1994). Experimental data was used to test a heterogeneous pore and surface diffusion model and to study the effect of energy distribution shape on the sorption dynamics.
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- Huang, R.T., Chen, T.L., and Weng, H.S., Adsorption of *o*-cresol and benzoic acid in an adsorber packed with an ion-exchange resin: A comparative study of diffusional models, *Sep. Sci. Technol.*, 29(15), 2019–2033 (1994). Use of solid- and pore-diffusion models to simulate adsorption in a fixed bed with anion-exchange resin. For linear isotherm (e.g. *o*-cresol), both models gave good agreement with experimental breakthrough data. The solid-diffusion model gave better agreement with a favourable isotherm (e.g. benzoic acid). Several other factors need to be considered when selecting a model, e.g. type of adsorbent, equilibrium data, and concentration dependence of the intraparticle diffusivity.
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