

Significant Role of Chemistry (Adsorption) in Environmental Control and Sustainable Development

Eva Chmielewska¹

¹Comenius University Bratislava, Faculty of Natural Sciences Department of Environmental Ecology and Landscape Management, Ilkovičova 6, Mlynská dolina B2, Bratislava 842 15, Slovakia

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*Comenius University Bratislava,
Faculty of Natural Sciences
Department of Environmental
Ecology and Landscape
Management, Ilkovičova 6,
Mlynská dolina B2, Bratislava
842 15, Slovakia
Email:eva.chmielewska@uniba.sk

Abstract: Adsorption technologies comprise some of the most important techniques and play a significant role in both environmental and human health control, as well as in the prevention of global warming and ozone layer depletion. The prospective demands for adsorption and related domains are based on a growing concern for environmental control and for improving quality of life. Mathematical equations of the most frequently used adsorption isotherms were introduced. A vision of human welfare development on Earth until the year 2100 is discussed and graphically recorded. In the Stabilized World scenario, societal priorities are shifted away from material consumption and industrial growth towards health and education services, as well as pollution abatement and resource-efficient technologies. Together with population stabilisation in the 21st century, this avoids collapse and leaves humanity with the highest levels of welfare. Chronology of significant milestones supporting environmental protection and sustainable development on Earth are introduced in this paper, respectively.

Keywords: adsorption, isotherms, sustainable development, adsorbents application

Introduction to Historical Background

Interest in the protection of nature and the environment in the modern sense started to be realized since begin of the middle of the 19th century. In 1972, the Meadows couple in the USA published the book *The Limits to Growth*, in which the authors, based on calculations and available information, concluded that people would soon completely exhaust some non-renewable natural resources (such as oil, natural gas, strategic mineral resources, etc.). Such a decline can be reversed by a so-called state of global balance, a rapid and drastic increase in efficiency in the use of materials and energy. However, such a transition to sustainability requires more than increased productivity and more than changes in technology. It also requires the maturity, compassion and wisdom of the population. The authors further claimed that today's humanity is living beyond its means and is only trying to extend these limits. According to them, market signals such as the price of oil are too distorted, amplified by speculation and manipulated by interest groups, and cannot predict a global collapse [1, 2]. Various indicators were therefore proposed to monitor the

societal development in order to accept sustainable life. The disadvantage of these sets of sustainable development indicators, according to [3] their continued focus on the outputs of the human economy (pollutant emissions, noise, waste production and other factors). In 1968, Paul Ehrlich published the book "The Population Bomb", and his forecasts later initiated the establishment of the international association the Club of Rome [4]. He later commissioned world-renowned and recognized authorities to develop a model of the development of civilization on Earth, based on certain assumptions and adjustable parameters. The last published report of the Club of Rome is a book by the Belgian entrepreneur and economist G. Pauli [5], the core of which is a business model called the Blue Economy. According to Pauli, the current dominant model of the Red Economy is based on borrowing, debt growth, unlimited drawing of resources and pushing problems into the future. The green economy is based on equipping the economy with ecological technologies, which are financially demanding and currently financially not feasible. His Blue Economy model is based on imitating nature, supporting the local economy and social capital, creating jobs at the local

level, cascading materials, nutrients and energy, and achieving zero waste production [1, 2, 6, 7, 8, 9]. In December 2019, the European Commission finally took over the so-called European Green Agreement and the European Council took note of it at its December meeting. The European Green Deal is a package of political initiatives, the purpose of which is to direct the EU on the path of green transformation with the ultimate goal of achieving climate neutrality by 2050. It emphasizes the need for a holistic and cross-sectoral approach all relevant policy areas contribute to the ultimate climate goal. The package includes initiatives on climate, environment, energy, transport, industry, agriculture and sustainable finance, all of which are closely linked. Fulfillment of the mentioned ambitious goals will be financially extremely demanding, especially for the member states that historically have a worse starting position related to the massive use of outdated and non-ecological sources of energy and heat. The Investment Plan for a Sustainable Europe can help overcome similar obstacles, which should mobilize investments from the resources of the European Union, while also counting on the participation of member states and the private sector [10-14, 21].

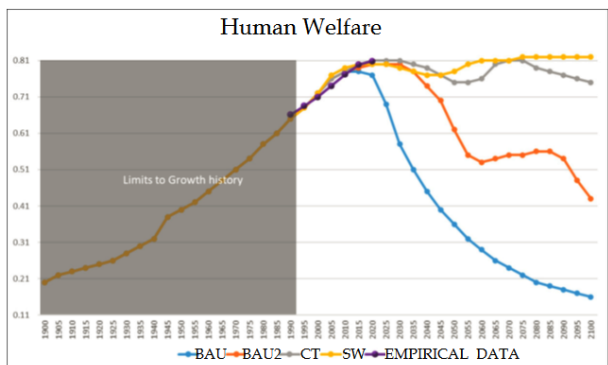


Fig.1. Empirical data (UN Human Development Index) are plotted against human welfare variables for all four scenarios. The best-known “business as usual” (BAU) “Business as usual 2” (BAU2) “Comprehensive technology” (CT) “Stabilised World” (SW) adopted according to Herrington, 2022

Herrington [15-20] published a vision of human welfare development on Earth until the year 2100 and graphically recorded according to Figure 1. The assumptions underlying each scenario span a range of technological, social and resource conditions. In each scenario, the cause of decline differs and its scale varies from a temporary dip to social collapse. The BAU scenario represents historical averages and keeps the growing of society forever until the natural resources depletion and social collapse. BAU 2 scenario means with double the natural resources occurring on Earth. This later version addressed criticism that natural resources had to be more abundant than estimated in the 1970s, however more abundant resources

do not avoid a collapse in this world and business as usual goes on for longer. Simultaneously, this creates so much pollution that agricultural output and human health break down. CT scenario suggests the following: The innovation rate in pollution abatement, food production and resource efficiency is set much higher than historical averages and the technology is assumed to be shared across the globe incl. with those who cannot pay for it. However, CT still results in some declines because so many resources need to be diverted towards technological innovation that not enough remain for agricultural, production, health and education services. In the SW scenario, societal priorities are shifted away from material consumption and industrial growth towards health and education services, as well as pollution abatement and resource-efficient technologies. Together with population stabilisation in the 21st century, this avoids collapse and leaves humanity with the highest levels of welfare. The author collected real-world data such as pollution, fertility, mortality, population, industrial output, food, health and education services, non-renewable natural resources, human welfare and ecological footprint. He plotted the empirical data together with the variables for each of the four scenarios and obtained good impressions of how closely empirical data aligned with the four scenario paths over time [3, 4, 11-15].

The term Anthropocene was used for the first time in 2000 by Paul J. Crutzen and Eugene Stoermer as the name of a geological period, which is distinguished from others primarily by the dominant influence of humankind on the planet and mainly by the speed with which changes are made. After all, since the beginning of the Anthropocene, the population on Earth has increased more than 6 times, the global economy 50 times, and the use of energy 40 times. While at the end of the war, 40 mil. cars, by the year 2000 there were already 700 million of them and today they are more than a billion cars on the streets [7-9].

Chronology of Significant Milestones Supporting Environmental Protection and Sustainable Development on Earth:

- 1960 – The beginnings of Hippies pop culture (first protests against nuclear tests in the Pacific).
- 1962 – Rachel Carson published the book *Silent Spring*, reacting to the inappropriate use of agrochemicals in the agriculture of the United States of America and promoting primarily biotic insecticides [2].
- 1966 – The first analysis of dangerous polychlorinated biphenyls PCBs (used as additives in paints, varnishes, hydraulic equipment and heat transfer media, in lubricants, plastics, adhesives,

cements, inks, copy paper) at the Department of Analytical Chemistry of Stockholm University by analytical chemist Sören Jensen.

- 1970 – The establishment of the Environmental Protection Agency in the USA (US EPA), which ensured interaction between scientific, industrial and governmental organizations with the aim of using Green Chemistry strategies in new technologies.
- 1971 – The establishment of the Greenpeace Organization in Vancouver (55 countries), Amsterdam Greenpeace international center (2,400 employees and 15,000 volunteers).
- 1977 – The first analysis of extremely dangerous polychlorinated dibenzo-dioxins PCDD in cow's milk fat at the University of Amsterdam by analytical chemist Kees Olie.
- 1980 – The establishment of the IPCC at the initiative of the UN and the World Meteorological Organization.
- 1985 – The discovery of the ozone hole by the British scientist Joseph Farman.
- 1987 – "Our common future" The International Commission for Environment and Development, defined the concept of sustainable development, which satisfies the needs of the present without endangering future generations to satisfy their own needs, i.e. Agenda 21.
- 1992 – The 1st UN Conference on Environment and Development (Earth Summit in Rio de Janeiro) – adopted Agenda 21 - a large-scale action plan for sustainable development.
- 1995 – The Nobel Prize in Chemistry was awarded jointly to Paul J. Crutzen (Max-Planck Inst., Mainz, Germany); Mario J. Molina (MIT Cambridge, MA, USA) and F. Sherwood Rowland (University of Irvin, CA, USA) " for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone".
- 1997 – Adoption of the Kyoto Protocol, which includes the obligation for industrialized countries to commit to limiting greenhouse gas emissions by 2012 entered into force in 2005.
- 1998 – The establishment of the Green Chemistry Center, University of York 1998 – Paul Anastas and John Warner published 12 principles of Green Chemistry in the first book on Green Chemistry, *Green Chemistry: Theory and Practice* [13]. In short, it concerns the use of maximum amounts of substances for reaction products, the lowest waste production, the safety of processes, the use of renewable resources and an increase in the efficiency of chemical production.
- 2001 – Stockholm Convention on the prohibition of the use of persistent organic pollutants (POPs).
- 2005 – Nobel Prize for the discovery of chemical catalysts, which made it possible to develop a new

method of transforming organic molecules. Synthesis means progress in the field of Green Chemistry and awarded were Robert Howard Grubbs (California Inst. of Technology, USA), Richard Royce Schrock (Massachusetts Inst. of Technology, USA) and Yves Chauvin (French Academy of Sciences) [6].

- 2007 – Nobel Prizes for the Intergovernmental Commission on Climate Change (IPCC) for the climate model and former US Vice President Albert Arnold Gore for peace [22].
- A 2010 study of the Institute for Climate Impact Research in Potsdam produced clear evidence that it is necessary to invest in climate protection and reverse its unfavorable development.
- 2015 – The climate conference in Paris; Africa: a green belt 15 km wide and 8000 km long is supposed to stop the expansion of the Sahara (lack of funds); EU from 2019 Green Deal - by 2050, Europe will reduce emissions by 60% and become the 1st climate-neutral continent in the world - by 2021, the EU has reduced CO₂ emissions, but they were increasing elsewhere in the world.
- 2018 – The banner "You stole our future" - the Fridays for Future FFF movement (Greta Thunberg's strike in front of the Swedish parliament by refusing to participate in classes until the election, later only on Fridays); the FFF movement influenced politicians in the cancellation of coal mining until 2038, the introduction of the Green Deal and emission permits in the EU.
- 2019 – The Nobel Prize in Chemistry for Li-Ion Battery Development was awarded to John B. Goodenough – University of Texas, Austin (USA), M. Stanley Whittingham – Binghamton University, State University of New York (USA), Akira Yoshino – Asahi Kasei Corporation, Tokyo, Meijo University, Nagoya (Japan).
- 2021 – The Nobel Prize in Physics and Global-Warming Climate Model was awarded to Syunkuro Manabe – Princeton University (USA), Klaus Hasselmann – Max Planck Institute (Germany), Giorgio Parisi – University of Rome (Italy).
- 2023 – COP 28 climate summit in Dubai focused on limiting the increase in global temperature max. by 1.5 °C [23].
- 2024 – The World Economic Forum (WEF) in Davos published a report on global risks, according to which the world may face the problem of a "polycrisis" in the next ten years - a cluster of interconnected global risks with mutually reinforcing effects, the combined impact of which will be greater than the sum of the individual ones.

General Aspects of Adsorption and its

Contribution to Environmental Protection

Adsorption science has a very long history, and the first practical adoption of adsorption was noted already in ancient times. The current adsorption theory and relevant applications initiated by Langmuir's fundamental work have been developed extensively more or less during the last 80 years [7, 27]. Now-a-day they comprise many advanced approaches including a wide spectrum of modern surface chemistry sciences. The autonomous existence of adsorption is based on the enormous complexity that is inherent to adsorption phenomena at various interfaces and the widespread, general occurrence and importance of adsorption and related domains in nature, including everyday life's product life's products and environmental applications.

The prospective demands for adsorption and related domains are based on a growing concern for environmental control and for improving quality of life. Many of the aspects aimed at this concept require both the use of new adsorbents or adsorbent-like materials and the development of the ecologically friendly, low-energy adsorption technologies, respectively.

Crucial progress in the theoretical description of adsorption has been achieved, mainly through the development of new theoretical approaches formulated on a molecular level, by means of computer simulation methods and owing to some new techniques which examine surface layers or interfacial regions. Moreover, during the last 20 years new classes of solid adsorbents have been developed, such as activated carbon fibres, carbon molecular sieves, fullerenes heterofullerenes, microporous glasses and nanoporous – both carbonaceous and inorganic – materials as well [24, 25].

In different periods of time, various adsorption materials have been fabricated and industrially applied, based on the raw materials accessible and the state of knowledge at that time. Before World War I, carbon adsorbents were mostly produced, during the period between World War I and World War II, the active carbons, silica gels and aluminum oxides, but after World War II revolutionary progress has been made in the discovery and application of synthetic zeolites and zeolite-like adsorbents traditionally known as molecular sieves (Tab.1).

Many hypothetical molecular sieves (MS) which obey quantitative topological and chemical rules as well as crystallochemical laws have been synthesised, respectively. Some of the novel applications of molecular sieves include membranes, chemical sensors, storage materials for both various compounds

and information as well as semiconductors. Other uses, such as high-tech materials in nano-chemistry and nano-physics, are being gradually implemented into practice. Their utilization in traditional areas, such as ion exchange, drying processes, animal feed improvement and processing, and detergent production is also anticipated to promote and arise. The main class of microporous materials is zeolites, which, according to the recommendation of the Structure Commission of International Zeolite Association (IZA), not only aluminosilicates, but also all other interrupted frameworks of zeolite-like materials, e.g. aluminophosphates, while provided that the framework atoms other than oxygen are tetrahedrally coordinated. There is, however, an ever-growing interest in expanding the pore sizes of zeotype materials from the micropore to mesopore region in response to the increasing demands in both industrial and fundamental studies (Tab.1). Traditional zeolites are the only existing crystalline materials with a well-defined pore structure in the microporous range. Their narrow pore size and tunable affinity to certain molecules make them ideal adsorbents for selective purification of gases in multicomponent mixtures or for

Table 1. Basic types of industrial adsorbents

| Carbon adsorbents | Mineral adsorbents | Other adsorbents |
|----------------------------|--------------------------------------|---------------------------|
| Active carbons | Silica gels | Synthetic polymers |
| Activated carbon fibres | Activated alumina | Composite adsorbents: |
| Molecular carbon sieves | Oxides of metals | (Complex mineral-carbons, |
| Mesocarbon microbeads | Hydroxides of metals | X-elutrilite; X = Zn, Ca) |
| Fullerenes | Zeolites | Mixed sorbents |
| Heterofullerenes | Clay minerals | |
| Carbonaceous nanomaterials | Pillared clays | |
| | Porous clay hetero-structures (PCHs) | |
| | Inorganic nanomaterials | |

the encapsulation of hazardous compounds from other contaminated media. Innumerable physical, chemical and biological processes take place at the boundary between two phases, while others are initiated at the interface. The concentration change of some substance at the interface compared with the neighbouring phases, is referred to as adsorption. In other words, the term adsorption deals with the process in which

molecules accumulate in the interfacial layer, and the desorption denotes the converse process. The term sorption – together with the terms sorbent, sorbate and sorptive – is also used to denote both adsorption and absorption, when both occur simultaneously, but it is not possible to distinguish whether adsorption or absorption predominates (Fig.2).

The fundamental concept of adsorption science is the adsorption isotherm (1-12). It is the equilibrium relation between the quantity of the adsorbed material on the adsorbent and the parent concentration in the bulk (aqueous) phase at constant temperature. Apart from the results of the calorimetric measurements, the adsorption isotherm is the primary source of information on the adsorption process. Its strict meaning can be derived from the so-called adsorption excess concept, which was introduced to surface science by Gibbs more than 100 years ago and forms an important tool for describing adsorption phenomena that occur at various types of interfaces [26]. The most advanced theories of adsorption are statistical ones and they should enable the calculation of ab initio the profile of component concentration at the solid-aqueous interface, by the standard methods of statistical thermodynamics. Due to the heterogeneity of the solid porous materials and thus by the majority of industrial adsorbents, a complete statistical description used to be rather complicated. Assuming the thermodynamic equilibrium between the surface and bulk phases and utilizing the equality of the chemical potentials of a component in the coexisting phases, various adsorption isotherms may be derived.

The equilibrium between a bulk phase and the surface layer used to be established in regard to neutral or ionic particles. If the adsorption process of one or several ionic species is accompanied by the simultaneous desorption of an equivalent amount of ionic species, this process is considered as an ion exchange reaction. The first description of adsorption phenomena was proposed in the years 1914–1918 associated with such names as Langmuir, Eucken or Polanyi. The Langmuir equation (3-7), initially derived from kinetic studies, was based on the assumption that on the adsorbent surface, there is a definite and energetically equivalent number of adsorption sites, at each of which one molecule of an ideal gas may be adsorbed. Bonding to adsorption sites was proposed to be either chemical or physical, sufficiently strong to prevent displacement of adsorbed molecules along the surface. The lateral interactions among the adsorbate molecules were neglected. The Langmuir equation describes relatively well physical (or chemical) adsorption on solid surfaces with one type of active centers. Nevertheless, he also noticed that one of the fundamental

assumptions of this theory, which refers to the homogeneity of the adsorbent surface, is not justified for many cases, because the surfaces of most solids are energetically heterogenous, and the adsorption sites are distributed over the energetically different levels. In 1932, he was awarded the Nobel Prize for Chemistry on the basis of his discoveries and research of surface chemistry. The Langmuir equation itself should be considered, however, as a useful equation that corresponds to the so-called ideal localised monolayer. The ideal localised monolayer model, despite its obvious imperfections, presents even today in surface and adsorption science the most frequent mathematical description. Another milestone in the development of the adsorption science was the multilayer isotherm equation (8), proposed in 1938 by Brunauer et al. The BET theory represents to some extent a generalisation of the Langmuir isotherm or a universal theory for physical adsorption. The other developed theory, i.e. the theory of volume-filling micropores, also named after Dubinin-Radushkevich (9), plays a significant role in describing of the most industrial adsorbents, which used to be characterized by well-developed porous structures [24-26].

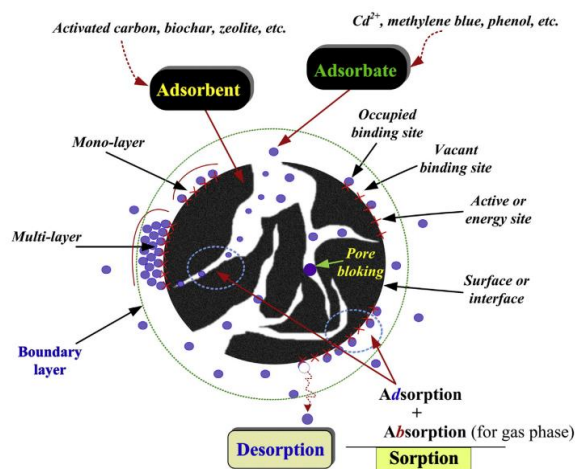


Fig.2. Some basic terms used in adsorption science and technology (adopted according to Hai Nguyen Tran, 2017)

1-parameter (K_H):

Henry izoterm

$$a = K_H \cdot c(eq) \quad (1)$$

2-parameters (K_F K_L K_{BET} n V_o E a_{max}):

Freundlich izoterm

$$a = K_F \cdot c(eq)^{\frac{1}{n}} \quad (2)$$

Langmuir izoterm

$$\frac{1}{a} = \left(\frac{1}{a(\max) \cdot K_L \cdot c(eq)} \right) + \left(\frac{1}{a(\max)} \right) \quad (3)$$

$$a = a_{\max} \cdot \frac{K_L \cdot c(eq)}{1 + K_L \cdot c(eq)} \quad (4)$$

$$\frac{C_{rov}}{a} = \frac{1}{a_{\max}} C_{rov} + \frac{1}{K_L a_{\max}} \quad (5)$$

$$C_{rov} \text{ vs. } \left(\frac{C_{rov}}{a_{rov}} \right)$$

$$a = a_{\max} - \left(\frac{1}{K_L} \right) \frac{a_{\max}}{C_{rov}} \quad (6)$$

$$\left(\frac{a_{rov}}{C_{rov}} \right) \text{ vs. } a_{rov}$$

$$\frac{a}{C_{rov}} = K_L a_{\max} - K_L a \quad (7)$$

$$a_{rov} \text{ vs. } \left(\frac{a_{rov}}{C_{rov}} \right)$$

Brunauer, Emmet, Teller (BET) izoterm

$$\frac{c(eq)}{a(C_{sat} - C_{eq})} = \frac{1}{K_{BET} \cdot a_{\max}} + \frac{K_{BET} - 1}{K_{BET} \cdot a_{\max}} \cdot \frac{c(eq)}{c(sat)} \quad (8)$$

Dubinín – Raduschkevitsch izoterm

$$a = \frac{V_o}{V_{mol}} \cdot \exp \cdot \left[- \left(\frac{RT \ln \frac{c(sat)}{c(eq)}}{E} \right)^2 \right] \quad (9)$$

3-parametrs (K_{LF} K_{RP} m n W_o V_{mol} E a_{\max}):

Langmuir-Freundlich (Sips) izoterm

$$a = a_{\max} \cdot \frac{K_{LF} \cdot c^n(eq)}{1 + K_{LF} \cdot c^n(eq)} \quad (10)$$

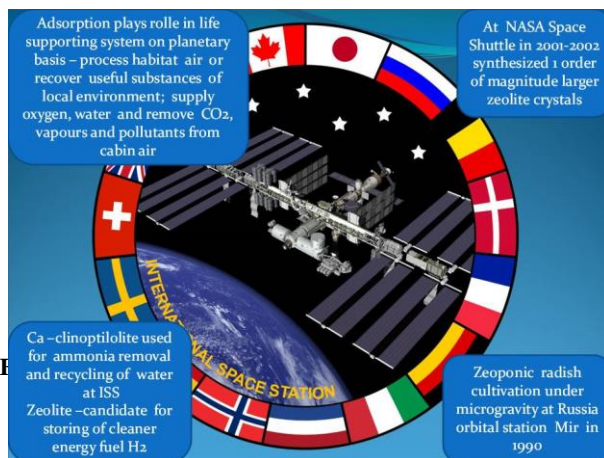
Redlich-Peterson izoterm

$$a = a_{\max} \cdot \frac{K_{RP} \cdot c(eq)}{1 + K_{RP} \cdot c^n(eq)} \quad (11)$$

Dubinín-Astachov izoterm

$$a = \frac{W_o}{V_{mol}} \cdot \exp \cdot \left[\left(\frac{RT \ln \frac{c(sat)}{c(eq)}}{E} \right)^m \right] \quad (12)$$

Adsorption technologies comprise the most important techniques and play a significant role in both environmental and human health control as well as in the prevention of global warming and ozone layer depletion. Adsorption can also be expected to play a significant role in the environmental control and life-supporting system on a planetary basis, where adsorbents are used to process the habitat air or to recover useful substances from the local environment. Adsorption processes were good candidates for separation and purification in space, by virtue of such characteristics as gravity independence, high reliability, relatively high energy efficiency, design flexibility, technological maturity and recovery [24]. For this reason, adsorption has historically played a key role in life support on piloted U.S. and Russian spacecraft (Fig.3). Thus, the environmental control and life support system on the spacecraft provided the safe and comfortable environment, in which the crew lived and worked by supplying oxygen, water and by removing carbon dioxide, water vapour and trace contaminants from cabin air. The design, ultimately selected for use on the international space station ISS, included activated carbon for high molecular weight compounds and ammonia removal, for which the impregnation with 10% phosphoric acid was used (besides the alternatively used zeolite). A catalytic oxidiser for removal of destroyed low molecular weight compounds and a postsorbent of LiOH for acid gas removal were sequenced in the series thereafter (Fig.3).



clinoptilolite onto the international space shuttles

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