Degradable systems and environment

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Abstract. In this paper degradable systems in an environment were studied. Equilibrium criteria for chemicals decomposition was considered. Degradable systems have various mechanisms for irreversible substance transformation. Discharged chemicals transformation or removing can be realized by physical, chemical and biological methods. Biodegradation is often transformation mechanism for organic compounds in nature. Rate of biodegradation depends from many factors and also from environmental conditions.

Keywords: Degradation, chemical decomposition, parameters, criteria of rate, environment.

1 Introduction

Methods for estimating fluxes, transformations, and resultant environmental concentrations of chemicals depend on the knowledge of how rapidly the chemicals are discharged to a specific compartment in the environment and how rapidly they are transformed or removed by physical, chemical, and biological processes. Apart from the specific structure of the receiving compartments, particularly its physical and chemical characteristics, these processes are largely controlled by the inherent molecular properties of the chemical released. These may be appropriately classified as sets of equilibrium and kinetic constants that defines the exposure potential, and a complementary set of data that characterize the effect potential[1],[2].

Here, the essential exposure and effects criteria will be described. With regard to the following quantitative specification, however, note that chemicals are never completely pure and that the very nature and quantity of the impurities can have a significant impact on many environment quantities. In particular, the following parameters are very sensitive to the presence of impurities, water solubility, odor characteristics and threshold values, biological oxygen demand, and toxicity[3]-[5].

The density of a substance, particularly in comparison to that of water or air, is of special environmental importance since it largely controls dispersion processes. For example, hydrocarbons are usually lighter than water[6],[7].

Normally, melting involves an increase in volume by about 10% exceptions are water, bismuth, and gallium. According to the sign of this change in volume, melting temperature rises or falls by 0.01-0.1 K/bar, which means that, under environmental conditions, pressure has little effect on melting point.

In this paper degradation reactions in an environment were studied.

2 Chemicals degradation by equilibrium partitioning

The melting and boiling points of the members of homologous series of hydrocarbons increases with increasing molar mass. When comparing organic compounds containing different halogens, however, the mass effect can be, partially, counterbalanced by polarization effects, in the case of methyl-fluoride (CH$_3$F) and methyl-bromide (CH$_3$Br). Substitution of another atom or group for hydrogen in an alkane results in an elevation of the boiling point. Thus, alkali halides, alcohols, aldehydes, ketones, and acids boil at higher temperatures than elementary hydrocarbons with the same carbon skeleton. The introduction of group promoting association brings about a marked rise in boiling point, which is especially pronounced in alcohols and acids since hydrogen bonds can be formed.

The vapor pressure of a liquid or solid in the pressure exerted by the gas in equilibrium with the liquid or solid at a given temperature. The evaporative loss, volatilization is a very important source of material for airborne transport and
subsequent transformation and deposition processes. Vapor pressure data permit, in combination with solubility data, calculations of rates of loss by evaporation of dissolved compounds from water by using Henry’s law constant.

Vapor density compared to density of air (=1), indicates whether a gas will be transported along the ground, possibly subjecting ecosystems to high exposure, or whether it will disperse rapidly. Vapor density is related to equilibrium vapor pressure through the fundamental state equation for a gas is easy derived. If the mass of substance and its molar mass are substituted for the number of moles the vapor density is obtained.

Vaporization of chemicals from water is an important transport process for a number of substances that have low water solubility and low polarity [8],[9]. Despite their very low vapor pressure, many compounds can volatilize rapidly because of their very high activity coefficients in solution.

Volatilization process from soil surfaces are complicated by variable contributions due to volatilization of the chemical from the water at the surface, evaporation of water itself, and the related capillary rise, which transports more water and dissolved chemical to the surface.

Water solubility is an important parameter for the environmental assessment of all solid or liquid chemicals. In general, molecules with highly polar bonds will be relatively strongly attracted to one another, consequently, water and alcohol are potent solvents for ionic compounds such as salts, as well as polar nonionic molecules such as sugar. In contrast, nonpolar molecules such as tetrachloromethane, benzene, or gasoline are more weakly as fats, grease, and paraffins, which are noted soluble in water. Some solids are so firmly bonded that they are not significantly soluble in any common solvents except those with which they react chemically, whereby the nature of the molecule being dissolved is altered. Quarts is of this type, its solubility in pure water is of the order of 5 mg/L, but if the water contains a 0.01M concentration of orthodiphenols, quarts is transformed into soluble states and the solubility is increased to 40 mg/L [9].

The composition of natural water varies considerably in space and time. Variables such as pH, water hardness, and concentration of cations, anions, and organic substances such as gelatin or fulvic and humic acids, all affects the solubility of chemicals in water.

Mixture of compounds behave differently from the individual compounds when brought in contact with water because each component partitions between the aqueous phase and the mixture. Compounds with a high water solubility tend to move into the aqueous phase, while the less soluble components have a greater tendency to remain in the mixture phase. Thus, the fractional composition of the water soluble fraction differs from the original composition of the mixture, and the concentration of the individual components of the water soluble fraction are generally lower than their maximum solubility.

The $n$-octanol-water partition coefficient $K_{OW}$ is defined as the ratio of the equilibrium concentration $c$ of a dissolved substance in the two phase system $n$-octanol and water, two solvent that are largely immiscible:

$$K_{OW} = \frac{c_{octanol}}{c_{water}}$$

Usually, $K_{OW}$ is given in decadic algorithm $\log K_{OW}$. Because, $K_{OW}$ is a dependent variable with regard to water solubility simultaneous use of both in structure=activity relationships or multivariate classification procedures will give spurious correlations. Experimental determination of both the aqueous solubility and the $n$-octanol-water partition coefficient led to the following regression [6].

$$\log K_{OW} = 5.00 - 0.670 \log s$$

where $s$ is the solubility in water in $\mu$mol/L. When solubility is expressed in mg/L, equations (2) becomes:

$$\log K_{OW} = 4.3 - 0.75 \log s$$
partition coefficient of a given chemical from solubility in water. However, the scatter increases considerably for solubility greater than 100 mg/L, as the example of L-tyrosine shows, where the experimental value of $\log K_{ow}$ is -2.26 while calculations using equation(2) yield values of +2.7 or +2.5.

Furthermore, whether the above equations would also apply to chemicals with high dissociation constants, such as salts and strong acids or bases, is questionable since their activities in solution can not be approximated by their concentration. Basically, the same restriction holds for aliphatic acids or bases whose partition coefficients can vary drastically with changes in pH [1]. Nevertheless, the n-octanol-water partition coefficient has proved useful as a simple means of predicting biological uptake, lipophilic storage, and biomagnification factors, whereas extrapolations of the multifactorial soil adsorption processes are much more difficult.

3 Exposure and criteria of rate of environment pollution

Every chemical reaction takes place at a definite rate depending on the specific conditions under which it occurs. These boundary conditions are the concentrations and/or pressure of the reacting substances, temperature, presence or absence of catalytic agent, and radiation. Chemical kinetics deals with the rates and mechanisms of these reactions whose understanding is rendered difficult by the fact that both time and intermediate products are involved, compared the subject of chemical equilibrium, which is concerned only with initial and final states of reactants. Because of the complexity of these subjects, the following presentation is limited two determination of the essential rate constants for environmental processes from structure alone by using structure-activity relationships.

Hydrolysis of compounds usually is the introduction of a hydroxyl function and is most commonly associated with the elimination of a leaving group X.

$$RX + H_2O \rightarrow ROH + HX \quad (4)$$

In water, the reaction is catalyzed mainly by $H^+$ and $OH^-$ ions, whereas in most soil, loosely complexed metal ions such as copper or calcium may also constitute important catalysts for the hydrolysis of several types of chemical structures. In addition, sorption of soil, of the chemical may increase its reactivity toward hydronium ions [12].

There are reviewed kinetic data for hydrolysis for hydrolysis of a variety of organic compounds in aquatic systems in relation to the chemical characteristics of most freshwater systems. Quantitative structure –activity relationships used as predective test methods to develop the essential kinetic data, generally take the form of that physical adsorption of gases by highly porous media such as silica gel, charcoal, and soil often exhibits hysteresis, a form of irreversibility due to condensation of liquid in pores is very important. Analogous phenomena occur with chemicals bonded at solid-liquid interface.

Molecules of a given substance may also be adsorbed from the liquid or gas phase by a solid through the activation of valence forces, its chemical adsorption. Consequently, they may be considered as reacting with atoms or molecule on the surface of the solid in a way analogous to any other chemical reaction, and the products of this reaction are usually conveniently considered to be species quite different from the original reacting molecules of the atoms (chemisorption or specific bonding in terms of soil chemistry). Temperatures at which chemisorption occurs are related not to the boiling point of the adsorbate (material being adsorbed), as is the case with physical adsorption, but to the stability of the surface compound and its rate of formation. Therefore, to the diffusion rates of chemisorption vary enormously with material and temperature as do those of ordinary chemical reactions, and may be very much slower than rates corresponding or gases or solutes to the surface. Further more the rates are likely to vary strongly with the amount of material adsorbed. Because of these rate characteristics, the amount of adsorbate at a given pressure or concentration and temperature, when observed over practical time periods, may depend strongly on the way these boundary conditions have been reached. Therefore, irreversibility is extremely common in chemisorption, which is characterized by enthalpy values $>100$ KJ/mol.

The pressure and extent of ionization also have a great influence on the chemical behavior of a substance, particularly on solubility, sorption,
toxicity, and other biological characteristics. Ion exchange as an important sorption mechanism for substance prone to ionization is viewed as an exchange with some other ion that initially occupies an adsorption site on the solid.

The ion exchanger property of a soil results mostly from the clay and silt fractions, organic matter, and hydrous oxides of iron. Soil particle have an amphoteric character but normally carry a net negative charge. Positive charges, as indicated by the amphoteric nature of the clay fraction, may originate matter from hydrous oxides of iron, ferrhydrites, aluminum, and manganese, and from exposed octahedral groups that react as bases by attracting protons from the surrounding soil solution. The negative charge increases and the positive charge decreases with rising pH as a result of increasing ionization of the acid groups and decreasing protonation of the basic groups. For decreasing pH, the corresponding change occurs in the opposite direction. The carboxyl groups of humans ionize under acid conditions, the phenolic hydroxyl groups mainly above pH =6. Because of the highly irregular shape of many clay minerals and the nonuniform distribution of charges in the particles, the surface charge density is quite variable.

To describe ion exchanger processes several formulas have been proposed in the course of exchanger studies. The first group is essentially empirical and intended mainly to provide mathematical formulations best fitting the experimental data. Among this group, the Freundlich, Langmuir, and Brunauer-Emmet-Teller (BET) are particularly very important [13],[14].

Freundlich equation, the concentration of a substance in solution is related to that adsorbed as follows:

$$\frac{x_{ad}}{m} = k c^{1/n_f}$$

where the $x_{ad}$ is the amount of substance adsorbed, $m$ the mass of the adsorbent, and $k$ and $n_f$ are specific constants.

4 Degradable transformation

Degradable system means compounds decomposition in the nature [10],[11]. Biodegradation is the most important transformation mechanism for organic compounds in the environment.

Biodegradation can occur under conditions in which oxygen is present, aerobic, or absent, anaerobic. In aerobic processes, organic carbon is oxidized to carbon dioxide, while in anaerobic processes it may ultimately be reduced to methane. In either case, the more important environmental variables affecting the rate and extent of biodegradation are temperature, pH, salinity, oxygen concentration, concentration of the chemical involved, ionic strength, composition of microbial associations and concentration of viable microorganisms, quantity and quality of nutrients (other than xenobiotic substances), trace metals and vitamins.

In general, microbial degradation is impeded by ether bonds and by triple substituted or condensed phenyl groups- particularly, if the latter have methoxyll, sulfone, nitro, or chlorine substituents in the meta position. Among the nitrophenols and chloroanilines, the ortho-isomers are relatively recalcitrant. Multiple substitution increases the recalcitrance of aromatic molecules considerably because their aerobic degradation is effected by relatively specific mono- and dioxy-genases[16]. Halogen substituents delay the electrophilic attack of these oxygenases considerably by reducing enzyme affinity. Therefore, multiple chlorine substituted aromatics form relatively persistent compounds, the more so because the delayed cometabolic attack yields dead-end metabolites, which can not be used for cell building purposes or as an energy source.

As a consequence, reliable conclusions about biodegradation are not generally possible on the basis of chemical structure alone. Therefore, many laboratory methods have been developed for studying the aerobic biodegradative potentials of chemicals. In comparison, tests for assessing anaerobic biodegradation have received less attention. Nevertheless, anaerobic degradation is an important process for substances that are not aerobically biodegradable or whose physicochemical properties are such that their occurrence in an aerobic environment is restricted.(chemicals that are strongly adsorbed or insoluble). For these substances, anaerobic biodegradation can be the major process responsible for breakdown in the environment.

Anaerobic biodegradation is complex and usually considered to occur in at least three
consecutive main stages, the first of which involves hydrolysis of complex organic molecules such as carbohydrates, proteins, and lipids by the action of extracellular enzymes. In the subsequent stage (acidogenic step), the hydrolysis products are fermented to yield mainly short-chain fatty acids, alcohols, hydrogen, and carbon dioxide. Alcohols and acids are then converted in the acetogenic step. The last degradation step is effected by methanogenic bacteria (methanogens), which utilize acetate and hydrogen to form methane.

Anaerobic processes tend to be self-inhibitory because the hydrolysis of complex substrates such as fats, proteins, and carbohydrates yields volatile organic acids. By lowering the pH of the system, these may inhibit the growth of methanogens unless the system has sufficient buffer capacity. Inhibition of gas production as a result of the toxicity of chemicals is also possible. Finally, some indications have been found that certain compounds (nitriloacetic acid, are degraded anaerobically only when aerobic organisms acclimatized to the compound are incorporated in the system.

When the organic compound liable to degradation or enzymatically induced metabolic transformations is utilized as a carbon source, the growth rate of the responsible microorganism depends on the concentration of the former. The rate of substrate utilization then becomes:

\[
\frac{dc_{\text{deg},r}}{dt} = \mu \frac{x}{y} = \left( \frac{\mu_m}{K_S} \right) \left( \frac{c_{\text{deg},r}}{K_S + c_{\text{deg},r}} \right) = k_b \frac{c_{\text{deg},r} x}{(K_S + c_{\text{deg},r})} \quad (4)
\]

where \( \mu \) is the specific growth rate of biomass, \( x \) is the biomass per unit volume, \( K_S \) is the concentration of substrate to support half maximum specific growth rate \( 0.5 \mu_m \), \( \mu_m \) is the maximum of the biomass specific growth rate, \( c_{\text{deg},r} \) is the concentration of degradation substance, \( k_b \) is the biodegradation constant, and \( y \) is the biomass produced from a unit amount of substrate consumed. The constants \( k_b \) and \( K_S \) depend on temperature, \( pH \), salinity, oxygen concentration, concentration of chemicals, composition of microbial associations, and concentration of viable microorganisms, quantity and quality of nutrients, trace metals, and vitamins.

**Bioconcentration and Bioaccumulation.** Bioconcentration is the concentration of a chemical in an organism due to direct uptake from the environment, ambient air or water, which does not include contaminated food. Bioaccumulation includes the latter pathway of concentration, while biomagnification considers only concentration processes via food uptake. Ecological magnification defines the increase in concentration of a substance in an ecosystem or a food when passing from a lower trophic level to a higher one.

Bioconcentration or bioaccumulation is the result of both kinetic diffusional transport and biotransformation, and equilibrium partitioning processes. It thus involves the following set of fundamental events[4].

- Partitioning of the xenobiotic between the environment and some surface of the organism.
- Diffusional transport of the molecules across cell membranes.
- Transport processes mediated by body fluids such as exchange between blood vessels and serum lipoproteins.
- Concentration xenobiotic in various tissues depending on its affinity for specific biomolecules such as nerve lipids.
- Metabolism, cometabolism, or biodegradation of the xenobiotic.

The relative importance of the above processes is likely to differ considerably as a result of both the physicochemical properties of the xenobiotic and the morphological and physiological structure of the target organisms. Therefore, an essential ecotoxicological requirement is that the determination of bioconcentration factors be complemented by an assessment of biomagnification values. Under real world conditions these would provide deeper insight into the complex bioaccumulation processes of xenobiotics as a result of transport and partitioning into higher levels of the food web, which may ultimately result in toxic concentrations.

On the basis of bioconcentration studies in different test organisms, correlations with both water solubility and \( n \)-octanol-water partition coefficients have been established. In some cases, the results proved excellent, in others, the
correlations yielded only satisfactory structure activity relationships, estimates bioconcentration factors to within and order of magnitude for chemicals of $\log K_{ow}$ ranging from 1 to nearly 7.

5 Conclusion
In this paper degradable systems in evaporation, water solubility and biodegradation were studied.

Evaporation loss in volatilization process, water solubility of compounds are important degradation processes. Dissociation constant and pH are determined parameters in water solubility processes.

For substances which have low water solubility and low polarity evaporation processes are very important for degradation. Biodegradation processes are very often in the nature, and bioaccumulation depends from diffusion transport and biotransformation kinetics.

Notation
- $c$ – the toxic substance concentration, mol/cm$^3$
- $c_{A,deg}$ - the concentration of degradation substance, mol/ cm$^3$
- $k_b$ - the biodegradation constant, s$^{-1}$
- $K_s$ - the concentration of substrate to support half maximum specific growth rate ($0.5 \mu_m$)
- $k_{b2}$ - the second order rate constant for biotransformation, dm$^3$mol$^{-1}$ s$^{-1}$
- $k_{m1}$ - the pseudo first order rate constant for biotransformation, s$^{-1}$
- $K_{ow}$ - the ratio of the equilibrium concentration in the liquid-liquid solution
- $x$ - biomass per unit volume
- $y$ - biomass produced from a unit amount of substrate consumed.

Greek Symbols
- $\mu$ - specific growth rate of biomass
- $\mu_m$ - maximum of the biomass specific growth rate

References