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Mass Transfer: Impact of Intrinsic Kinetics on the Environment

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1. Introduction

Emerging trends in environmental engineering and biosystem analysis indicate that a clean, safe and healthy ecosystem is still possible regardless of the increased quest for technology and industrialization by a dynamic society where the fuel requirements of the energy sector and the chemical and petrochemical needs of the chemical and allied industries are greatly dependent on the petroleum industry in which the downstream sector is a key player. These needs range from the feedstock requirements of the chemical industries, polymeric industrial sector, the solvent sector, the cosmetics industries etc. The concern over industrial and technological expansion, energy utilization, waste generation from domestic and industrial sources viz a viz their attendant negative effects on the environment cannot be overemphasized.

This chapter is intended to expose the reader to the role of mass transfer on the topical issue of environmental remediation. This is against the backdrop of the interrelationship between mass transfer and the major processes such as biological, chemical and phyto-oxidation acting during the removal of toxic substances from the environment and the dependence of these processes on the availability of these substances which over time compromise the integrity of the environment. Research reports advanced in this chapter is aimed at highlighting the crucial need to very seriously exploit the principles of mass transfer in addressing the critical issue of environmental degradation. The underlying mechanisms involved in the removal process and the systematic protocol developed for accelerated clean up are incorporated.

Basically, mass transfer is one of the important three transport operations commonly encountered and employed in chemical transformations. It has been described fundamentally, as the movement of the components of a mixture from one point to another as a result of observed

differences in concentration [1]. The material transfer is usually in the direction of decreasing concentration gradient.

The concept of mass transfer is very important in the fields of engineering (particularly Chemical Engineering) and sciences in general where it is applied for physical processes. From the standpoint of chemical engineering, mass transfer is of prime significance because most of the unit operations involving separation of mixtures into their component parts employ mass transfer operation. The relevance of mass transfer operations is continuously a subject of discourse as specifically, there is hardly any chemical process which does not require a preliminary purification of raw materials or final separation of desired products from by-products. In essence it can be described as the process that determines the rate at which separation will occur. Issues relating the removal of certain materials from fluid streams typically by adsorption are important industrial applications of the mass transfer operation.

The challenges of maintaining a clean environment stem primarily from the increasing pollution of waters and land by heavy metals that are difficult to decompose biologically and organic compounds which are persistent, recalcitrant and ubiquitous. This is because these substances resist the self-purification capabilities of the rivers as well as decomposition in conventional wastewater treatment plant. Consequently, conventional mechanical-biological purification no longer suffices. It thus becomes imperative to supplement an additional stage of processing and this improvement has been augmented by adsorption; an innovative treatment method based on the principle of diffusion (a mechanism of mass transfer). Literature reports have shown that the mechanism of the process of material transfer is by diffusion and this is dependent to a large extent on the physical characteristics and attributes of the mass been considered for transfer. The transfer process which is dependent on concentration gradient is basically of two types; molecular diffusion and convective transfer. While the former is known to be involved with movement of a material between two points i.e from a high to low area of concentration, the latter relates to the flow of liquids around a solid surface in forced convection motion. Interestingly, the two transfer types are governed by Fick's first law of diffusion under the condition of unchanging concentration gradient with the passage of time. However, Fick's second law becomes applicable under unsteady-state diffusion. The principles of Fick's laws which suggest that the rate of diffusion is a linear function of the solute concentration gradient has continuously been affirmed by research results involving material transport. In general, mass transfer cannot really be separated from adsorption and desorption processes as the transport of materials from one phase to another is principally by the mechanism of diffusion. Sorption is the primary process in the evaluation of availability while mass transfer is the mechanism of movement from the fluid phase to the surface of the soil particle. Various isotherm correlations have been used to describe the surface adsorption of the solutes and their subsequent desorption from the soil surface [1]. The sorption of contaminant tends to separate the direct contact between microorganisms, adsorbents and contaminants, which is necessary for biodegradation detoxification to occur. The practical effect of the adsorption and desorption rate, is that it controls the overall reaction rate. The transport (mobility) of contaminant solute therefore is significantly dependent on two possible scenarios: fast sorption/desorption and slow sorption/ desorption.

Development of surface modified activated carbon from low cost and readily available natural materials and agricultural wastes have been advanced for the generation of activated carbon with far superior adsorption capacity for the treatment of contaminated water. The removal of pollutants from aqueous waste stream by adsorption in fixed beds has therefore progressively become an important treatment process and a subject of many excellent research works.

Laboratory and field studies results abound to demonstrate the applications of mass transfer in the management of the environment in terms of pollution monitoring and control. The intrinsic kinetics of the mass transfer process has through systematic and sustained researches become a relevant area of interest which provides information on availability, mobility and toxicity as a function of the measured concentration and the mechanism of sequestration of the solutes in the containing system.

2. Applications of mass transfer in water treatment technology

The demand for clean water for fishing activities, recreation etc and its non-ready availability has caused considerable attention to be focused towards recovery and re-use of waste waters. In water treatment procedures where the process of adsorption has been effectively engaged, the use of adsorbent materials has served as the solid surface onto which molecules of the adsorbates such as organic compounds, heavy metals, attach themselves. The removal of contaminant solutes from the environment has not been effectively accomplished by traditional methods. Hence it has now become universally recognized that adsorption technology provides a feasible and effective method for the removal of pollutants from polluted water resources and waste waters. Activated carbons are the most commonly used adsorbent in the adsorption process due to their high adsorption capacity, high surface area and high degree of surface reactivity. Adsorbents have been sourced variously from refinery residue, coal but mostly from agricultural waste materials such as coconut shell, soya bean, cotton seed, walnut and rice hulls, melon husk, orange peels etc.

The effectiveness of low density adsorbents dried (ground ripe and unripe orange peels) in the removal organics typified using naphthalene and pyrene from an aqueous stream has been extensively studied [2]. The influence of the variation in process conditions such as concentration, adsorbent dosage, agitation time and particle size, pH, and initial solute concentration were analyzed to highlight the contributions of mass transfer in the treatment of contaminated water. Under the operating conditions specified above, laboratory and experimental results showed that the removal efficiency defined by adsorption capacity increased with an increase in adsorbent dosage, contact time and initial solute concentration but decreased with an increase in the particle size. This experimental result clearly demonstrates that the transfer of any organic compound under consideration from one point to another is a linear function of the operating variables which positively improve the reliability of the process.

Following the same adsorption principle for mass transfer, the removal of mono and polycyclic aromatic hydrocarbons (PAHs) from bulk fluid stream onto adsorbents from periwinkle and coconut shell (PSC) also provides an alternative technology for effective mass transfer process in

the reduction of pollutant level of waste water. Naphthalene, phenanthrene and anthracene were used as the representative PAHs and the effluent stream was simulated refinery wastewater.

The result for the characterization of the refinery effluent before and after treatment with periwinkle shell activated carbon showed that the total suspended solids (TSS) reduced from an initial value of 53 mg/l to 2 mg/l after treatment.

Further insights into the role of adsorption on the contaminated water has revealed that the biochemical and chemical oxygen demand of the wastewater reduced drastically from an initial value to specifications recommended by the environmental protection agency (EPA) using activated carbon from materials such as periwinkle shell [3]. As contact time increased, percentage removal of the organic and inorganic contaminants present in the wastewater also increased. From the bench scale results [3], the total dissolved solids and total hydrocarbon content of the wastewater treated with activated periwinkle shell carbon reduced significantly. A maximum percentage removal of 78.5% was achieved. The clarity of the effluent water was observed to be greatly improved after the first hour of treatment where the turbidity dropped from 66 NTU to 6 NTU. Again the percentage turbidity increased with contact time until 100% removal was achieved following complete clarity.

The result showed comparatively, that the treated effluent water had maximum percentage reduction of approximately 83.26%, 91.19% (BOD, COD) for periwinkle shell carbon (PSC) and commercial activated carbon (CAC) respectively. The periwinkle shell carbon displayed the capacity to reduce the turbidity of the water contaminated with organic compounds via transfer of the contaminant solute from the bulk wastewater where their concentration is high to the external surface of the activated periwinkle shell carbon acting as the adsorbent.

In the development of alternative fixed filter bed for water treatment, the application of the mass transfer process by adsorption has also been shown to be feasible by examining the influence of modified clay on the rates of adsorption. The modifiers used were inorganic and organic acids, bases and salts. The results obtained showed that equilibrium adsorption of naphthalene i.e the transfer of naphthalene molecules from the bulk solution was attained at a faster rate using modified clay when compared with the unmodified clay. Amongst the modified clay used for the study, acids were found to be most suitable for the modification purpose [4].

This is attributable to the fact that the solutes in the acid medium had higher diffusive mobility defined by their dispersion coefficient/diffusivity as shown in Table 1 and higher influence on the physicochemical properties (porosity, surface area, bulk and particle density).

Overall, results from this study affirm that sediment modification directly affects the availability of the contaminant chemicals.

3. Applications in soil remediation

In soil remediation, the availability of the contaminant is of prime significance and it is commonly approached from the premise that chemicals are immediately accessible for

Modifying agents	D _{AB} (cm ² /s)
HCl	4.88 x 10 ⁻⁶
H ₂ SO ₄	4.5 x 10 ⁻⁶
HNO ₃	4.33 x 10 ⁻⁶
H ₃ PO ₄	2.97 x 10 ⁻⁶
KOH	5.15 x 10 ⁻⁷
NaOH	4.36 x 10 ⁻⁷

*Adapted from Oladele, A.O. (2012). M.Eng. Thesis. University of Benin, Nigeria.

Table 1. Parameter estimation for naphthalene diffusivity in modified-clay sediment*

microbial uptake only when in aqueous solution. The rationale behind this premise is that the small pore spaces internal to aggregates of soil and sediment particles exclude microbes, such that compounds that are dissolved or sorbed within these immobile-water domains must first be transported to the external aqueous phase (i.e., bulk aqueous phase) before they can be metabolized [5]. This premise is supported by several laboratory studies that have found biodegradation to occur only, or predominantly, in the bulk aqueous phase [6], [7]. A variety of factors, including physical characteristics of the sorbent (e.g., particle shapes, sizes, and internal porosities), chemical properties of the sorbates and sorbents, and biological factors (e.g., microbial abundance and affinity for the contaminant) influence availability.

In a study conducted [8], the experimental data from a soil microcosm was analyzed using the method of temporal moments (MOM) which interprets solute transport with linear equilibrium sorption and first order degradation and the analytical solutions of a transport model CXTFIT version 2.0. This was with a view to estimating the transport parameters (pore-water velocity, *V* and dispersion coefficient, *D*) using non-reactive solute and the degradation parameters (retardation factor *R* and first order degradation rate λ) of the contaminant PAHs.

A dimensionless parameter called the retardation factor was used to represent bioavailability (i.e the accessibility of a chemical for assimilation and possible toxicity). This parameter increased with increasing solute hydrophobicity.

The result from the study is summarized in Table 2 and it showed that naphthalene had the lowest retardation factor with a corresponding higher degradation rate constant. The observed trend is similar and comparable to previous estimates from the Michaelis-Menten kinetics. The finding from this study can be attributed to the aqueous solubility, diffusivity and mobility of each contaminant solute.

PAHs	R			λ (per day)		
	MOM	CXTFIT	ϵ	MOM	CXTFIT	E
Naphthalene	25.77	20.23	0.21	3.54	4.22	-0.19
Anthracene	41.62	28.43	0.32	1.21	2.05	-0.69
Pyrene	35.66	25.89	0.27	2.25	3.26	-0.45

*Adapted from Owabor, C.N. (2007) PhD Thesis, University of Lagos, Nigeria.

Table 2. Comparison of the Degradation and Transport parameters for the Contaminant PAHs*

In general, the result is significant as it affirms that the biodegradation of the contaminant organic compound or specifically PAHs is a function of their bioavailability.

Studies have led researchers to conclude that some microorganisms are capable of degrading compounds directly from the sorbed phase. Also, for many studies where solid-phase degradation was reported, biodegradation rates were nonetheless observed to decrease with contaminant soil-water contact time. Access to contaminants is increasingly inhibited as solutes migrate deeper into submicron pores of impermeable sorption domains in soil/sediment-water environments. From the foregoing, if solutes are degraded in the mobile aqueous phase, it then becomes pertinent to state that the rates of remediation will be reduced by sorption and/or diffusion into impermeable regions, with the overall rate controlled by the slowest process of desorption or biotransformation. For example, in batch systems where the solids have a large sorption capacity, only a small fraction of the contaminant mass may be present in the bulk water. Evolving experimental reports is thus emphasizing that sorbate *diffusion* is often the limiting step, particularly in systems involving contaminants with large organic-carbon partition coefficients (k_{OC}) and large fine-pored aggregates with high organic matter content.

Studies on mass transfer effects for the evaluation of bioavailability and biodegradation parameters of contaminant solutes in aqueous solid/sediment matrix applicable for biodegradation of the environmentally persistent and recalcitrant chemicals have been extensively investigated using models [7], [9] which incorporates a two-site sorption/desorption kinetics.

The applications of mass transfer by diffusion in multi-component mixtures were carried out by comparing the adsorption and desorption behavior of polycyclic aromatic hydrocarbons and benzene, toluene, ethylbenzene and xylene (BTEX) in sand and clay sediments fractions. Using equilibrium time as a basis for argument, research result showed that the contaminants in sand attained equilibrium faster than in the clay sediment for both sorption and desorption studies as a result of the higher permeability of sand sediment. The desorption equilibrium time in both sediment types was found to be slower than adsorption an indication that it may be the limiting step in the event of mineralization.

The adsorption and desorption kinetics of naphthalene using calcined and modified clay soil fractions at ambient temperature has also been investigated to demonstrate the role of mass

transfer in the removal of toxic chemicals from soil. Result of the batch experiments showed that adsorption equilibrium was attained at 24, 28 and 32 hours for modified, calcined and untreated soils; while the desorption equilibrium occurred at 46 hours for modified and 52 hours for calcined and untreated soils. Following the equilibrium time, the percentage of an initial 100mg/l of naphthalene in the slurry phase system unadsorbed was 30%, 32% and 35% for the calcined, modified and untreated soils respectively; while 12.3%, 11.2% and 9.5% of the adsorbed naphthalene resisted desorption by the calcined, modified and untreated samples respectively at equilibrium. The mass transfer rate was estimated using the Lagergren equation and found to be 0.12 mg/g.hr, 0.11mg/g.hr and 0.08mg/g.hr during adsorption while the desorption rate (k_{des}) were 0.06mg/g.hr, 0.05mg/g.hr and 0.07mg/g.hr for calcined, modified and untreated soil respectively. The results clearly confirm that the rate of adsorption and desorption of naphthalene differ among soil types and this directly affects its effective removal from the soil. Studies on the dynamic behavior of the adsorption of naphthalene onto natural clay with various modifying agents have shown that adsorption increased to a large extent with increasing surface area and porosity of the modified clay. The results using acids, bases and salts showed that equilibrium adsorption of naphthalene from the bulk solution were attained at a faster rate using inorganic acids. Further investigations revealed that of all the acids used, the diffusivity of naphthalene was highest in the HCl-modified clay which had the largest surface area and porosity.

Comparing this result with the data from the desorption study showed that while adsorption was inversely proportional to the pH of the medium, desorption was directly proportional. The implication of the retention time obtained from the equilibrium study is significant as it provides the bench mark for the interplay between sorption and degradation for transport and transformation of contaminant solutes within the soil matrix.

The adsorption and desorption kinetics of naphthalene, anthracene, and pyrene in a soil slurry reactor at ambient conditions was also investigated with a view to ascertaining the mechanisms controlling the retention and release rates of the compounds in the soil matrix. A stirred-flow method was employed to perform the experiments [10].

Analysis of the results of the batch adsorption/desorption kinetics and equilibria indicated that the desorption rate was slower than the adsorption rate. The cumulative extent of desorption for the tested chemicals (naphthalene, anthracene and pyrene) suggested that the desorption step was also the rate limiting for biodegradation. This may not be unrelated to the fact that diffusion in the pores may have been retarded by surface adsorption effects on soil organic carbon. The observed resultant effect was the lowering of the aqueous phase concentration of the contaminant PAHs which renders them not readily available to the microorganisms. The biodegradation will thus in the long run be controlled by the slow desorptive and diffusive mass transfer into biologically active areas. The extent of partitioning for the polycyclic aromatic hydrocarbons tested was found to be dependent on their solubility and diffusivity in the aqueous phase see Table 3. Experimental results from this study affirm that diffusivity/diffusion coefficient is a property dependent on the physical properties of a system as well as the molecularity, structural configuration and angularity of the solute [8].

Properties	Naphthalene	Anthracene	Pyrene
Molecular formula	C ₁₀ H ₈	C ₁₄ H ₁₀	C ₁₆ H ₁₀
Molecular weight (g/mol)	128	178	202
Density (g/cm ³)	1.14	1.099	1.271
Melting point (°C)	80.5	217.5	145-148
Boiling point (°C)	218	340	404
Aqueous solubility (g/m ³)	0.93	0.07	0.14

*Adapted from Zander et al., (1993), Perry's Handbook of Chemical Engineers' (1998) and Oleszczuk and Baran, (2003).

Table 3. Some properties of investigated PAHs*

Overall, discussion of the subject under consideration indicates that mass transfer is assessed by the rate of adsorption/desorption and it must be emphasized that this is both the measured concentration of the solute with time and the mechanism of distributing the solutes into surfaces and pores of individual adsorbent medium. The successful predictions of the fate and transport of solutes in the environment is hinged on the availability of accurate transport parameters.

Solute transport with linear equilibrium therefore must as a matter of necessity be accounted for and be accommodated as an integral component of the mineralization of toxic chemicals.

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