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Microcontaminant Sorption and Biodegradation in Wastewater Modeled as a Two-Phase System

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1. Introduction

It has only been within the past 15 years that concern about the presence of pharmaceutical compounds and other emerging contaminants in water and wastewater has garnered the attention of the scientific community. Although earlier research can be documented, it was not until the publication of the overarching analysis by Daughton and Ternes (1999) that scientific investigations began to take off, as evidenced by being cited over 900 times (As of March 2011). One of the key contributions of their research was to highlight the ubiquitous nature of those compounds in the environment and to highlight that their potential impact on human and environmental health was unknown. This work helped to spur one of the largest studies conducted, to date, the 1999 National Reconnaissance conducted by the U.S. Geological Survey (USGS 2003, Kolpin et al. 2003). As part of that study, investigators sampled 139 streams in 30 states and tested for 149 emerging compounds of interest to include hormones, steroids, prescription pharmaceuticals, insecticides, and pesticides. Perhaps the key finding from that survey was that every compound that was tested for was found to be present in the environment. Subsequent studies (Richardson and Ternes 2005, Daughton 2009, Bartelt-Hunt et al. 2009) have reinforced the need for continued research, both in regards to occurrence in surface water systems, as well as wastewater treatment plants.

As the research on the origination of these microcontaminants has progressed, it has become more apparent that wastewater treatment plants play a critical role (Lietz and Meyer 2004, Glassmeyer et al. 2005, Vanderford and Snyder 2006, Yu et al. 2006). These facilities are located at the nexus connecting the anthropogenic with the ecological and, as such, have become a focal point for environmental research, especially in regards to the fate, transport, and occurrence of emerging contaminants. A closer examination of the wastewater treatment process reveals two key fundamental processes: sorption and biodegradation (Joss et al. 2006, Ottmar et al. 2010a). These two processes are intrinsically linked as, in almost all instances, the rate of biodegradation will be related to the concentration of compound present in the aqueous phase, which, itself, is linked to the concentration in the solid phase by the process of sorption. It is this linkage that provides the motivation behind the development of a two-phase model that will account for both of these processes.

2. Model development

The examination of concurrent sorption and biodegradation in environmental systems is not actually a recent development. The method of volume averaging described by Hassanizadeh and Gray (1979) has frequently been used to examine contaminant transport in porous media. These analyses proceed by defining the groundwater system as containing two phases, the aqueous phase (groundwater) and the solid phase (soils). Of note, in some cases a more elaborate system could be defined with the solid phase actually consisting of multiple phases (i.e. an organic phase along with an inorganic phase), however it is the corollary with the two-phase system that will be used here. In the groundwater systems, the solid phase is stationary with the aqueous phase moving through it, as indicated below in Figure 1.

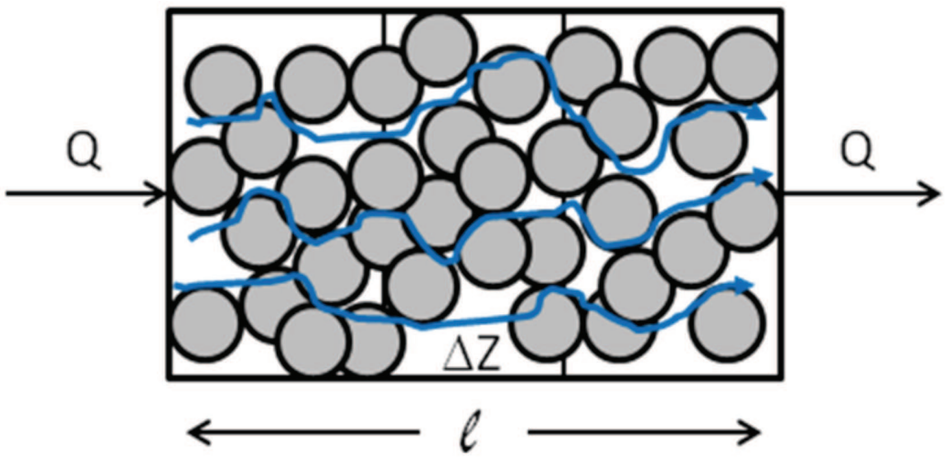

Fig. 1. Representation of porous media characteristic of groundwater systems

The analysis begins with a microscopic differential volume that is then expanded through volume averaging, with the ultimate result being the series of advection-dispersion-reaction (ADR) equations that are frequently encountered in groundwater research. This underlying methodology will now be applied to an activated sludge basin, with the key difference being that the solid phase will move in conjunction with the aqueous phase, rather than being stationary.

2.1 Modeling of the activated sludge basin

In broad terms, the wastewater treatment plant's activated sludge basin will be modeled as a plug flow reactor, with the key underlying assumption being that while there will be longitudinal variances along the length of the reactor, there will not be any vertical or latitudinal variances (i.e. for a given differential volume, it will be assumed to be completely mixed).

As seen in the folowing figures, the activated sludge basins are modeled as being a plug flow reactor (PFR) with a specified length, l, cross-sectional area, A, and volumetric flow rate, Q.

This process is defined as being a two-phase system, consisting of the solids phase and the aqueous phase. Inherent to this definition is the presumption that mass transfer of the target compounds to/from the gas phase due to deposition/volatilization is negligible based on their chemical properties (primarily pKa and Henry's Law coefficient).

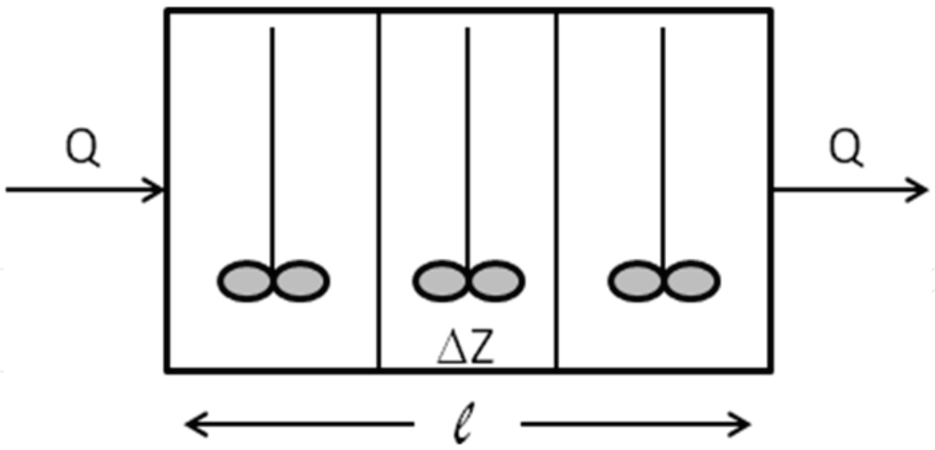

Fig. 2. Schematic of a plug flow reactor (PFR)

Having defined it as a two-phase system, the initial focus will be on the differential volume indicated by the ΔZ (and multiplied by A) in Figure 3. This differential volume is shown more clearly in the following figure.

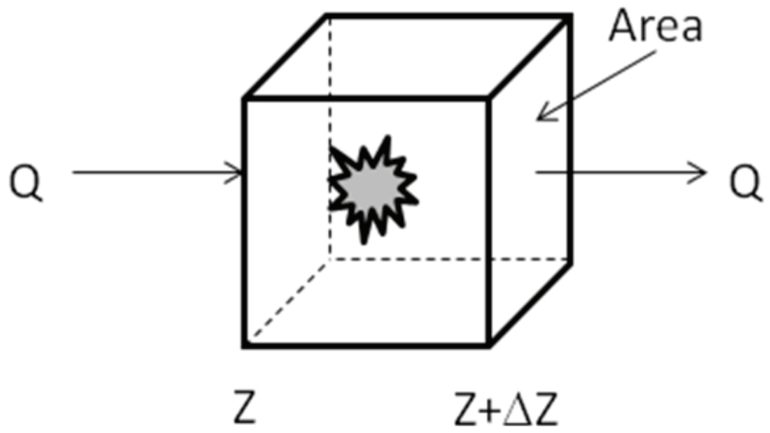

Fig. 3. Close-up of the differential volume

For this volume, a mass balance on the target compound in both phases is performed. First, as a word formulation and then as the mathematical representation of that phase:

2.1.1 Compound mass in the aqueous phase in the differential volume

(Change) = (Flow in with aqueous phase) – (Flow out with aqueous phase) + (flux from aqueous phase to solid phase) – (biodegradation in aqueous phase)

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{sorb\_flux} - \dot{m}_{bio} \tag{1}$$

Because the differential volume is extremely small, it is assumed to be at steady state, and so the overall change is mass is zero.

$$0 = QC\big|_{Z} - QC\big|_{Z+\Delta Z} + V_{aq} j_{sl} - V_{aq} r_{bio} \tag{2}$$

Where C is the concentration in the aqueous phase (µg/L), V_{aq} is the aqueous phase volume, j_{sl} is the mass flux to the solid phase (µg/L-time) and r_{bio} is the biodegradation rate expression (µg/L-time)
At this point, it is important to highlight the differences in the volumes presented so far. V is the total differential volume and V_{aq} is the volume of the aqueous phase within that differential volume, and V_s is the volume of the solid phase.

$$V = V_{aq} + V_s \Rightarrow A\Delta Z = V_{aq} + V_s \tag{3}$$

A further examination of the activated sludge system allows for a simplifying assumption in regards to the aqueous phase volume. The average solids concentration in an activated sludge tank is 3,250 mg/L for completely mixed tanks (Metcalf and Eddy 1991). These solids have a specific gravity of 1.25, meaning that in one liter of activated sludge, the 3,250 mg of solids will have a volume of 2.6 milliliters. Consequently, the aqueous volume (997.4 milliliters) is almost equal to the total volume (1,000 milliliters).
Returning to equation 2, by dividing both sides by Q and V results in:

$$\frac{C\big|_{Z+\Delta Z} - C\big|_Z}{\Delta Z} = \frac{A}{Q} j_{sl} - \frac{A}{Q} r_{bio} \tag{4}$$

Taking the limit as the differential length approaches zero yields:

$$\lim_{\Delta Z \to 0} \frac{C\big|_{Z+\Delta Z} - C\big|_Z}{\Delta Z} = \frac{A}{Q} j_{sl} - \frac{A}{Q} r_{bio} \Rightarrow \frac{dC}{dz} = \frac{A}{Q} j_{sl} - \frac{A}{Q} r_{bio} \tag{5}$$

Which is the PFR governing equation for the aqueous phase. The process is repeated for the solid phase.

2.1.2 Compound mass in the solid phase in the differential volume

(Change) = (Flow in with solid phase) – (Flow out with solid phase) + (flux from solid phase to aqueous phase)

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{sorb\_flux} \tag{6}$$

Again, because the differential volume is extremely small, it is assumed to be at steady state, and so the overall change in mass is zero.

$$0 = Q\,X\big|_Z\,S\big|_Z - Q\,X\big|_{Z+\Delta Z}\,S\big|_{Z+\Delta Z} + V\,X\big|_{Z+\Delta Z}\,j_{ls} \tag{7}$$

Where X is the solids concentration (kg/L), S is the compound concentration in the solid phase (µg/kg solids), and j_{ls} is the mass flux to the aqueous phase (µg/kg solids-time). Dividing both sides by Q and V results in:

$$\frac{X\big|_{Z+\Delta Z}\,S\big|_{Z+\Delta Z} - X\big|_Z\,S\big|_Z}{\Delta Z} = \frac{A}{Q} X\big|_{Z+\Delta Z}\,j_{ls} \tag{8}$$

Again, taking the limit as the differential length approaches zero yields:

$$\lim_{\Delta Z \to 0} \frac{X\big|_{Z+\Delta Z} S\big|_{Z+\Delta Z} - X\big|_{Z} S\big|_{Z}}{\Delta Z} = \frac{A}{Q} X\big|_{Z+\Delta Z} j_{ls} \Rightarrow \frac{d(XS)}{dz} = \frac{A}{Q} X\big|_{Z+\Delta Z} j_{ls} \tag{9}$$

Because the solids concentration varies minimally throughout the reactor (varying by less than 3% from one end to the other), it can effectively be treated as a constant, resulting in:

$$X \frac{dS}{dz} = \frac{A}{Q} X j_{ls} \tag{10}$$

At this point it can be seen that there are two governing equations for a target compound in the two different phases present in the PFR.

$$\frac{dC}{dz} = \frac{A}{Q} j_{sl} - \frac{A}{Q} r_{bio} \tag{5}$$

$$X \frac{dS}{dz} = \frac{A}{Q} X j_{ls} \tag{10}$$

At this point, two additional assertions can be made to simplify the governing equations and provide a unified theory encompassing transport in both phases. First, it should be noted that mass is conserved throughout the inter-phase mass transfer flux. Because of this, the following equation holds:

$$0 = \frac{V_{aq}}{V} j_{sl} + X j_{ls} \Rightarrow j_{sl} = -X j_{ls} \tag{11}$$

Equation 11 can then be combined with equation 10 to yield:

$$X \frac{dS}{dz} = -\frac{A}{Q} j_{sl} \tag{12}$$

Adding equation 12 to equation 5 gives:

$$\frac{dC}{dz} + X \frac{dS}{dz} = -\frac{A}{Q} r_{bio} \tag{13}$$

The second assertion to be made is in regards to the sorption mechanism occurring. If the assumption is made that sorption occurs very rapidly, is linear, and is essentially at equilibrium (as shown in Ottmar et al. 2010), then the following relation holds:

$$S = K_d C \tag{14}$$

Taking the derivative with respect to movement through the reactor yields:

$$\frac{dS}{dz} = K_d \frac{dC}{dz} \tag{15}$$

This can then be substituted into equation 13, giving:

$$\frac{dC}{dz} + K_d X \frac{dC}{dz} = -\frac{A}{Q} r_{bio} \Rightarrow \left(1 + K_d X\right) \frac{dC}{dz} = -\frac{A}{Q} r_{bio} \tag{16}$$

Then by defining that $(1 + K_dX) = R$, where R is the retardation factor, equation 16 ultimately reduces to:

$$R\frac{dC}{dz} = -\frac{A}{Q}r_{bio} \Rightarrow \frac{dC}{dz} = -\frac{1}{vR}r_{bio} \tag{17}$$

Where v is the linear velocity along the length of the reactor as defined by Q/A. At this point, the next step is to further examine r_{bio}, the biodegradation rate term. One of the most common approaches is to model biodegradation under a first-order process. This is manifested by:

$$r_{bio} = k_1 C(z) \tag{18}$$

Adding equation 18 back into equation 17 gives:

$$\frac{dC}{dz} = -\frac{k_1}{vR}C(z) \tag{19}$$

This expression can then be integrated:

$$\int \frac{dC}{C(z)} = -\frac{k_1}{vR}\int dz \Rightarrow \ln|C| = -\frac{k_1}{vR}z + Const_{Integration} \Rightarrow C = Be^{-\frac{k_1}{vR}z} \tag{20}$$

By applying the initial conditions that when $z = 0$, $C = C_0$, the equation can then be defined:

$$C_0 = B \Rightarrow C = C_0 e^{-\frac{k_1}{vR}z} \tag{21}$$

For the final step, the concentration at the end of the basin can be calculated by setting $z = l$.

$$C = C_0 e^{-\frac{k_1}{vR}l} \Rightarrow C_0 e^{-\frac{k_1\theta}{R}} \tag{22}$$

Where θ is the hydraulic retention time, which is equal to the length divided by the linear fluid velocity.

As has been observed experimentally, however, biodegradation sometimes does not quite appear to follow true first-order kinetics, but rather, a sort of substrate-enhanced process. One of the challenges with this is developing a relevant mathematic model that is grounded in physical principles and observations. To this end, the following expression is proposed for the biodegradation rate:

$$r_{bio} = k_1 X C(z)\left(1 + \frac{L(z)}{K_L}\right) \tag{23}$$

Where $L(z)$ is the concentration of substrate (BOD or COD) present and K_L is the Monod half saturation coefficient. Substituting this equation into equation 17 gives:

$$\frac{dC}{dz} = -\frac{k_1 X}{vR}C(z)\left(1 + \frac{L(z)}{K_L}\right) \tag{24}$$

Rearranging equation 24 and configuring it for integration yields:

$$\frac{dC}{C(z)} = -\frac{k_1 X}{vR}\left(1 + \frac{L(z)}{K_L}\right)dz \tag{25}$$

At this point, the challenge is in finding the appropriate mathematical expression for how the concentration of substrate (BOD or COD) changes as it moves through the reactor. The simplest model is that of a linear decrease from the concentration entering the reactor, L_0, to the concentration leaving the reactor, L_f:

$$L(z) = L_0 - \frac{1}{l}\left(L_0 - L_f\right) \tag{26}$$

Substituting this back into equation 25 gives:

$$\begin{aligned} &\frac{dC}{C(z)} = -\frac{k_1 X}{vR}\left(1 + \frac{L_0 - \frac{1}{l}\left(L_0 - L_f\right)z}{K_L}\right)dz \\ &\Rightarrow \frac{dC}{C(z)} = -\frac{k_1 X}{vRK_L}\left(K_L + L_0 - \frac{1}{l}\left(L_0 - L_f\right)z\right)dz \end{aligned} \tag{27}$$

This equation can then be integrated, giving:

$$\begin{aligned} &\ln|C| = -\frac{k_1 X}{vRK_L}\left[\left(K_L + L_0\right)z - \frac{1}{2l}\left(L_0 - L_f\right)z^2\right] + Const_{Integration} \\ &\Rightarrow C = Be^{-\frac{k_1 X}{K_L vR}\left[\left(K_L + L_0\right)z - \frac{1}{2l}\left(L_0 - L_f\right)z^2\right]} \end{aligned} \tag{28}$$

Applying the initial condition that at the beginning of the reactor, when $z = 0$, $C = C_0$, it can be seen that $B = C_0$, which results in the following governing equation for the aerobic basins:

$$C = C_0 e^{-\frac{k_1 X}{K_L vR}\left[\left(K_L + L_0\right)z - \frac{1}{2l}\left(L_0 - L_f\right)z^2\right]} \tag{29}$$

From this, the concentration at the end of the PFR can be calculated by setting $z = l$, and:

$$\begin{aligned} &C = C_0 e^{-\frac{k_1 X}{K_L vR}\left[\left(K_L + L_0\right)l - \frac{1}{2l}\left(L_0 - L_f\right)l^2\right]} \\ &\Rightarrow C = C_0 e^{-\frac{k_1 Xl}{K_L vR}\left[\left(K_L + L_0\right) - \frac{1}{2}\left(L_0 - L_f\right)\right]} \\ &\Rightarrow C = C_0 e^{-\frac{k_1 X\theta}{K_L R}\left(K_L + \frac{1}{2}L_0 + \frac{1}{2}L_f\right)} \end{aligned} \tag{30}$$

From this governing equation, the aqueous drug concentration at the end of the reactor, can then be determined. The mass of drug compound in the sorbed phase is calculated from the equilibrium sorption condition by means of the following equations:

$$Mass_{drug,total} = Mass_{drug,aq} + Mass_{drug,sorbed}$$
$$Mass_{drug,sorbed} = f_{sorbed} Mass_{drug,total}$$
$$\Rightarrow \frac{Mass_{drug,sorbed}}{f_{sorbed}} = Mass_{drug,aq} + Mass_{drug,sorbed}$$
$$\Rightarrow Mass_{drug,sorbed} - f_{sorbed} Mass_{drug,sorbed} = f_{sorbed} Mass_{drug,aq}$$
$$\Rightarrow Mass_{drug,sorbed} = \frac{f_{sorbed} Mass_{drug,aq}}{1 - f_{sorbed}}$$

The reduction in COD and the change in solids masses are based on the treatment plants operating characteristics.

2.2 Overall approach for wastewater treatment processes

Having developed a governing equation for simultaneous sorption and biodegradation, the model could then be applied to a wastewater treatment, as a single entity. Each wastewater treatment plant process is characterized by a set of ten parameters, each of which has been assigned to a specific cell in a table with five rows and two columns, as shown in Figure 4.

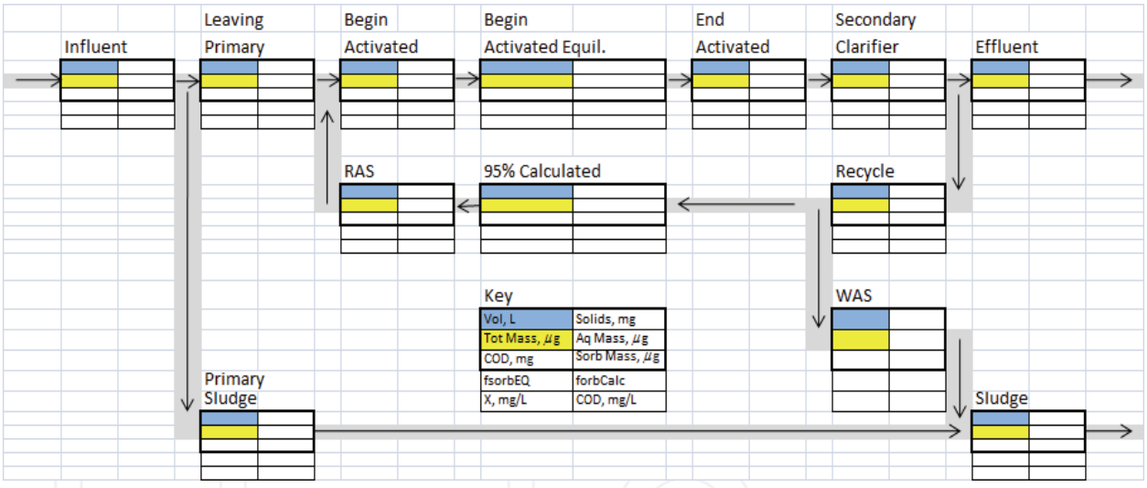

Fig. 4. Overall model schematic of a wastewater treatment plant. Note the key for the definition of individual cell values

The first row of each box contains the aqueous volume (V) of each compartment, as scaled to one liter, and the known mass of solids in that compartment. The second row contains the total mass of drug within each compartment (at left) and the mass of drug that exists in the aqueous phase within each compartment (at right). These drug masses are in units of μg. The third row contains the mass of COD substrate within each compartment (at left) and the mass of each drug that exists as sorbed phase (at right). COD mass is in mg, and drug mass is in μg. The total mass of drug compound (second row, first column) will always be equal to the sum of the mass in the aqueous phase (second row, second column) and the mass in the sorbed phase (third row, second column). The left-hand side of the fourth row contains the estimated fraction of each drug that exists in the sorbed phase assuming equilibrium conditions. This is based on the K_d value for each drug, as measured previously, and the

solids concentration in each compartment. The right-hand side of the fourth row contains the estimated fraction of each drug that exists in the sorbed phase, as calculated using mass in the aqueous phase and the mass in the sorbed phase. The equilibrium sorbed fraction and computed sorbed fraction are only different from each other when two streams with markedly different solids concentrations mix. For our model, this happens at the beginning of the aerobic basin, where effluent from the primary clarifiers mixes with return activated (RAS) sludge from underneath the secondary clarifiers. The fifth row contains two concentrations calculated from the aforementioned parameters: the biosolids concentration (X) at left and COD concentration (L) at right, both in mg/L.

2.2.1 Influent

The first modeled location corresponds to WWTP influent. The aqueous volume for this compartment is set to 1L, but this could be scaled based on actual flow rates. Masses and concentrations for COD and solids are set to match the characteristics of any specific WWTP. The total suspended solids (TSS) in the raw influent and the COD concentration (L) can be based on information from a treatment plant or from various references. Influent total drug masses can be taken from projection calculations by Ottmar et al. (2010b) for a plant with P/Q (service population over daily flow) equal to the target plant. Aqueous-phase and sorbed-phase drug masses can then be calculated assuming equilibrium conditions, using K_d values previously determined and the presumed TSS concentration in influent wastewater. Equation 31, below, can be re-arranged to solve for this:

$$K_d = \frac{1}{X_{ss}}\left(\frac{1}{1-f_{sorbed}} - 1\right) \Rightarrow K_d X_{ss} + 1 = \frac{1}{1-f_{sorbed}} \Rightarrow f_{sorbed} = 1 - \frac{1}{1+K_d X_{ss}} \tag{31}$$

From this, the mass in the sorbed phase is equal to the total mass multiplied by the sorbed fraction. The mass in the aqueous phase is equal to the total mass minus the mass in the sorbed phase.

2.2.2 Primary clarification

The second modeled location corresponds to the exit of the primary (1°) clarifiers. It was assumed that the overall flow splits into two smaller flows at this location, namely: primary sludge and primary effluent. For an example, it can be said that 60% of TSS and 40% of COD are removed into the primary sludge stream. The remaining TSS and COD flow from the primary clarifier into the activated sludge basin with the primary effluent. Based on these parameters and an assumed solids concentration of 45,000 mg/L for the primary sludge, a mass balance on the solids can be used to calculate the mass of solids (first row, second column) and the aqueous volume (first row, first column) leaving the primary clarifier as effluent or primary sludge. The following two equations are used, with the first being the mass balance equation and the second being the balance equation for a non-compressible aqueous fluid:

$$Mass_{solids\_in} = Mass_{solids\_primaryeff} + Mass_{solids\_primarysludge}$$
$$\Rightarrow X_{in}Q_{in} = X_{primaryeff}Q_{primaryeff} + X_{primarysludge}Q_{primarysludge}$$

$$Q_{in} = Q_{primaryeff} + Q_{primarysludge}$$

X_{in} is the solids concentration in the influent, Q_{in} is the aqueous flow rate (unit volume), $X_{primaryeff}$ is the solids concentration in the primary effluent, $Q_{primaryeff}$ is the flow rate leaving the primary clarifier, $X_{primarysludge}$ is the solids concentration in the primary sludge, and $Q_{primarysludge}$ is the sludge flow rate. Of these six, only $Q_{primaryeff}$ and $Q_{primarysludge}$ are unknown, but with two equations, they can be determined.
Concerning the transport of COD, a similar mass balance approach was used:

$$Mass_{COD\_in} = Mass_{COD\_primaryeff} + Mass_{COD\_primarysludge}$$
$$\Rightarrow L_{in}Q_{in} = L_{primaryeff}Q_{primaryeff} + L_{primarysludge}Q_{primarysludge}$$

The flow rates have already been determined (previously with the solids mass balance), and the amount of COD leaving the primary clarifier is set as part of this plant's operating characteristics (40% removal). Consequently, the masses of COD (third row, first column) and the concentrations (fifth row, second column) can be calculated.
For evaluation of drug compound transport, each phase is treated as a separate process. Beginning with the aqueous phase, we begin with the familiar mass balance. Here, we assume that substantial biodegradation does not occur in the primary clarifier due to the short hydraulic retention time and anoxic conditions:

$$Mass_{drug,aq,In} = Mass_{drug,aq,primaryeff} + Mass_{drug,aq,primarysludge}$$
$$\Rightarrow C_{in}Q_{in} = C_{primaryeff}Q_{primaryeff} + C_{primarysludge}Q_{primarysludge}$$

Because the drug compound will be dissolved in the aqueous phase, the concentrations (in μg/L) will not change, so C_{in} will be equal to $C_{primaryeff}$ and $C_{primarysludge}$. Consequently, the transport of drug mass in the aqueous phase will be proportional to the transport of the aqueous phase itself. For example, if the aqueous phase flow rate (first row, first column) leaving the primary clarifier as the primary sludge is equal to 0.4% of the volume in the influent, then the mass of drug compound in the aqueous phase of the primary sludge (second row, second column, Primary Sludge) will be equal to 0.4% of the mass of drug compound in the aqueous phase of the influent (second row, second column, Influent).
The transport of drug compound in the sorbed phase will be similarly governed, with the basis being a mass-balance approach, as outlined in the following equation:

$$Mass_{drug,sorb,in} = Mass_{drug,sorb,primaryeff} + Mass_{drug,sorb,primarysludge}$$
$$\Rightarrow S_{in}X_{in}Q_{in} = S_{primaryeff}X_{primaryeff}Q_{primaryeff} + S_{primarysludge}X_{primarysludge}Q_{primarysludge}$$

Because the only transport process occurring is a physical separation of the sludge, the sorbed concentration (in mg/kg sludge) will not change, so S_{in} will be equal to $S_{primaryeff}$ and $S_{primarysludge}$. For example, if 60% of the solids from the influent (first row, second column, influent) go to the primary sludge (first row, second column, primary sludge), then 60% of the total drug mass in the sorbed phase from the influent (third row, second column, influent) will go with the primary sludge (third row, second column, primary sludge).

2.2.3 Preliminary activated sludge treatment

Entrance into secondary (2°) treatment, "Start A.S. Basin," marks the third modeled location, in particular inlet to the activated sludge basins. Here, the effluent from the primary clarifier

is merged with recycled activated sludge (R.A.S.). Modeling at this location requires a two-step mathematical process. The first step comprises arithmetic addition of the physical properties from the two feeder streams:

$$Q_{StartASbasin} = Q_{leaving1^o\,clarifier} + Q_{R.A.S.}(1stRow, 1stColumn)$$

$$Mass_{Solids,StartASbasin} = Mass_{Solids,Leaving1^0\,Clarifier} + Mass_{Solids,R.A.S.}(1stRow, 2ndColumn)$$

$$Mass_{drug,aq,StartASbasin} = Mass_{drug,aq,Leaving1^0\,Clarifier} + Mass_{drug,aq,R.A.S.}(2ndRow, 2ndColumn)$$

$$Mass_{drug,sorb,StartASbasin} = Mass_{drug,sorb,Leaving1^0\,Clarifier} + Mass_{drug,sorb,R.A.S.}(3rdRow, 2ndColumn)$$

$$Mass_{COD,StartASbasin} = Mass_{COD,Leaving1^0\,Clarifier} + Mass_{COD,R.A.S.}(3rdRow, 1stColumn)$$

As mentioned previously, the addition of the masses of drug compound in the solids phases and in the aqueous phases produces a condition whereby the equilibrium sorption conditions are not satisfied, owing to the marked increase in solids concentration (a jump from 120 mg/L to 3000 mg/L). This can be seen by re-visiting equation 31 and by the fact that the fraction of drug compound sorbed that is calculated based the masses in the aqueous phase and in the solids phase is not the same as the fraction sorbed calculated based on the solids concentration and the distribution coefficient. Because laboratory batch tests have shown that sorption happens quite rapidly and can be assumed be essentially at equilibrium, a subsequent series of data cells is used to make the conversion to an equilibrium condition. This is done by setting the mass of drug in the sorbed phase (3rd row, 2nd column) of the "Start A.S. EQM" data set equal to the total mass (2nd row, 1st column) in the "Start A.S. Basin" data set multiplied by the fraction sorbed at equilibrium (4th row, 1st column). The mass of drug in the aqueous phase (2nd row, 2nd column) of the "Start A.S. EQM data set is then calculated by subtracting the aforementioned calculated mass in the sorbed phase from the total mass.

2.2.4 Aerobic activated sludge treatment

The fourth modeled process is the activated sludge basin. This compartment is modeled as a plug flow reactor, which makes it possible to compute extent of pharmaceutical biodegradation and sorption as a function of travel time. A more rigorous, first-principles-based approach is needed for this process because both sorption and biodegradation are occurring and need to be accounted for simultaneously. The use of a plug-flow model allows for the appropriate formulation of the fate and transport of the compounds and phases (aqueous and solid).

2.2.5 Secondary clarification

The fifth modeled location comprises the secondary clarifier. Secondary clarification, like the equilibrium portion of the activated sludge basin, is modeled assuming plug flow conditions with equilibrium sorption. Extent of pharmaceutical biodegradation in this compartment is once again computed as a function of time in the reactor and the biodegradation rate coefficient, in this case, $k_1/2$. A decreased rate constant is used to account for the lack of aeration during secondary clarification and the presumption that the biomass are less actively degrading COD and drugs in the clarifiers relative to the activated sludge basins. After the secondary clarifier, the process stream splits into two streams: the effluent stream and the sludge recycle stream. The volume (first row, first column), the

solids mass (first row, second column), and the COD mass (third row, first column) in the effluent are set to match the plant operating characteristics (and also effluent regulatory requirements, 5 mg/L solids and 3 mg/L COD). The volume, solids mass, and the COD mass for the sludge recycle are calculated by subtracting the effluent values from the secondary clarifier values:

$$Q_{\mathrm{Re}cycle} = Q_{Leaving\,2^0\,Clarifier} - Q_{Effluent.}(1stRow, 1stColumn)$$
$$Mass_{Solids,\mathrm{Re}cycle} = Mass_{Solids,Leaving\,2^0\,Clarifier} - Mass_{Solids,Effluent.}(1stRow, 2ndColumn)$$
$$Mass_{COD,StartASba\sin} = Mass_{COD,Leaving\,2^0\,Clarifier} - Mass_{COD,Effluent}(3rdRow, 1stColumn)$$

As with separation after the primary clarifier, the transport of drug compound is modeled to mirror the transport of the phase containing the drug compound (i.e. inter-phase flux, or *j*, is assumed to not be significant owing to equilibrium conditions). If 66% of the aqueous phase goes into the effluent stream (first row, first column, Effluent), then 66% of the drug mass present in the aqueous phase leaving the secondary clarifier will go into the effluent stream (second row, second column, Effluent). The drug masses in the sludge recycle stream are the calculated by subtracting the effluent masses from the masses leaving the secondary clarifier.

2.2.6 Sludge recycle

After separation following the secondary clarifier, the next modeled process is the sludge recycle stream. As mentioned above, the values for the aqueous volume (first row, first column), the solids mass (first row, second column), the mass of COD (third row, first column), the aqueous drug mass (second row, second column), and the sorbed drug mass (third row, second column) for the recycle stream are calculated by subtracting the effluent values from the values leaving the secondary clarifier. The recycle stream is then split into two separate streams, the return activated sludge (RAS), which is pumped back to the beginning of the activated sludge basins, and the waste activated sludge (WAS), which is merged with the primary sludge stream and pumped to the anaerobic digesters (not modeled here). In this case, the treatment plant's operating characteristics define the separation between these two streams, specifically, the RAS is 95% of the recycle stream, whereas the WAS is 5% of the stream. Both the aqueous phase (first row, first column) and the solids phase (first row, second column) are split proportionately with 95% moving to the RAS and 5% moving to the WAS. Additionally, the COD mass dissolved in the aqueous phase (third row, first column) and the drug mass in the aqueous phase (second row, second column) are split proportionately to the phase (95% to RAS, 5% to WAS), as is the mass of drug in the sorbed phase (third row, second column).

The final component of the model is the iterative step that is part of the RAS stream. This two-step process was necessary to eliminate circular calculation errors that arise due to the recycle stream which otherwise would have produced an indeterminate system. This error can be highlighted by looking at just the aqueous phase drug mass. The mass at Start A.S. Basin is calculated from the mass leaving the primary clarifier and the mass in the RAS stream. The mass at Start A.S. EQM is calculated from the mass at Start A.S. Basin. The mass at Leaving A.S. Basin is calculated from the mass at Start A.S. Basin. The mass Leaving 2° Clarifier is calculated from the mass at Leaving A.S. Basin. The mass at Recycle is calculated from the Effluent and the mass at Leaving 2° Clarifier. Finally, the mass in the RAS stream is

calculated from the Recycle stream. This value then would be fed into the calculation for Start A.S. Basin, resulting in a circular calculation error. This error is resolved by essentially creating two separate entries in the model for the same process. The first, RAS, provided the values that feed into the Start A.S. Basin process. The second, 95% Calculated, is calculated from the Recycle stream, as described previously. Initially, two arbitrary values are inputted for the mass of drug compound in the aqueous phase (second row, second column) and the in the sorbed phase (third row, second column) for the RAS process. An optimization routine is then executed to minimize the sum of the squared residuals between the drug masses in the RAS line that feed into the activated sludge basin and the RAS line that is calculated as being 95% of the recycle line. By minimizing the difference between the two processes, the recycle loop is effectively closed, allowing for a complete modeling of the wastewater treatment process.

3. Conclusions

Modeling the simultaneous sorption and biodegradation in wastewater systems has proven to be a challenging problem for researchers. Because the two processes are intrinsically linked, a novel approach was needed to develop a comprehensive mathematical expression to be used in modelling analyses. To that end, the volume averaging methodology commonly employed in groundwater systems was used with one key difference: rather than the having the solid phase be stationary, it was mobile. This paradigm shift allowed for fate and transport modelling throughout a wastewater treatment plant. This new model is sufficiently robust that it can have applications with many different types of compounds in different treatment plants with varying operational characteristics.

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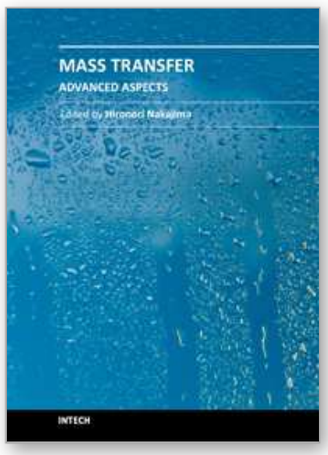

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Our knowledge of mass transfer processes has been extended and applied to various fields of science and engineering including industrial and manufacturing processes in recent years. Since mass transfer is a primordial phenomenon, it plays a key role in the scientific researches and fields of mechanical, energy, environmental, materials, bio, and chemical engineering. In this book, energetic authors provide present advances in scientific findings and technologies, and develop new theoretical models concerning mass transfer. This book brings valuable references for researchers and engineers working in the variety of mass transfer sciences and related fields. Since the constitutive topics cover the advances in broad research areas, the topics will be mutually stimulus and informative to the researchers and engineers in different areas.

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