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Grado en Ingeniería Civil
Universidad Politécnica de Cartagena

TEMA 3.
BALANCES DE MATERIA Y ENERGÍA EN MASAS DE AGUA

1. Introducción
2. Sistemas en estado estacionario
3. Sistemas en estado no estacionario
4. Balances de energía

1. Introducción

Conservación

1ª LEY DE LA TERMODINÁMICA

Sistema cerrado

$$\Delta E_p + \Delta E_c + \Delta U = q - w$$

$$\Delta E_p = 0 \qquad \Delta E_c = 0$$

$$\Delta U = q - w$$

$q = 0$ → Adiábatico

$\Delta V = 0$ (reactor) → $\Delta U = q$

DISTRIBUCIÓN DEL CONTAMINANTE

AIRE/AGUA

$$K_{aw} = \frac{C_{ia}}{C_{iw}}$$

LEY DE HENRY (1803)

- Temperatura
- Otros disolventes
- Coloides
- pH

$$K_{aw} = \frac{P_i}{C_{iw}} = \frac{C_{ia} RT}{C_{iw}} \left(\frac{Pa}{mol \cdot m^{-3}} \right)$$

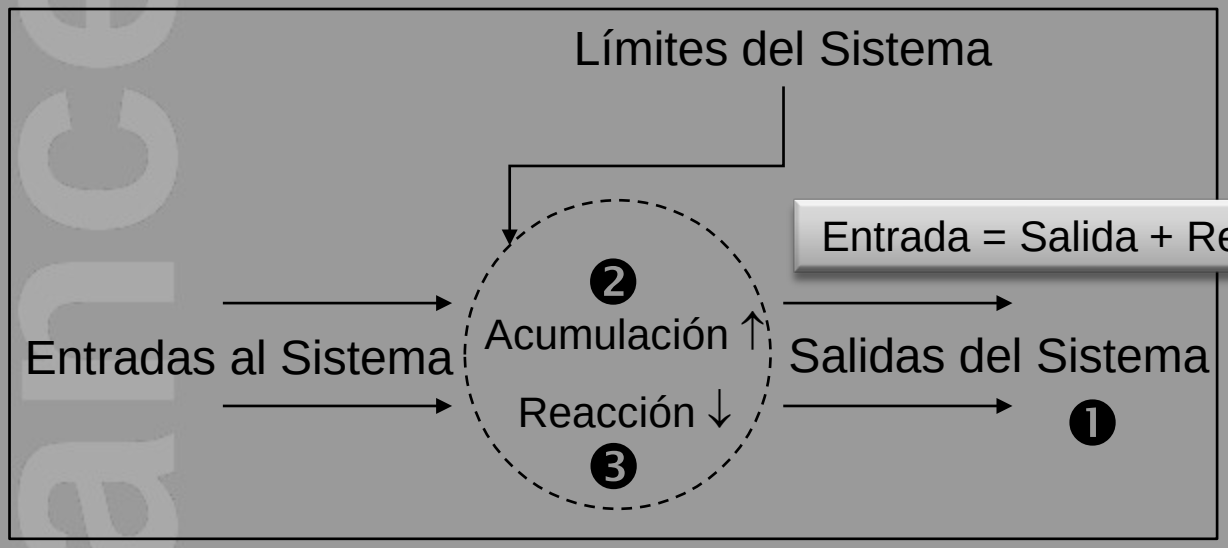
SUELO/AGUA

$$K_{sw} = K_{sw}^{om} + K_{sw}^{mm}$$

$$K_{om} = \frac{K_{sw}^{om}}{f_{om}} \qquad K_{mm} = \frac{K_{sw}^{mm}}{S_a}$$

2. Sistemas en estado estacionario

DEFINICIÓN DE LOS LÍMITES DEL SISTEMA



Entrada = Salida + Reacción + Acumulación

ESTADO ESTACIONARIO

Acumulación = 0

CONTAMINANTE CONSERVATIVO

Reacción = 0

Entrada = Salida

CONTAMINANTE NO CONSERVATIVO

Entrada = Salida + Reacción

ESTADO NO ESTACIONARIO

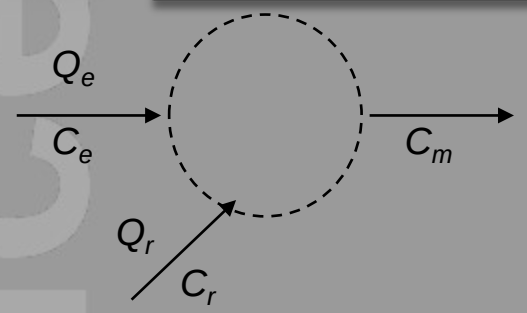
Entrada - Salida = Transporte + Dispersión + Reacción + Fuentes + Sumideros

Conservativo

2. Sistemas en estado estacionario

MODELO DE MEZCLA

Distancia de mezclado → $L = 0{,}1u\dfrac{W^2}{\varepsilon_t}$



Mezclado vertical: 90 veces más rápido que mezclado transversal

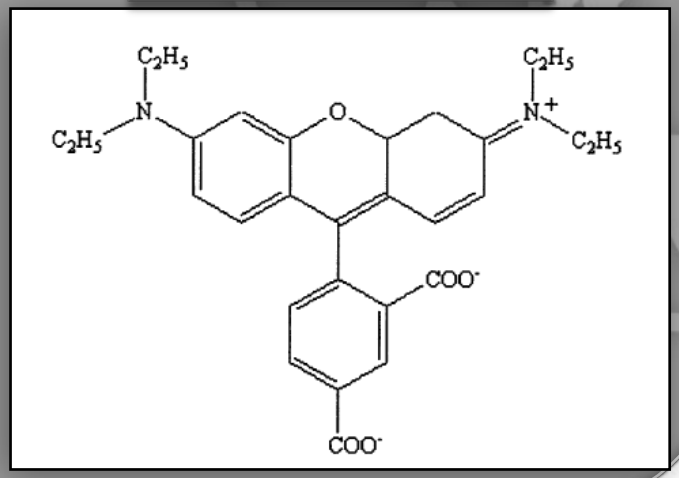
CONTAMINANTE CONSERVATIVO

Entrada = Salida

$$C_m = \frac{Q_e \cdot C_e + Q_r \cdot C_r}{Q_e + Q_r}$$

→ Metales pesados, NO_3^-, trazadores, Cl^-

RODAMINA-WT



Predicción de la concentración (1D)

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D_x \frac{\partial C}{\partial x}\right) - v_x \frac{\partial C}{\partial x}$$

IMAGEN TOMADA DE:
Lin *et al.* (2003). Comparison of rhodamine WT and bromide in the determination of hydraulic characteristics of constructed wetlands. Ecological Engineering 20: 75-88.

Orden 0

2. Sistemas en estado estacionario

CONTAMINANTE REACTIVO O NO CONSERVATIVO

Entrada = Salida + Reacción

OD, DBO, T, Cl"a", R-N, NH_3-N, NO_2^-, NO_3^-, P, µ.o.

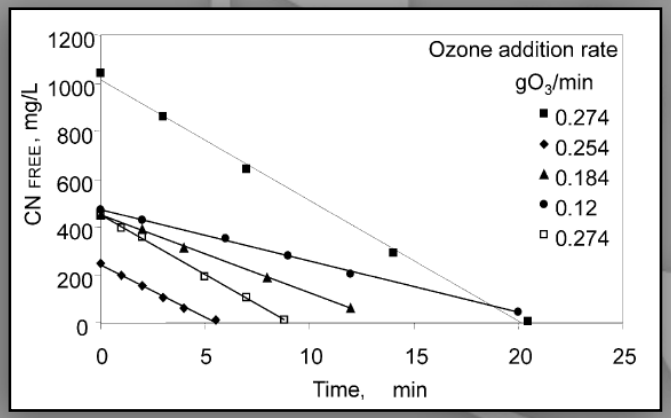
Cinética de orden cero

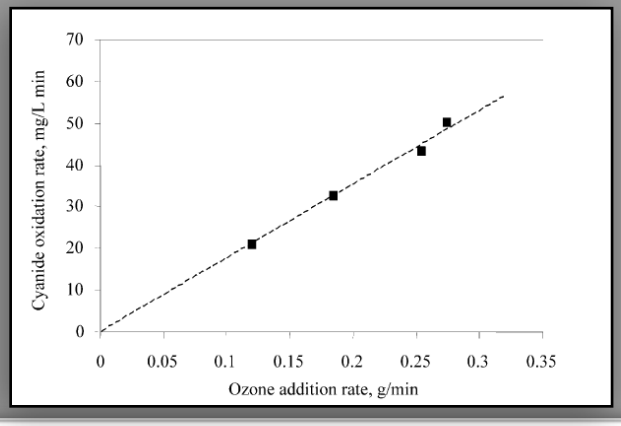
$$r(C) = \frac{dC}{dt} = k_0$$

$$r(C) = \frac{dC}{dt} = -k_0$$

$$V\frac{dC}{dt} = -Vk_0 \longrightarrow \boxed{C = C_0 - k_0 t}$$

$CN^- + O_3 \rightarrow CNO^- + O_2$





IMÁGENES TOMADAS DE:
Parga *et al.* (2003). Destruction of cyanide waste solutions using chlorine dioxide, ozone and titania sol. Waste Management 23: 183-191.

Orden 1

2. Sistemas en estado estacionario

CONTAMINANTE REACTIVO O NO CONSERVATIVO

Entrada = Salida + Reacción

Cinética de primer orden

$$r(C) = k_1 C$$

$$r(C) = -k_1 C$$

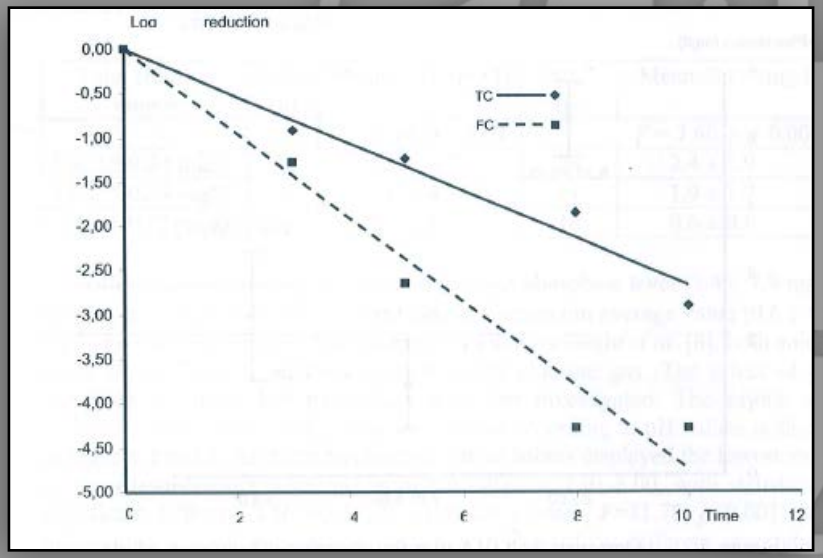
$$V\frac{dC}{dt} = -Vk_1 C \longrightarrow \boxed{C = C_0 e^{-k_1 t}}$$

Degradación del Cl_2 en agua desinfectada

$$\frac{dC_{Cl}}{dt} = -k * C_{Cl}$$

$$C_{Cl}(t) = C_{Cl_0}\exp(-kt)$$

IMAGEN TOMADA DE:
Bayo *et al.* (2008). Disinfection efficiency of secondary effluents with ultraviolet light in a Mediterranean area. WIT Transactions on Ecology and the Environment 111: 511-520.



IMÁGENES TOMADAS DE:
Kohpaei y Sathasivan (2011). Chlorine decay prediction in bulk water using the parallel second order model: An analytical solution development. Chemical Engineering Journal 171: 232-241.

Cinética del proceso de eliminación de microorganismos en aguas desinfectadas

Orden 1

2. Sistemas en estado estacionario

CONTAMINANTE REACTIVO O NO CONSERVATIVO

Entrada = Salida + Reacción

Cinética de primer orden

Eliminación de contaminantes en humedales empleados como tanques de tormenta

SÓLIDOS EN SUSPENSIÓN

FÓSFORO TOTAL
AMONIO
NITRATO

$$f(y) = \frac{C(y)}{C_{in}} = \exp\left(-\frac{k_a y}{q}\right)$$

$$f(t) = \frac{C(t)}{C_{in}(t)} = \exp(-k_v t)$$

$$\ln\left(\frac{C - C^*}{C_i - C^*}\right) = -\frac{k_a}{q}$$

$$\frac{C}{C_i} = e^{-k_a/q}$$

$$\frac{C}{C_i} = e^{-k_v \tau}$$

IMÁGENES TOMADAS DE:
Holland *et al.* (2005). Analysis and modeling of suspended solids from high-frequency monitoring in a stormwater treatment wetland. Ecological Engineering 24: 159-176.

IMÁGENES TOMADAS DE:
Carleton *et al.* (2001). Factors affecting the performance of stormwater treatment wetlands. Water Research 35: 1552-1562.

Orden 1

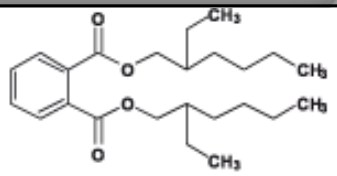
2. Sistemas en estado estacionario

CONTAMINANTE REACTIVO O NO CONSERVATIVO

Entrada = Salida + Reacción

Modificación a la cinética de orden 1

Eliminación de DEHP del agua residual en CSTR



DEHP

di(2-etil-hexil) ftalato

IMAGEN TOMADA DE: Lemos de Souza *et al.* (2009). Application of infrared and raman techniques in the identification and quantification of plasticizers in commercial films of PVSC. Qumica Nova 32: 1452-1456.

IMÁGENES TOMADAS DE: Vavlin (2007). Corrected first-order model of DEHP degradation. Chemosphere 68: 1992-1995.

$$\frac{dS}{dt} = -k(S - \alpha S_0)$$

$$S = S_0(1-\alpha)e^{-kt} + \alpha S_0$$

$$\frac{dS}{dt} = \frac{1}{T}(S_{inf} - S) - k(S - \alpha S_{inf})$$

$$S = S_{inf}\frac{1+\alpha kT}{1+kT}\left[1 - e^{-(k+1/T)t}\right] + S_0 e^{-(k+1/T)t}$$

Pseudo-primero

2. Sistemas en estado estacionario

CONTAMINANTE REACTIVO O NO CONSERVATIVO

Entrada = Salida + Reacción

Cinética de pseudo-primer orden → Procesos de adsorción de metales pesados en agua

$$\frac{dq}{dt} = k_1(q_e - q) \longrightarrow \boxed{\log(q_e - q) = \log q_e - \frac{k_1}{2{,}303}t}$$

$$\boxed{v_1 = k_1 q_e}$$

Modelo de Lagergren (1898)

(1)

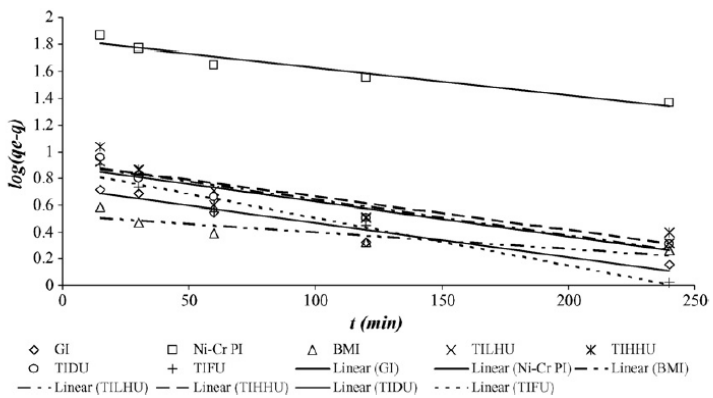


Fig. 2. Lagergren pseudo-first-order sorption kinetics plot of Ni(II) biosorption from industrial wastewater onto *C. fistula* biomass.

(2)

Table 3. Rate constants and equilibrium Cd^{2+} uptake according to pseudo-first- and pseudo-second-order kinetic models.

	Native grapefruit	Protonated grapefruit
$q_{e,exp}$ (meq g^{-1})	0.1870	0.1812
Pseudo-first-order kinetic model		
$q_{e,cal}$ (meq g^{-1})	0.2291	0.1694
k_1 (min^{-1})	0.0046	0.0046
r	0.726	0.772
r^2	0.528	0.597
r^2_{adj}	0.433	0.462
S_e	0.1956	0.1757
SS_{REG}	0.214	0.137
SS_{RES}	0.191	0.093
F-test (p value)	5.583 (<0.1)	4.438 (<0.1)
Durbin–Watson	2.492	2.101
Pseudo-second-order kinetic model		
$q_{e,cal}$ (meq g^{-1})	0.1819	0.1821
k_2 (g meq^{-1} min^{-1})	1.8562	0.5357
h (meq g^{-1} min^{-1})	0.0614	0.0178
r	0.945	0.991
r^2	0.892	0.983
r^2_{adj}	0.866	0.974
S_e	148.1593	42.8149
SS_{REG}	728,397.761	208,019.246
SS_{RES}	87,800.725	3666.233
F-test (p value)	33.184 (<0.01)	113.478 (<0.01)
Durbin–Watson	2.757	2.073

(r) Correlation coefficient; (r^2) determination coefficient; (r^2_{adj}) adjusted determination coefficient; (S_e) standard error of the estimate; (SS_{REG}) regression sum of squares; (SS_{RES}) residual sum of squares

IMÁGENES TOMADAS DE:

(1) Hanif *et al*. (2007). Kinetic studies for Ni(II) biosorption from industrial wastewater by *Cassia fistula* (Golden Shower) biomass. Journal of Hazardous Materials 145: 501-505; (2) Bayo *et al.* (2012). The use of native and protonated grapefruit biomass (*Citrus paradisi* L.) for cadmium(II) biosorption: equilibrium and kinetic modelling. Environmental Technology 33: 761-772.

Orden 2

2. Sistemas en estado estacionario

CONTAMINANTE REACTIVO O NO CONSERVATIVO

Entrada = Salida + Reacción

Cinética de segundo orden

$$r(C) = k_2 C^2$$

$$r(C) = -k_2 C^2$$

$$V\frac{dC}{dt} = -Vk_2C^2$$

$$C = \frac{C_0}{1 + C_0 k_2 t}$$

$$\frac{1}{C} = k_2 t + \frac{1}{C_0}$$

Depuración de agua residual de la industria textil mediante reactor UAFB

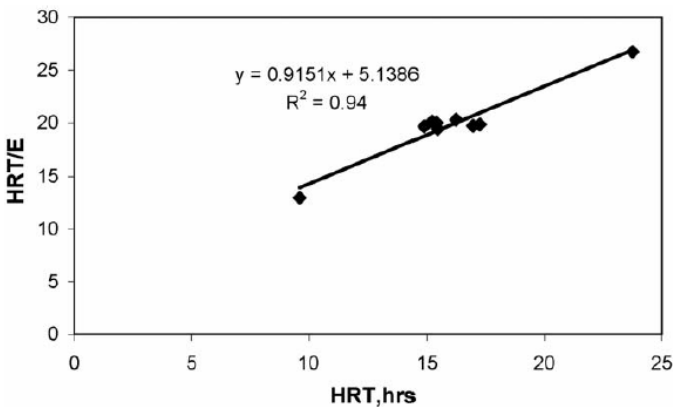


Fig. 5. Second-order kinetic model application for UAFB.

$$\frac{-ds}{dt} = k_{2(S)} X \left(\frac{S}{S_o}\right)^2$$

$$\frac{\theta}{E} = a + b\theta$$

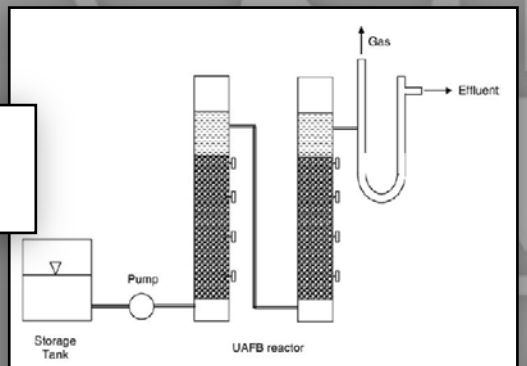


Fig. 1. Schematic diagram of hybrid column UAFB reactor.

IMÁGENES TOMADAS DE: Sandhya and Swaminathan (2006). Kinetic analysis of treatment of textile wastewater in hybrid column upflow anaerobic fixed bed reactor. Chemical Engineering Journal 122: 87-92.

Pseudo-segundo

2. Sistemas en estado estacionario

CONTAMINANTE REACTIVO O NO CONSERVATIVO

Entrada = Salida + Reacción

Cinética de pseudo-segundo orden → Proceso de bioadsorción de Cd(II)

$$\frac{dq}{dt} = k_2 (q_e - q)^2$$

$$v_2 = k_2 q_e^2$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

$$q = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$$

Modelo de Ho and McKay (1999)

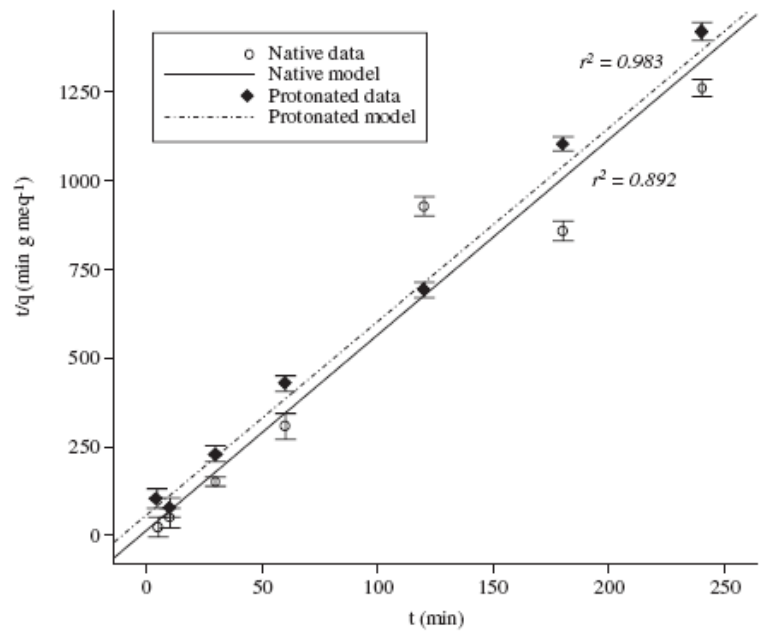


Figure 7. Linearization of pseudo-second-order kinetic for native and protonated grapefruit biomass (pH = 4.5; grapefruit concentration = 16.67 g l^{-1}; initial Cd^{2+} concentration = 250 mg l^{-1}; 60 rpm).

IMAGEN TOMADA DE:
Bayo *et al.* (2012). The use of native and protonated grapefruit biomass (*Citrus paradisi* L.) for cadmium(II) biosorption: equilibrium and kinetic modelling. Environmental Technology 33: 761-772.

Pseudo-segundo

2. Sistemas en estado estacionario

CONTAMINANTE REACTIVO O NO CONSERVATIVO

Entrada = Salida + Reacción

Cinética de pseudo-segundo orden

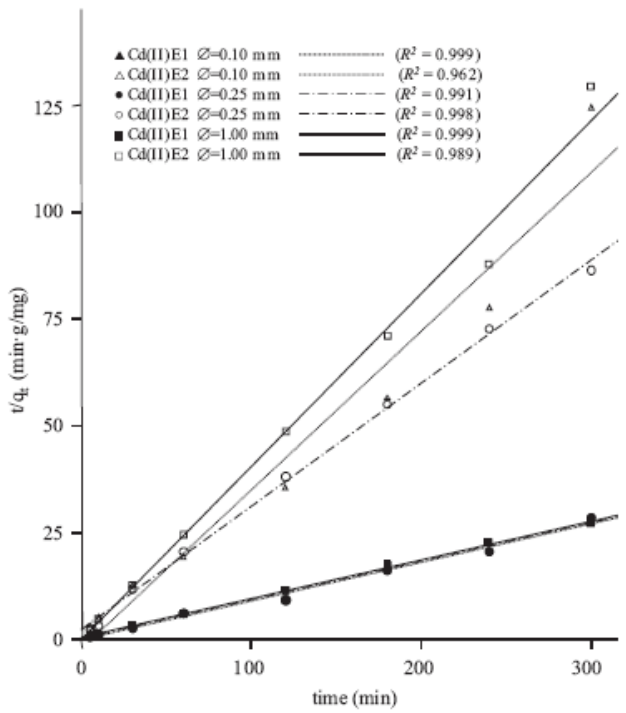


Fig. 2. Pseudo-second-order kinetic models for the biosorption of Cd(II) onto NGB for experiments E1 and E2 [pH = 4.5; Cd(II) concentration = 100 mg/L; biomass concentration = 5 g/L; 60 rpm; t = 5 h; room temperature].

Eliminación de Pb(II), Cu(II), Ni(II) y Cd(II) del agua residual mediante bioadsorbentes naturales

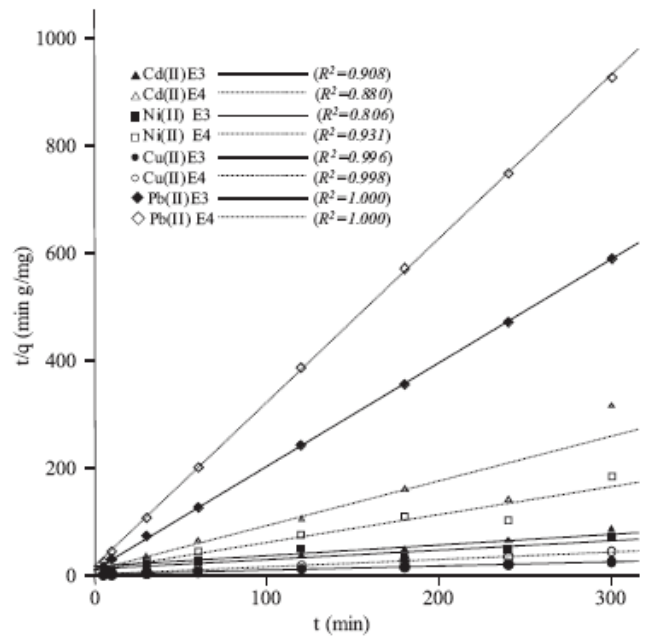


Fig. 4. Pseudo-second-order kinetic models for the biosorption of four heavy metals onto NGB for experiments E3 and E4 [pH = 4.5; biomass concentration = 5 g/L; 60 rpm; t = 5 h; room temperature].

IMÁGENES TOMADAS DE:
Bayo (2012). Kinetic studies for Cd(II) biosorption from treated urban effluents by native grapefruit biomass (*Citrus paradisi* L.): The competitive effect of Pb(II), Cu(II) and Ni(II). Chemical Engineering Journal 191: 278-287.

2. Sistemas en estado estacionario

MODELO DE FLUJO PISTÓN

No existe mezcla de los contaminantes a lo largo del recorrido
(en el reactor de flujo pistón ideal no existe difusión axial)

$$C = C_0 - kt$$ ORDEN 0

$$C = C_0 e^{-kt}$$ ORDEN 1

$$\frac{dq}{dt} = k_1 (q_e - q)$$ PSEUDO-1

$$C = \frac{C_0}{1 + C_0 kt}$$ ORDEN 2

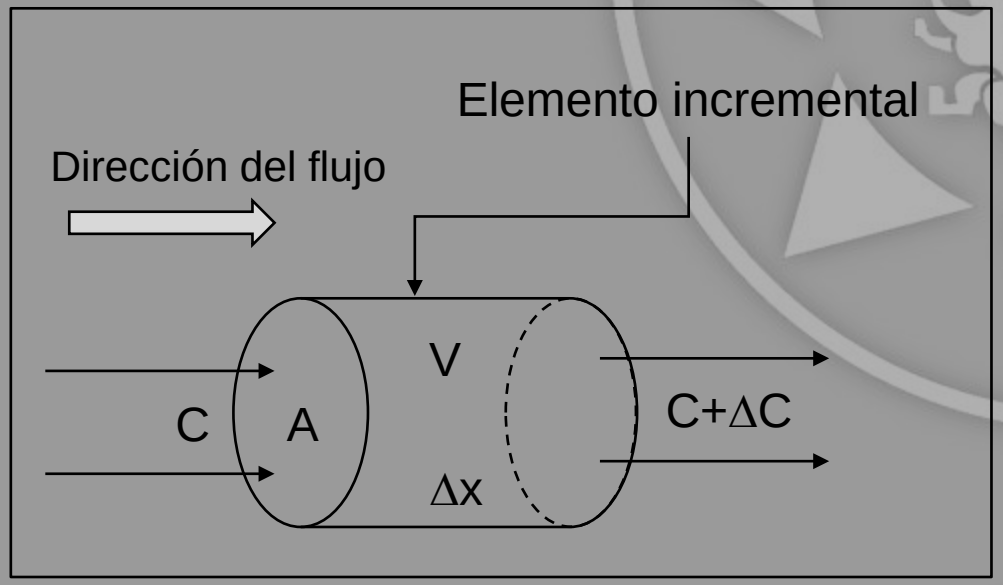
$$\frac{dq}{dt} = k_2 (q_e - q)^2$$ PSEUDO-2

$$t = \frac{l}{v} = \frac{V}{Q}$$

Entrada – Salida + Reacción = 0

$$QC - Q(C + \Delta C) + \Delta V k_d C = 0$$

$$\Delta V = A \Delta x$$



PFR

2. Sistemas en estado estacionario

MODELO DE FLUJO PISTÓN

Decoloración de agua residual mediante sistema UV/H_2O_2 en reactor de flujo pistón

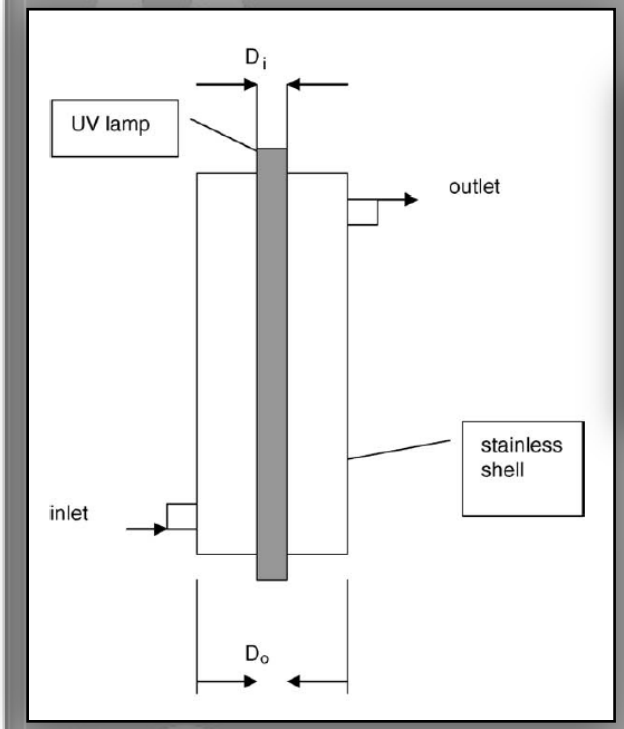
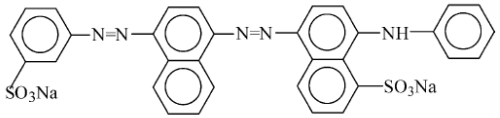


Table 1
The characteristics of C.I. Acid Blue 113 (AB 113)

Azo dye	C.I. Acid Blue 113
Formula	$C_{32}H_{21}N_5Na_2O_6S_2$
λ_{max} (nm)	566
MW	681.66
Solublity in water (mg/ml)	40

Chemical Structure



CINÉTICA DE PSEUDO-PRIMER ORDEN

$$R = \left(1 - \frac{C}{C_0}\right) \times 100\% = (1 - e^{-kt}) \times 100\%$$

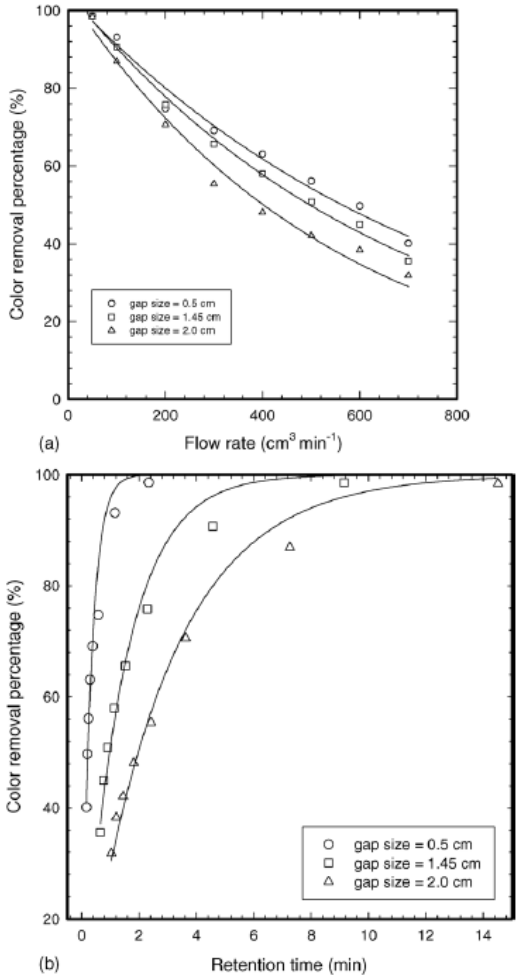


Fig. 5. (a) The color removal percentage of C.I. Acid Blue 113 vs. flow rate in plug flow UV/H_2O_2 process under various gap sizes. (b) The color removal percentage of C.I. Acid Blue 113 vs. retention time in plug flow UV/H_2O_2 reactor under various gap sizes. The operating condition was under H_2O_2 initial dosage 46.53 mM. C.I. Acid Blue 113 initial concentration was 29.30 μM, initial pH was 5.5. Reactor gap sizes were 0.5, 1.45 and 2.0 cm, respectively.

IMÁGENES TOMADAS DE:
Shu *et al.* (2005). Effects of gap size and UV dosage on decolorization of C.I. Acid Blue 113 wastewater in the UV/H_2O_2 process. Journal of Hazardous Materials B118: 205-211.

PFR

2. Sistemas en estado estacionario

MODELO DE FLUJO PISTÓN

Análisis del destino de contaminantes en humedales empleados como tanques de tormenta

Tratamiento de escorrentías urbanas y agrícolas debidas a tormentas

Parámetros de funcionamiento

CARGA HIDRÁULICA

TIEMPO DE RETENCIÓN

- Intensidad de tormenta
- Volumen de escorrentía
- Tamaño del humedal

CINÉTICA DE PRIMER ORDEN

FÓSFORO TOTAL

NITRATO

AMONIO

$$\ln\left(\frac{C - C^*}{C_i - C^*}\right) = -\frac{k_a}{q}$$

$$\frac{C}{C_i} = e^{-k_a/q}$$

$$\frac{C}{C_i} = e^{-k_v \tau}$$

$$1 - \frac{RE}{100} = e^{-k_a/q}$$

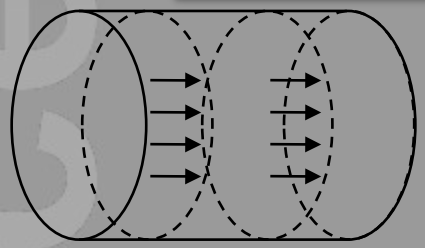
$$1 - \frac{RE}{100} = e^{-k_v \tau}$$

IMÁGENES TOMADAS DE:

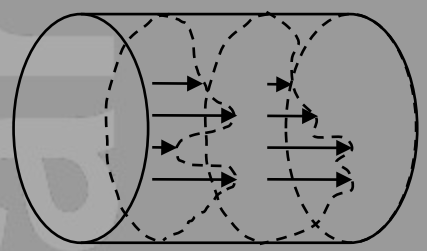
Carleton *et al.* (2001). Factors affecting the performance of stormwater treatment wetlands. Water Research 35: 1552-1562.

2. Sistemas en estado estacionario

MODELO DE FLUJO PISTÓN NO IDEAL



Comportamiento ideal



Comportamiento no ideal

PFR (D=0)

↓

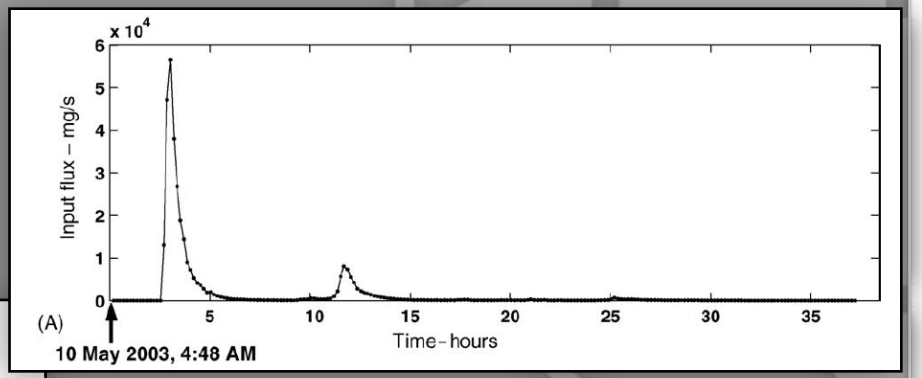
CSTR ($D \rightarrow \infty$)

Ley de Fick →

$$\frac{\partial C}{\partial t} = -D\frac{\partial^2 C}{\partial x^2}$$

Coeficiente de dispersión axial (m^2/s)

Modelización de sólidos en suspensión en un tanques de tormenta mediante análisis de la distribución de tiempos de residencia



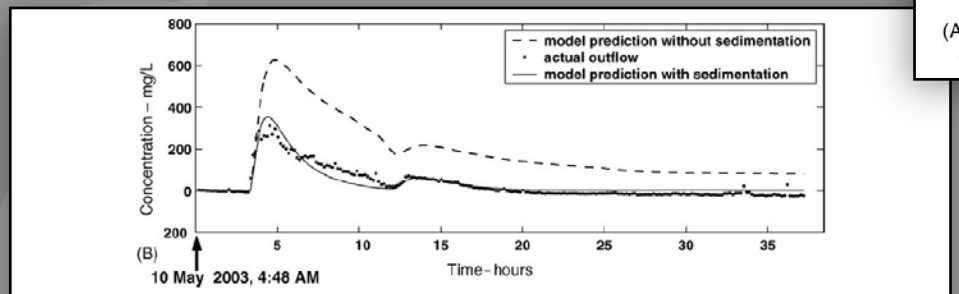


Fig. 10. Input mass flux of suspended solids to stormwater treatment wetland during a precipitation event (A). Predicted outflow concentration of suspended solids from RTD model (Model 4) with and without sedimentation dynamics compared with actual outflow concentration (B).

IMÁGENES TOMADAS DE:
Holland *et al.* (2005). Analysis and modeling of suspended solids from high-frequency monitoring in a stormwater treatment wetland. Ecological Engineering 24: 159-176.

Definición

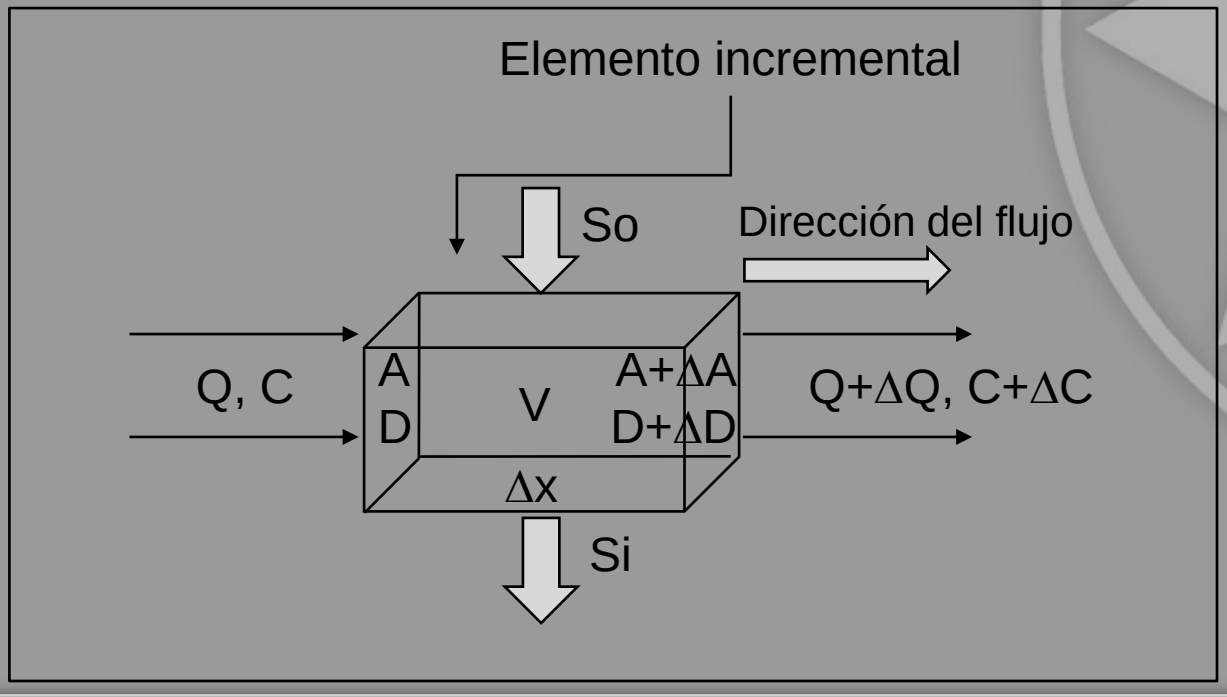
3. Sistemas en estado no estacionario

VARIACIÓN DE LA CONCENTRACIÓN DE UN CONTAMINANTE CON EL TIEMPO EN LA MASA DE AGUA

Sistema de respuesta dependiente del tiempo ➔ Modelizado por elementos incrementales
➔ Se asume modelo de mezcla completa en dicho elemento

Entrada - Salida = Transporte + Dispersión + Reacción + Fuentes + Sumideros

(Advección) (Difusión) (Transformación: generación o descomposición)



Ecuación

3. Sistemas en estado no estacionario

So

Entrada - Salida = Transporte + Dispersión + Reacción + Fuentes + Sumideros

Si

- Difusión molecular
- Movimiento browniano

- Generación → Orden 0
- Descomposición → Orden 1

Ley de Fick → $J = -D\dfrac{\Delta C}{\Delta x}$

$$Vk_g - Vk_d C$$

$$QC\Delta t - \left[(Q+\Delta Q)(C+\Delta C)\right]\Delta t = V\Delta C$$

$$D_{agua} \approx 10^{-5} cm^2/s$$

SIMPLIFICACIÓN

Acumulación = Entrada – Salida + Generación - Descomposición

$$V\frac{dC}{dt} = QC_i - QC + Vk_g - Vk_d C$$

Si: $\dfrac{dC}{dt} = 0 \longrightarrow C_\infty = \dfrac{QC_i + k_g V}{Q + k_d V}$

Ecuación

3. Sistemas en estado no estacionario

Para cualquier tiempo *(t)*:

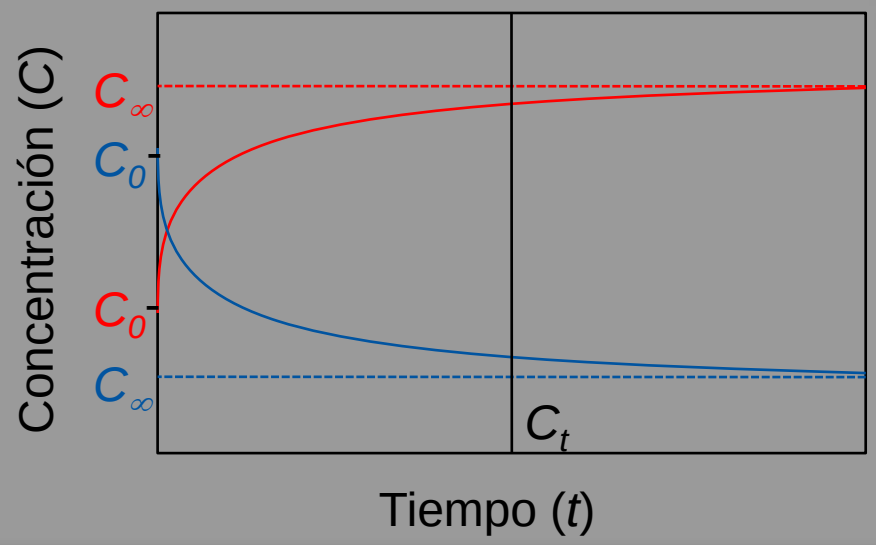
$$C(t) = C_\infty + (C_0 - C_\infty)\exp\left[-\left(k_d + \frac{Q}{V}\right)t\right]$$

A tiempo $t = 0$

$$C = C_\infty + (C_0 - C_\infty)\exp 0 = C_0$$

A tiempo $t = \infty$

$$C = C_\infty + (C_0 - C_\infty)\cdot 0 = C_\infty$$



$$C_\infty = \frac{QC_i + k_g V}{Q + k_d V}$$

$$C_\infty = \frac{QC_i}{Q + k_d V}$$

Ecuación

4. Balances de energía

Entrada = Salida + Variación de la energía interna

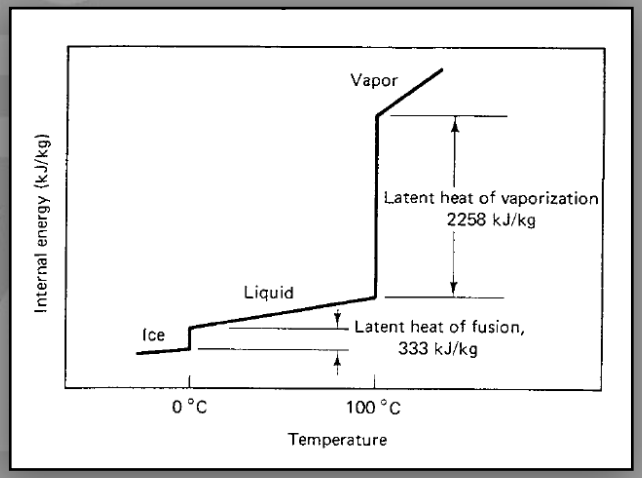
Energía almacenada en el sistema

$$\Delta U = mC_e\Delta T$$

AGUA

4.184 J/kg·ºc
1 cal/g·ºC
1 Btu/lb·ºF

CALOR ESPECÍFICO → Cantidad de energía necesaria para elevar en 1 ºC (15 ºC – 16 ºC) la temperatura de 1 kg de materia [J/kg·ºC]



Calores latentes de fusión y vaporización del agua

IMAGEN TOMADA DE:
Masters (1991). *Introduction to Environmental Engineering and Science*. Prentice-Hall: New Jersey.

SOME ENGLISH TERMS TO BE FAMILIAR WITH

- ✓ Balance de materia → Mass balance
- ✓ Contaminante conservativo → Conservative pollutant
- ✓ Contaminante no conservativo → Non-conservative pollutant (Reactive pollutant)
- ✓ Distancia de mezclado → Mixing length
- ✓ Estado estacionario → Steady state
- ✓ Estado no estacionario → Unsteady state (Dynamic state)
- ✓ Fuente → Source
- ✓ Modelo de mezcla → Mixing model
- ✓ Reactor continuo de tanque agitado → Continuously stirred tank reactor (CSTR)
- ✓ Reactor de flujo pistón → Plug flow reactor (PFR) (Tubular reactor)
- ✓ Reactor discontinuo → Batch reactor
- ✓ Régimen turbulento → Tidal regime
- ✓ Sumidero → Sink

One step beyond!

WATER QUALITY BY A CIVIL ENGINEER

MASS BALANCE TECHNIQUE

SOURCES AND SINKS

PLUG FLOW REACTOR

DYE TRACERS

BROWNIAN MOTION

IMAGEN TOMADA DE: www.gifmania.com.es

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