Phosphorus Removal Mechanisms in Soil and Slag Media

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ABSTRACT

Excessive phosphorus (P) is one of the major pollutants in natural water that are responsible for algal blooms and eutrophication. P removal by soil and slag is an attractive solution if the P sorption capacity of soil or slag is significant. To design an efficient land treatment facility, basic information on the behaviour of P in the media-water environment is required. In this study, detailed experiments were conducted to study P removal under static and dynamic conditions, and mathematical models were developed to describe these processes.

The kinetic studies on P sorption onto a sandy loam soil from North Sydney, Australia, and dust and cake waste products from the BHP steel industry revealed that P sorption is a slow process. More than 90% of the P was adsorbed within 70, 12 and 60 hours in a mixing system for soil, dust and cake respectively while it was within 240, 24 and 120 hours respectively in a static (no stirring) system. Dust adsorbed P the most, compared to the other adsorbents (220-225 times and 4-5 times of the sorptivity of soil and cake respectively). P sorption in the batch experiments was described better by an equation using the Langmuir isotherm than one using the Freundlich isotherm. The kinetics of P sorption were satisfactorily explained by a static, physical, non-equilibrium sorption model (SPNSM).

The pH of the P solution played a critical role in the extent of removal and the removal mechanisms of P. Removal was at a minimum at pH 2. The effect of pH on P removal varied depending on the type of adsorbents and the initial P concentration. The dominant removal mechanism of P at pH<8 was physical sorption, while it was chemical precipitation at pH>10. Batch flocculation experiments revealed that the P removal efficiency increased with an increase of adsorbent dose, flocculation (contact) time and mixing rate. P sorption is affected by the presence of NH_4 which competes for available sites on the adsorbents. The amount of P adsorbed by dust and cake in the presence of NH_4 was less than that in a single solute system. The reduction percentage of P for dust ranged from 33 to 57%.

Detailed column experiments conducted with soil, dust and cake as media indicated that dust and cake have much higher sorption capacities than soil. The solid phase P concentrations on dust and cake calculated from batch experimental isotherm constants are substantially higher than those estimated

from the dynamic column experiments. A program to fit a generalised, non-linear, advective, dispersion model (MCMFIT) was used to estimate the optimal model parameter values. All the columns exhibited characteristic S-shaped or curvilinear breakthrough curves. The simulated results from a dynamic physical non-equilibrium sorption model (DPNSM), based on Freundlich isotherm constants K and N (obtained from column experimental results) satisfactorily matched the corresponding experimental breakthrough data. P removal under dynamic conditions was explained better as a physical non-equilibrium process than an equilibrium one. The mobility of P is restricted by the adsorbing medium and it is proportional to the sorption capacity of the adsorbents. The DPNSM predictions were better than those of the equilibrium sorption model (ESM). The ESM predictions were similar to DPNSM predictions at high influent P concentrations for dust and cake.

An increase of pH value occurred at the initial stage of P removal. This is due to the liberation of Mg^{2+} and Ca^{2+} ions into the solution from the dust and cake media. The sorption capacity of P in dust and cake columns decreased in the presence of NH_4 due to the competition for sorption sites.

Dust and cake can be applied (i) as an adsorbent in sewage treatment plants, (ii) as a substratum in constructed wetland systems and (iii) as a suppressing material for the release of P from sediments due to their high sorption capacity. The effluent concentrations of heavy metals in the dust and cake column were low enough not to harm any living organisms.

CERTIFICATE

I certify that this thesis has not already been submitted for any degree and is not being submitted as part of candidature for any other degree.

I also certify that the thesis has been written by me and that any help that I have received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

Signature of Candidate

ACKNOWLEDGMENTS

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NOTATION

A	Cross sectional area of column (m^2)
C_r	Courant number
C	Liquid phase concentration (mg/L)
C_f	Liquid phase concentration in the film (mg/L)
C_i	Liquid phase concentration of solute i in the mixture (mg/L)
C_m	Liquid phase concentration in mobile water (mg/L)
C_o	Influent liquid phase concentration (mg/L)
D_s	Dispersion / Diffusion coefficient (cm^2/s)
$D(\Theta)$	Diffusivity as a function of water content
$D_s(\Theta,w)$	Diffusion coefficient as a function of water content (cm^2/s)
f(C)	Function of C (sorption isotherm)
H	Column filter depth (cm)
K	Freundlich isotherm constant, $[mg/g(L/mg)^N]$
$K(\Theta)$	Permeability as a function of water content (cm/s)
N	Freundlich isotherm constant (dimensionless)
Q	Flow rate (m^3/d)
R	Solid particle radius (m)
R_d	Retardation factor (dimensionless)
ROH	Ratio of bulk density to porosity
S	Solid phase concentration at any instant (mg/g)
S_1	Solid phase concentration on equilibrium sites (equivalent liquid phase) (mg/g)
S_2	Solid phase concentration on kinetic non-equilibrium sites (equivalent liquid phase) (mg/g)
S_{2e}	Equilibrium solid phase concentration on kinetic nonequilibrium sites (equivalent liquid phase) (mg/g)
S_f	Solid phase concentration in equilibrium with the influent liquid phase concentration (mg/g)
S_m	Maximum capacity of the filter medium to adsorb P solute (mg/g)
S_i	Sorption site i (mg/g)
X	Normalised liquid phase concentration
Y	Normalised solid phase concentration
a	Langmuir isotherm constant (mg/g)
α	Mass transfer coefficient (day^{-1})
α_i	Isotherm fitting parameter (i=1,2,3,4)
α_5	Kinetic sorption rate constant (day^{-1})

α_6	Fraction of the sites available for instantaneous sorption
b	Langmuir isotherm constant (L/mg)
β	Mass of the medium (g)
c(i)	Parameter values, i=1,NVAR.
$c_{max}(i)$	Maximum of the ith parameter
$c_{min}(i)$	Minimum of the ith parameter
d_{max}	Maximum observed concentration (mg/L)
d_{min}	Minimum observed concentration (m/gL)
ε	Porosity
Θ	Amount of liquid (water) (L)
Θi	Initial water content in the column (L)
Θ_m	Water content in the mobile phase (L)
Θ_{im}	Water content in the immobile phase (L)
k_r	Rate constant (day^{-1})
p	Column Peclet number
ρ	Bulk density (g/cm^3)
t	Time (s)
t_1	Pulse period (m)
Δt	Time step (s)
v	Darcy velocity (cm/s)
w	Pore water velocity (cm/day)
w_m	Pore water velocity in the mobile phase (cm/day)
w_s	Pore solute velocity (cm/day)
z	Distance (m)
Δz	Spatial step (m)

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