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Intraparticle phosphorus diffusion in a drinking water treatment residual at room temperature

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Abstract

Phosphorus (P) has been recognized as one of the major limiting nutrients that are responsible for eutrophication of surface waters, worldwide. Efforts have been concentrated on reducing P loads reaching water bodies, via surface runoff and/or leaching through a soil profile. Use of drinking water treatment residuals (WTRs) is an emerging cost-effective practice to reduce soluble P in poorly P-sorbing soils or systems high in P. Literature suggests that WTRs have huge P sorption capacities. We hypothesized that P sorption would be limited by diffusional constraints imposed by the WTR particles. Selected chemical and physical (specific surface area, particle size distribution) characteristics of an iron-based WTR were measured. Sorption P isotherms at room temperature were constructed, and sorption kinetics were monitored. An intraparticle diffusion model was utilized to fit the kinetic data. Results showed that the WTR dramatically reduced soluble P, showing nonequilibrium characteristics, even after 80 d of reaction. Specific surface area (SSA) measured with CO_2 gas was significantly greater than the traditional BET–N_2 value (28 versus 3.5 $m^2\,g^{-1}$), suggesting that a large amount of internal surfaces might be present in the WTR. The intraparticle P diffusion model was modified to include the wide particle size distribution of the WTR. The intraparticle diffusion model fitted the data well ($r^2 = 0.83$). We calculated a maximum apparent P diffusion coefficient value of 4×10^{-15} $cm^2\,s^{-1}$, which agrees with published values for intraparticle diffusion in microporous sorbents. This work may be useful for predicting long-term sorption characteristics of WTRs, since WTRs have been suggested as potential long-term immobilizers of sorbed P in P-sensitive ecosystems.
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1. Introduction

Increased phosphorus (P) levels in water bodies have been recognized as one of the major limiting factors responsible for eutrophication-related decrease in water quality [1]. Agricultural activities have resulted in current elevated P inputs in soils. Elevated soil P concentrations are usually above a soil's P sorption capacity and they are prone to advective/convective transport towards water bodies. Poorly P-sorbing soils are abundant in Florida and other eastern states of USA. Their low P sorbing capacity accompanied by high water tables and coarse textures make these soils vulnerable to P losses [2]. The main P pathways to sur-

face waters are lateral (surface and subsurface) and vertical movement of P with water moving towards the water bodies.

Soluble P reduction may be achieved by the use of traditional chemical coagulants, such as alum [3]. Drinking water treatment residuals (WTRs) are an emerging alternative to alum use, since they can be obtained free of charge from the water treatment plants. WTRs are primarily amorphous masses of Fe, Al oxides or $CaCO_3$, that also contain sediment and humic substances removed from the raw water, that are produced during the water purification process [4]. Recent research has shown that WTRs can immobilize P susceptible to leaching or soil surface runoff. Gallimore et al. [5], Peters and Basta [6] studied the effect of WTR application to poultry litter-amended soils. WTR significantly reduced soluble P levels in surface runoff. Codling et al. [7] and Ippolito et al. [8] observed a positive linear relationship between increasing WTR rate and grass yield after

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co-mixing of WTR and biosolids. Brown and Sartain [9] showed that a 2.5% (by weight) Fe–WTR application rate significantly reduced P leaching from applied fertilizer P with minimal negative impact on plant P uptake.

WTRs have considerable P sorption capacities as previous work on Florida-produced WTRs showed; WTRs exhibited P retention capacities ranging from 3500 (Fe–WTR) to 5000 (Al–WTR) mg kg^{-1} [10]. An Al–WTR from Bradenton, FL sorbed essentially all of the added P (6000 mg kg^{-1}), suggesting that it can dramatically reduce soluble P levels when applied to a poorly P-sorbing soil amended with different P sources. The P adsorption maximum of the WTR could not be determined, but it was greater than 6000 mg P kg^{-1}. The cumulative percent of P desorbed from the WTR was less than 1%, suggesting that the WTR has the potential to be an ultimate P immobilizer.

Reactions between phosphate molecules and soils, or Fe, and/or Al hydr(oxides) are initially fast, becoming slower with time, without reaching true equilibrium [11]. The fast reaction is explained by simple Coulombic interactions between adsorbent/adsorbate. The slow fraction of sorption has been attributed to intraparticle diffusion in meso- and micropores of mineral particles [12], and/or diffusion within soil organic matter (SOM) [13]. SOM is recognized as a dual-functional sorbent possessing a soft or rubbery state, and a hard or glassy carbon state [13]. The hard carbon or condensed organic domain is believed to exhibit nonlinearity in the sorption of organics by SOM. Total elemental carbon content of WTRs varies, but can be as much as 15–20% [10]. Preliminary results on other WTRs showed that P continues to slowly sorb, even at prolonged contact times. We hypothesized that intraparticle P diffusion into the porous network of the WTR particles was responsible for the slow P sorption kinetics. Use of the intraparticle diffusion model to fit the sorption kinetic data for the WTR would permit the calculation of an apparent P diffusion coefficient. Matching the calculated P diffusion coefficient with published values from direct determination of diffusion coefficients of solutes into porous sorbents, would possibly explain the slow P sorption kinetics by the WTR. Slow sorption into micropores of the WTR would significantly increase the activation energy of desorption, immobilizing P into the pores of WTRs. Slow P sorption by WTRs may be an indicator for the long-term stability of sorbed P in P-sensitive areas that have been amended with WTRs.

Thus, the objectives of this work were to characterize the P sorption kinetics and determine the apparent diffusion coefficient of P sorption by the Fe–WTR, at room temperature.

2. Experimental

2.1. Materials and methods

An Fe–WTR was obtained from the Hillsboro River water treatment plant in Tampa, FL, where $Fe_2(SO_4)_3$ is used as the coagulant. The pH of a 0.01 M KCl solution of the WTR was measured after 20 d reaction (1:10 solid:solution ratio). Determination of percent solids was performed by drying the material at 105 °C [14]. KCl-extractable P was measured at a ratio of 1:10 in a 0.01 M KCl solution after 40 d. Total C and N were determined by combustion at 1010 °C using a Carlo Erba NA-1500 CNS analyzer. The WTR was analyzed for total P, Fe, and Al by ICP following digestion according to the EPA Method 3050B [15]. Oxalate-extractable P, Fe, and Al were determined by ICP after extraction at a 1:60 solid:solution ratio, following the procedures of McKeague et al. [16].

P adsorption maxima of the WTR at different initial P loads were determined with a batch equilibration test, based on the work of O'Connor and Elliott [17]. Representative air-dried (<2 mm) samples of the WTR were reacted for 1, 10, 20, 40, and 80 d with inorganic P solutions at loads of 2500 mg P kg^{-1} to 10,000 mg P kg^{-1} in a 1:10 WTR: 0.01 M KCl solid to solution ratios to determine P sorption capacities and kinetics, at 23 ± 2 °C. The selection of the above range of P loads was based on preliminary sorption experiments. The pH was not controlled and the suspensions were not shaken. No mechanical energy (shaking) was applied because our focus was on monitoring of diffusion processes. After equilibration, suspensions were centrifuged, filtered (0.45 μm), and supernatants were analyzed for P by ICP.

The particle size distribution of the WTR was generated with a particle size analyzer (Coulter, LS230). The Coulter LS230 measures particle sizes from 40 nm to 2000 μm by laser diffraction. The technique is based on the principle that particles scatter and diffract light at certain angles based on their size, shape, and optical properties. Calculations assume the scattering pattern is due to single scattering events by spherical particles.

Specific surface area (SSA) of the WTR was measured at 77 and 273 K using N_2 and CO_2, respectively, as adsorbates in a volumetric apparatus (Quantachrome Autosorb-1, Quantachrome Corporation, Boynton Beach, FL), after outgassing at 70 °C for 4 h. Based on preliminary thermogravimetric analysis, four hours were adequate to evaporate all physisorbed water released at 70 °C from the WTR particles. Dinitrogen and CO_2 gas sorption experiments were performed in a liquid N_2 (77 K), and ethylene glycol (273 K) baths using a thermostat, respectively. BET-N_2 SSA was measured using the classic BET equation using the 0.03–0.3 relative pressure region [18]. Micropore (CO_2) volume of the WTR was calculated using the Dubinin–Radushkevich (DR) model [19]. The linear form of the DR model is shown below:

$$\log V = \log(V_0) - \frac{BT^2}{\beta}\left[\log \frac{P_0}{P}\right]^2, \qquad (1)$$

V is the volume sorbed at standard pressure and temperature (cm^3 g^{-1} STP), V_0 is the micropore capacity (cm^3 g^{-1} STP), P_0 is the vapor saturation pressure of CO_2 (26,140 mm Hg), P is the equilibrium pressure (mm Hg), B is a constant

representing adsorption energy, and β is the affinity coefficient of CO_2 gas relative to P_0. The monolayer capacity V_0 is obtained by plotting the log V against $[\log P_0/P]^2$. The intercept of the linear plot is the monolayer micropore volume of CO_2 gas sorbed in the micropores. The model assumes a Gaussian pore size distribution, volume filling instead of layer-by-layer adsorption on the pore walls, and the degree of filling in micropores is a function of the negative differential free energy of adsorption. Micropore monolayer surface area is calculated from the DRK equation, which is a special case of the DR equation. The DRK equation assumes layer-by-layer gas sorption on the walls, so the only modification to Eq. (1) is that the amount of gas sorbed (expressed as a liquid volume) is used, instead of the volume sorbed.

2.2. P diffusion considerations

Diffusion processes plays major role in solute sorption/desorption dynamics [20]. Slow sorption ascribed to diffusional limitations seems to apply to many types (inorganic/organic) of compounds and sorbents (Pignatello et al. [21]). To model P intraparticle diffusion in the WTR, the continuity equation was coupled with Fick's second law in spherical coordinates [20]:

$$D_a\left[\left(\frac{\partial^2}{\partial r^2}C(r,t)\right) + \frac{2\left(\frac{\partial}{\partial r}C(r,t)\right)}{r}\right] = \frac{\partial}{\partial t}C(r,t). \quad (2)$$

WTR particles, for modeling purposes, were assumed to be homogeneous spheres. The above partial differential equation assumes that the apparent diffusion coefficient (D_a) is constant. D_a can be constant in cases where the adsorption isotherm is linear (independent of concentration) or in cases of small incremental concentration changes; r is the average particle radius where $r = 0$ at the center of the sphere. Sorption occurred at ambient constant pressure and temperature in a bath of limited volume. A pulse input of solute (phosphate) was initiated at time zero, followed by the monitoring of the decrease in aqueous P decrease with time. Initial and boundary conditions were:

$$\begin{aligned}
C &= 0, & t &= 0, & 0 &< r < a, \\
C &= C_{eq}, & t &= \text{infinity}, & r &= a, \\
\partial C/\partial r &= 0, & t &> 0, & r &= 0 \text{ (center of sphere).}
\end{aligned} \quad (3)$$

The batch experiments were mathematically treated as a "bath of limited volume" (Grathwohl [20]). The analytical solution of the corresponding partial differential equation (Eq. (2)), based on the initial and boundary conditions described above, is shown below [22]:

$$\frac{M}{M_{eq}} = 1 - \left(\sum_{n=1}^{400} \frac{6\beta(\beta+1)e^{\left(-\frac{q_n^2 D_a t}{a^2}\right)}}{9 + 9\beta + q_n^2\beta^2}\right), \quad (4)$$

where M/M_{eq} denotes the mass of P (M) in the WTR sphere after time t normalized by the mass of P in the WTR sphere

at equilibrium (M_{eq}). D_a is the apparent diffusion coefficient of P ($cm^2\,s^{-1}$). The ratio of the mass of P dissolved in the aqueous phase at equilibrium divided by the mass of P in the WTR particle at equilibrium is denoted as β. a is the WTR particle radius in cm.

The qns are the positive nonzero roots of: $\tan(qn) = 2qn/(3 + \beta qn^2)$. At large values of n (>50) the qns approach $n \times \pi$ [20]. We assumed that $qn = n \times \pi + dqn$, where dqn is the differential qn value. We calculated that n had to be at least equal to 400 terms to get $dqn = 0.002$, thus, qn could be approximated by $n \times \pi$. Thus, four hundred ($n = 400$) terms were used for the subsequent calculations. We hypothesized that P sorption is diffusion-controlled and not reaction-controlled with hydroxyls on surfaces (external and internal sites). Phosphorus reaction with external and internal sites of the WTR was assumed to be homogeneous, since reaction is not limited on the external solid/liquid interface but involves reaction with pore walls of the interior. As a result, the rate of reaction decreases due to diffusion limitations, although reaction at the micropore walls may be heterogeneous (react with the surface, produce the product, which will diffuse back out (Cussler [23])). Based on the analytical solution (Eq. (4)) and the actual P sorption kinetics data, we performed a nonlinear optimization routine with the General Algebraic Modeling System (GAMS software) [24]. The GAMS optimization routine fitted the intraparticle diffusion model to the actual data by varying the apparent D_a values (one for each size class).

3. Results and discussion

3.1. General characterization of the WTR

Selected chemical characteristics of the WTR are presented in Table 1. The pH of the material was circumneutral (6.3). KCl-extractable P represented only 0.2% (6.2 mg kg^{-1} Fe–WTR) of the total P. KCl–P is considered to be the most available pool of P, and varies among different P sources. Low levels of KCl–P may suggest that the WTR is an ideal P immobilizer for reducing P losses in poorly P-sorbing soils. Total C value (14.1%) was much greater than the median OC value of 6.3% reported by Dayton et al. [25] for 21 WTRs, and may be responsible for diffusional limitations imposed on P molecules. Total P content of the WTR (3.2 g P kg^{-1}) was much greater than the median value (1.3 g kg^{-1}) reported by Dayton et al. [25] for a host of WTRs. Total Fe was 250 g Fe kg^{-1}, exceeding typical range of total values for WTRs (50–150 g kg^{-1} [26]). X-ray diffraction analysis (data not shown) revealed that amorphous Fe and Al oxides appeared to dominate in the WTR, with no apparent crystalline Fe and/or Al oxides. Oxalate extractable P, Fe, and Al are usually associated with the amorphous fraction of the particles. The Fe–WTR had oxalate extractable P and Fe values equal to ∼64% of total P and Fe.

Table 1
Selected chemical properties of the Fe–WTR, Tampa, FL

pH	KCl–P (mg kg^{-1})	C (%)	N (%)	Total (g kg^{-1})			Oxalate (g kg^{-1})		
				P	Al	Fe	P	Al	Fe
6.3	6.21 ±0.8	14.1 ±0.6	0.8 ±0.04	3.2 ±0.1	9.8 ±0.1	251 ±5.6	2.6 ±0.05	6.0 ±0.1	161 ±8.0
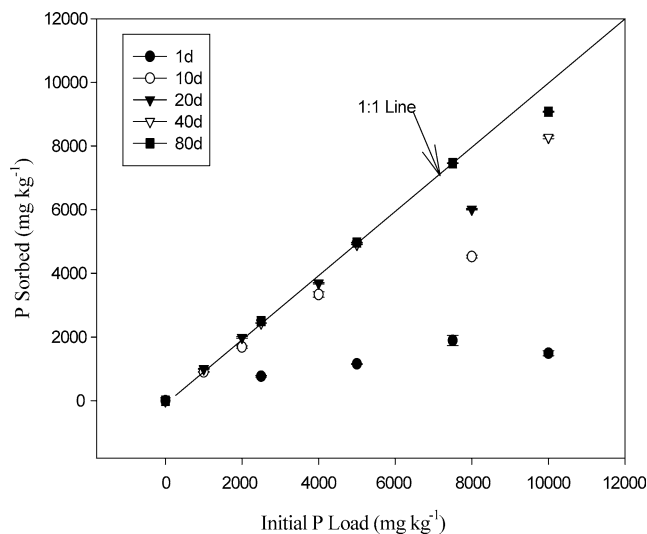
Fig. 1. P sorption with time at room temperature by the Fe–WTR, Tampa, FL.

Fig. 2. The semi-log normalized particle size distribution of the Fe–WTR, Tampa, FL.

3.2. Phosphorus sorption kinetics

A specific mass of WTR particles was contacted with variable initial pulse P inputs and reacted for 1 to 80 d. After 1 d, the WTR sorbed ~2000 mg P kg^{-1} based on the determination of the Langmuir sorption maximum. After 10 d, the Fe–WTR sorbed even more P, reaching ~4500 mg P kg^{-1} at the highest initial P load. The nonequilibrium P sorption character of the Fe–WTR continued with longer reaction times. After 40 and 80 d, the Fe–WTR sorbed nearly all of the P in solution, reaching 8270 and 9100 mg sorbed P kg^{-1}, respectively (Fig. 1). Slow reaction time seemed to be an important factor since P sorption followed a nonequilibrium slow reaction, implying P diffusional limitations. Complete removal of the maximum (10,000 mg P kg^{-1}) initial pulse input used in the batch experiments may have eventually occurred (>80 d).

3.3. Particle size distribution and specific surface area

WTR particles used in the batch experiment had passed a 2-mm sieve. However, the particle size distribution of the <2-mm WTR particles was log-normal due to the broad range of size classes measured (Fig. 2). Based on the % number distribution of particles, the greatest number of WTR particles was found in the 0.1–1 μm (Fig. 2). The % volume distribution showed that the greatest volume of WTR particles was found in the range of 100–2000 μm (Fig. 2). Specific surface area (SSA) measured using the BET–N$_2$ method
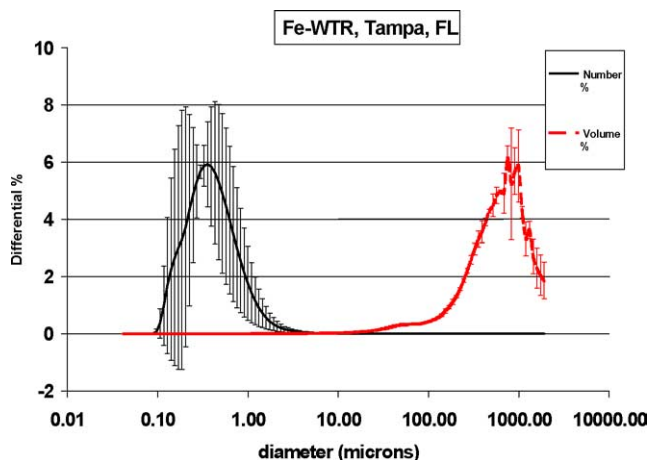
was 3.5 m^2 g^{-1}. Despite the high P sorption capacity of the WTR, BET–SSA was surprisingly low, and led us to suspect that the BET–N$_2$ method failed to characterize the true SSA of the WTR. Recent work has shown that the major factor for the decreased BET–SSA is the presence of increased organic matter content (Kaiser and Geggenberger [27]). The Fe–WTR had an unusually large % C value (14.1) that may be associated with the internal porosity of the WTR. Diffusional restrictions imposed on N$_2$ molecules attempting to diffuse through micropore-associated with organics doorways, may be overcome using CO$_2$ at a higher temperature (273 K) and greater saturation pressure than used in the BET–N$_2$ method. Carbon dioxide gas sorption at OC has been used to evaluate microporosity in soils high in organic carbon content (Xing and Pignatello [28]). CO$_2$ molecules have a higher diffusion coefficient than N$_2$ molecules since they have approximately 32 times greater saturation pressure and much greater (0 versus −196 °C) temperature than what N$_2$ molecules encounter for the BET method. This permits CO$_2$ molecules to access micropores associated with organic molecules that N$_2$ cannot, due to energetic barriers. CO$_2$-based micropore SSAs of WTRs were greater than the BET–N$_2$ suggesting the presence of narrow micropores, or constrictions in the pore opening that restrict N$_2$ diffusion (Makris et al. [29]). CO$_2$ micropore SSA was significantly greater than the BET–N$_2$ SSA (28 > 3.5 m^2 g^{-1}), suggesting that the Fe–WTR had a large amount of micropores. The presence of micropores would greatly affect the diffusion of P molecules in and out of internal sorption sites, and might explain the observed slow P kinetics. We hypothesized that

Table 2
The pooled five size classes from the particle size distribution and its corresponding geometric diameters

% number	Geometric diameter (cm)	D_a (cm^2 s^{-1}) fitted
0.44	3.4×10^{-6}	1.34×10^{-20}
17.62	0.75×10^{-5}	6.46×10^{-20}
73.26	4.5×10^{-4}	2.32×10^{-16}
8.62	1.6×10^{-4}	2.94×10^{-17}
0.06	1.2×10^{-3}	1.65×10^{-15}

The fitted D_a are the result of the nonlinear optimization method.

the intraparticle diffusion model could adequately explain the observed slow P sorption kinetics.

3.4. Intraparticle P diffusion model

The analytical solution (Eq. (4)) of the diffusion model was used to fit the P sorption data. The % number particle size distribution data were pooled in five size classes, and a geometric diameter for each size class was calculated based on the following equation:

$$d\sqrt{d_1 d_2}, \tag{5}$$

where d_1 is the smallest diameter of the pooled size class and d_2 is the largest diameter of the pooled size class. Particle size effects on the nonequilibrium diffusion of solutes in porous media have been acknowledged [30]. Carta and Ubiera [31] showed that particle size distribution effects were significant for modeling of pore diffusion-controlled batch sorption experiments. Thus, the analytical solution (Eq. (4)) was modified to include the broad range of particle sizes measured. The modified intraparticle diffusion equation was the sum of five terms that corresponded to the geometric diameters of the five pooled size classes weighted by the corresponding % number probabilities. By minimizing the squared residuals between the actual and the predicted (model) values for all 400 terms × 5 size classes data points, we were able to precisely quantify the apparent P diffusion coefficients (Table 2).

The overall mean squared error of the fit was small (5%), and the model fit the sorption data well (Fig. 3). M_{eq} was assumed to correspond to the maximum amount of P sorbed by the WTR particles (initial pulse input of 10,000 mg P kg^{-1}). Fitted D_a values ranged from 10^{-20} to 10^{-15} cm^2 s^{-1} (Table 2). There seems to be an increasing fitted D_a with particle radius (Table 2). The percent number of particles within a size class (probability) was assumed responsible for the artificial D_a/particle diameter positive trend. In order to calculate a single value for D_a based on the actual sorption data, we plotted the M/M_{eq} versus the dimensionless time t' (Fig. 4).

$$t' = t D_a a^{-2}. \tag{6}$$

Fig. 4 helped us perform a simple calculation to determine the maximum apparent P diffusion coefficient. The minimum dimensionless time necessary to allow all aqueous P
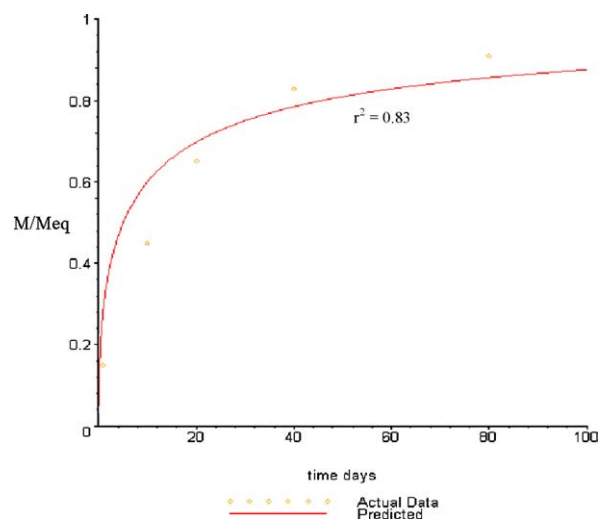

Fig. 3. Intraparticle diffusion model fit to the P sorption kinetics data for an initial pulse input of 10,000 mg P kg^{-1}.
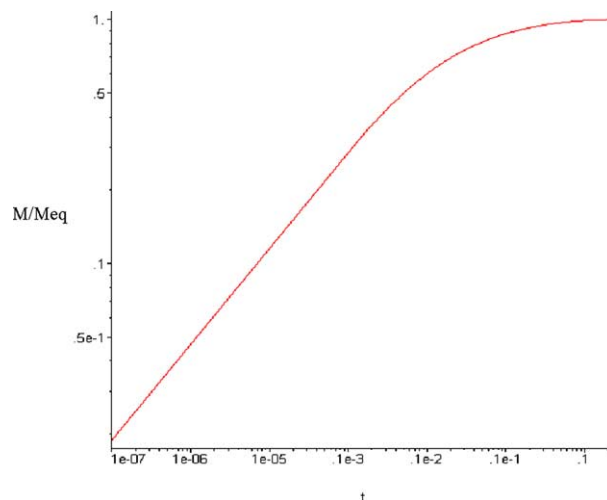

Fig. 4. Double logarithmic plot of the M/M_{eq} versus the dimensionless time. The trend seems to reach equilibrium at a value of 0.15 dimensionless time.

to diffuse into a WTR particle with the most probable (0.73; Table 2) measured radius (4.5×10^{-4} cm), after 80 days of reaction, was 0.15. We hypothesized that the largest WTR micropore would be equal to the particle radius [32]. Substituting into Eq. (6), we found that the maximum P diffusion coefficient for the WTR particles at room temperature was $D_a = 4 \times 10^{-15}$ cm^2 s^{-1}.

This value is within the range of published diffusion coefficients in microporous oxides. Intraparticle diffusion of heavy metals in model microporous Al and Fe oxides was shown to occur under steady supplement of the metal in solution [33]. Axe and Trivedi [33] reported that cation (Zn, Cu, etc.) diffusion coefficients at "infinite bath" initial and boundary conditions, ranged from 10^{-10} to 10^{-14} cm^2 s^{-1}. Effective diffusion coefficient of phosphate molecules in free liquid solution has been calculated to be 8.9×10^{-6} cm^2 s^{-1} [34]. Several studies have been performed to de-

termine P diffusion coefficients in soils. Direct determination of P bulk diffusion coefficients in soil was in the order of 10^{-13} $cm^2\,s^{-1}$ at 298 K [34]. P diffusion coefficient measured in iron alloy was 10^{-19}–10^{-17} $cm^2\,s^{-1}$ at 550–850 K [35]. Effective P intraparticle diffusion coefficient into activated alumina at 298 K was measured based on P breakthrough curves, and was in the order of 10^{-15} $cm^2\,s^{-1}$ [36]. Micropore diffusion of organic contaminants in soil is usually in the order of 10^{-16}–10^{-8} $cm^2\,s^{-1}$ [32]. The calculated maximum apparent diffusion coefficient (4×10^{-15} $cm^2\,s^{-1}$) in this work, matches the published effective P diffusion coefficients for sorption into porous sorbents, as determined directly from diffusion experiments.

4. Conclusions

Land or water application of WTRs to systems high in P is an emerging practice to reduce soluble P levels in soils or water bodies (lakes, ponds, etc.). The sorption isotherm at room temperature showed that the Fe–WTR removed nearly all of the aqueous P without reaching true equilibrium. Phosphorus sorption kinetics by the Fe–WTR exhibited nonequilibrium characteristics, even after prolonged contact times (80 d). SSA measured with CO_2 gas (micropore SSA) was significantly greater than the BET–N_2 SSA. The observed increase in SSA was attributed to internal surfaces of microporous nature. The high content of carbon present in the WTR was speculated to be responsible for the low BET–N_2 and the high CO_2–SSA measured in the WTR. An intraparticle diffusion model was used to explain the slow P kinetics. The analytical solution of the appropriate partial differential equation of the intraparticle diffusion model was modified according to the particle size distribution data, since the particle size distribution was broad, covering 3 orders of magnitude.

Use of a nonlinear optimization routine fitted the diffusion model to the sorption data well ($r^2 = 0.83$). The maximum value for the apparent P diffusion coefficient was 4×10^{-15} $cm^2\,s^{-1}$, which agreed with published values from direct determinations of effective P diffusion coefficients, assuming intraparticle diffusion in porous sorbents. The observed consistency in P diffusion coefficients may provide indirect evidence for intraparticle P diffusion into the WTR particles. Various sources of WTRs have different physicochemical properties and sorption characteristics. However, they have some common characteristics that affect sorption mechanisms. Ongoing research in our laboratory has shown that a suite of WTRs exhibited significant internal surface area associated with micropores, as well as abundant organic carbon that is uniformly distributed throughout the particles. Organic carbon distribution and concentration would influence P diffusion towards the interior of the particles, being a rate-limiting factor for P sorption. WTRs also contain high concentrations of oxalate-extractable Fe or Al, a mea-

sure currently used to predict WTRs reactivity. We suggest the combined evaluation of the three parameters mentioned above, as the key components controlling WTR reactivities, to help account for sources differences in WTR sorption properties. Calculated P diffusion coefficients may be used to different batches of the Fe–WTR, Tampa, as well as, to other WTRs that resemble the Fe–WTR, Tampa in pore size and volume distribution, and organic carbon content. Phosphorus diffusion coefficients may then be applied to predict the long-term maximum P sorption capacities of WTRs, when applied to P-sensitive ecosystems.

Long-term stability of sorbed P is an issue of major concern for state and federal regulatory agencies. We propose the use of WTRs as effective long-term P immobilizers in agricultural fields, lakes, ponds, and animal waste lagoons high in P by taking advantage of the WTRs' internal sorption sites and dramatic P sorption capacities. Future work should include the application of advanced spectroscopic methods to directly probe the nature and distribution of the diffused phosphate molecules to the internal surfaces of the WTR.

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