# Modelling of the closed equilibrium system $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$ for wastewater treatment applications

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## ABSTRACT

Water pollution caused by nitrogen and phosphorus compounds triggers algal blooms and poses challenges to aquatic organisms. Wastewater treatment applications represent critical areas where fundamental models of phosphorus equilibria, prevalent in municipal and reject water streams, are essential. This paper focuses on studying the closed equilibrium system $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$, elucidating the structural distribution of ions and molecules within this system. Utilizing the iteration method, we calculate pH, concentrations of formed ions and molecules, and proton transfer parameters based on a developed proton transfer model. Upon the initial formation of the equilibrium system $H_2O–(CO_2)_W–CaCO_3$, $CO_3^{2-}$ ions released from the dissolution of $CaCO_3$ bind protons ($\Delta[H^+]_{CO_3^{2-}}$) originating from the reversible dissociation of water ($\Delta[H^+]_{H_2O}$) and $H_2CO_3$ ($\Delta[H^+]_{H_2CO_3}$). In the equilibrium system $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$, at low initial $CO_2$ concentrations ($< 3.39 \times 10^{-5}$ mmol·L$^{-1}$), the majority of protons ($\Delta[H^+]_{H_2PO_4^-}$) originate from the $H_2PO_4^-$ dissociation. Conversely, with increased initial $CO_2$ concentrations, the dissociation of $H_2CO_3$ ($\Delta[H^+]_{H_2CO_3}$) becomes the primary proton source. Experimental validation confirms the developed model's accuracy.

## 1. Introduction

The decline in water quality and pollution resulting from nitrogen and phosphorus species are linked to algal blooms, leading to the damage and subsequent death of aquatic organisms and health issues for humans. Wastewater treatment systems require fundamental approaches to remove phosphorus species from municipal and wastewater streams, necessitating optimization of biological and chemical treatment systems, which, in turn, requires mathematical modelling of the related processes. The system $H_2O–(CO_2)_W–CaCO_3$ served as the foundation for modelling the closed system $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$ [1]. Models for the equilibrium system of $H_2O–(CO_2)_W–CaCO_3$, based on proton-centred acid-base equilibria, have been developed and published for both open [2] and closed systems [1–4]. Similar models have also been developed for the CaS-$H_2O$ and SrS-$H_2O$ systems [5–8]. These models can primarily be utilized in environmental engineering and for assessing greenhouse gas emissions [2]. The current model can be employed in wastewater treatment to estimate bacterial inhibition based on different substrate concentrations. In an aqueous medium, all acid-base equilibria are interconnected through proton concentration, meaning that a change in the concentration of any component of the system affects the concentrations of all components. In the equilibrium system $H_2O–(CO_2)_W–CaCO_3$, reducing the concentration of $[CO_2]_W$ within the range of $3.39 \times 10^{-5}$ mmol·L$^{-1}$ – $3.39 \times 10^{-7}$ mmol·L$^{-1}$ leads to an increase in pH up to 9.88 [1,3]. Consequently, protons bind to $CO_3^{2-}$ ions, resulting in an increase in the concentration of [$OH^-$] ions in the medium. At lower concentrations of [$CO_2$]$_W$, water dissociation provides the majority of protons for the equilibrium system, while the dissociation of $H_2CO_3$ can be neglected at small concentrations of [$CO_2$]$_W$.

Equilibrium systems comprising carbonaceous and phosphorus species are prevalent in various wastewater sources [9,10]. In instances such as landfill leachate and reject water from anaerobic digestion of organic substrates, wastewater often contains elevated concentrations of phosphorus ions ($H_2PO_4^-$ and $HPO_4^{2-}$). For example, total phosphorus concentrations can reach up to 3.22 $mmol{\cdot}L^{-1}$ in landfill leachate [11–13] and 1.61–3.22 $mmol{\cdot}L^{-1}$ in reject water [14,15], originating from the dewatering of digested sludge or manure from anaerobic methane digesters [15,16].

The present study aims to develop a model for the closed equilibrium system $H_2O$–($CO_2$)$_W$–$CaCO_3$–$NaH_2PO_4$, utilizing iteration and square root equations, to ascertain equilibrium pH, concentrations of all formed ions and molecules, and proton transfer parameters at equilibrium state. The model's accuracy was further validated through experimental dissolution and potentiometric methods.

## 2. Materials and methods

### 2.1. Modelling the system $H_2O$–($CO_2$)$_W$–$CaCO_3$–$NaH_2PO_4$

When modelling the self-regulating complex system $H_2O$–($CO_2$)$_W$–$CaCO_3$–$NaH_2PO_4$, it is crucial to consider that acid-base reactions in aqueous solutions proceed rapidly. For instance, the dissociation reaction of water into $H^+$ and $OH^-$ ions is recognized as one of the fastest reaction rates in aqueous solutions, with a rate constant of $k = 1.4 \times 10^{11}$ $L{\cdot}mol^{-1}{\cdot}s^{-1}$ [17,18]. The calculations' results prior to the addition of $NaH_2PO_4$ to the $H_2O$–($CO_2$)$_W$–$CaCO_3$ system are presented in Table 1 [1]. The term $\Delta[H^+]_{H_2O}$ represents the molar concentration of protons released in the dissociation of water, the term $\Delta[H^+]_{H_2CO_3}$ denotes the concentration of protons released from the dissociation of carbonic acid, and the term $\Delta[H^+]_{CO_3^{2-}}$ represents the concentration of protons bonded to carbonate ions released by dissolving $CaCO_3$.

The data presented in Table 1 illustrate that within the closed equilibrium system of $H_2O$–($CO_2$)$_W$–$CaCO_3$, the pH value reaches a maximum of 9.88 as the concentration of [$CO_2$]$_{W0}$ decreases [1]. At lower concentrations of [$CO_2$]$_{W0}$, the dissociation of water primarily contributes to proton formation, while the dissociation of $H_2CO_3$ can be disregarded due to the minimal proton production. As observed from Table 1, when [$CO_2$]$_{W0}$ is below $3.39 \times 10^{-4}$ $mmol{\cdot}L^{-1}$, the concentration of [$HCO_3^-$] ions matches that of [$H^+$] ions generated by water dissociation. Consequently, the equilibrium of the system is determined by the dissociation of water and the solubility of $CaCO_3$.

The distribution of ions and molecules within the $H_2O$–($CO_2$)$_W$–$CaCO_3$–$NaH_2PO_4$ system aligns quantitatively with the equilibrium constants depicted in the structural scheme (Fig. 1). The designations of the symbols in Fig. 1 are as follows:

- $K_h$ is the hydration constant of $CO_2$
- $K'_{a1}$ is the dissociation constant of $H_2CO_3$
- $K_{a2}$ is the dissociation constant of $HCO_3^-$
- $K_{SP}$ is the solubility product constant of $CaCO_3$
- $K_W$ is the ion-product constant of water
- $K_{a2,P}$ is the dissociation constant of $H_2PO_4^-$
- $K_{a3,P}$ is the dissociation constant of $HPO_4^{2-}$

**Table 1.** Results of the calculated proton mass-transfer and pH values, along with the concentrations of ions and molecules after $CaCO_3$ was added into the system $H_2O$–($CO_2$)$_{W0}$ at T = 25 °C

| [$CO_2$]$_{W0}$ $mmol{\cdot}L^{-1}$ | $\Delta[H^+]_{H_2O}$ $mmol{\cdot}L^{-1}$ | $\Delta[H^+]_{H_2CO_3}$ $mmol{\cdot}L^{-1}$ | $\Delta[H^+]_{CO_3^{2-}}$ $mmol{\cdot}L^{-1}$ | Equilibrium pH | [$Ca^{2+}$] $mmol{\cdot}L^{-1}$ | [$HCO_3^-$] $mmol{\cdot}L^{-1}$ |
|---|---|---|---|---|---|---|
| $3.39 \times 10^{-7}$ | $7.63 \times 10^{-2}$ | $-2.03 \times 10^{-5}$ | $-7.63 \times 10^{-2}$ | 9.88 | $1.03 \times 10^{-1}$ | $7.63 \times 10^{-2}$ |
| $3.39 \times 10^{-5}$ | $7.62 \times 10^{-2}$ | $1.09 \times 10^{-4}$ | $-7.63 \times 10^{-2}$ | 9.88 | $1.03 \times 10^{-1}$ | $7.63 \times 10^{-2}$ |
| $3.39 \times 10^{-4}$ | $7.56 \times 10^{-2}$ | $7.00 \times 10^{-4}$ | $-7.63 \times 10^{-2}$ | 9.87 | $1.03 \times 10^{-1}$ | $7.70 \times 10^{-2}$ |
| $1.32 \times 10^{-2}$ | $6.19 \times 10^{-2}$ | $1.57 \times 10^{-2}$ | $-7.75 \times 10^{-2}$ | 9.79 | $1.04 \times 10^{-1}$ | $9.32 \times 10^{-2}$ |
| $3.39 \times 10^{-1}$ | $2.43 \times 10^{-3}$ | $3.46 \times 10^{-1}$ | $-3.49 \times 10^{-1}$ | 8.38 | $3.56 \times 10^{-1}$ | $6.95 \times 10^{-1}$ |
| 2.45 | $-1.55 \times 10^{-7}$ | 1.73 | –1.73 | 7.00 | 1.73 | 3.46 |
| 33.9 | $-1.11 \times 10^{-3}$ | 5.78 | –5.78 | 5.95 | 5.78 | 11.6 |

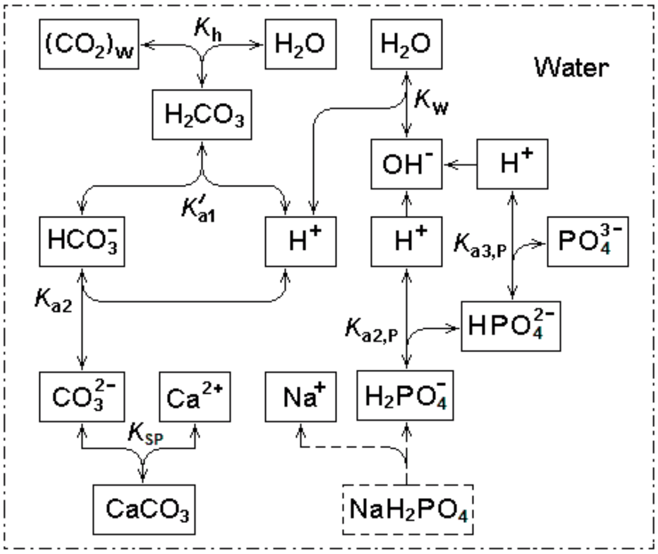

**Fig. 1.** The structural scheme of the equilibrium distribution of ions and molecules in the final closed equilibrium system $H_2O–[CO_2]_W–CaCO_3–NaH_2PO_4$.

The equilibrium constants of the system under investigation are represented by Eqs (1–7):

$$K_h = \frac{[H_2CO_3]}{[CO_2]_W} = 2.58\times10^{-3}\ [19], \tag{1}$$

$$K'_{a1} = \frac{[H^+]\times[HCO_3^-]}{[H_2CO_3]} = 1.72\times10^{-4}\ \text{mol}\cdot\text{L}^{-1}\ [20], \tag{2}$$

$$K_{a2} = \frac{[H^+]\times[CO_3^{2-}]}{[HCO_3^-]} = 4.7\times10^{-11}\ \text{mol}\cdot\text{L}^{-1}\ [21], \tag{3}$$

$$K_W = [H^+]\times[OH^-] = 1.01\times10^{-14}\ (\text{mol}\cdot\text{L}^{-1})^2\ [22], \tag{4}$$

$$K_{SP} = [Ca^{2+}]\times[CO_3^{2-}] \cong 2.8\times10^{-9}\ (\text{mol}\cdot\text{L}^{-1})^2\ [23], \tag{5}$$

$$K_{a2,P} = \frac{[HPO_4^{2-}]\times[H^+]}{[H_2PO_4^-]} \cong 6.2\times10^{-8}\ \text{mol}\cdot\text{L}^{-1}\ [23], \tag{6}$$

$$K_{a3,P} = \frac{[PO_4^{3-}]\times[H^+]}{[HPO_4^{2-}]} \cong 4.2\times10^{-13}\ \text{mol}\cdot\text{L}^{-1}\ [24]. \tag{7}$$

Taking into account that in the equilibrium system $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$ the concentration of $[HPO_4^{2-}–P]$ exceeds the concentration of $[PO_4^{3-}–P]$ by a factor of several orders of magnitude ($[HPO_4^{2-}]>>[PO_4^{3-}]$), the charge balance equation can be expressed as:

$$2[Ca^{2+}]+[H^+]+[Na^+] \cong 2[CO_3^{2-}]+[HCO_3^-]+[OH^-]+[H_2PO_4^-]+2[HPO_4^{2-}]. \tag{8}$$

The molar balance equation of carbonaceous species can be expressed as follows:

$$\Sigma[CO_X]_W = \Sigma[CO_X]_{W0}+[Ca^{2+}] = [CO_3^{2-}]+[HCO_3^-]+[H_2CO_3]+[CO_2]_W, \tag{9}$$

where $\sum[CO_X]_W$ is the total concentration of all carbonaceous species. It is noteworthy that this equation does not change when $NaH_2PO_4$ is supplemented.

Taking into account that in the equilibrium state of the system the concentration of $[HPO_4^{2-}–P]$ exceeds the concentration of $[PO_4^{3-}–P]$ by a factor of several orders of magnitude ($[HPO_4^{2-}]>>[PO_4^{3-}]$), the molar balance equation of phosphorus-containing particles can be expressed as follows:

$$c[NaH_2PO_4] \cong [H_2PO_4^-]+[HPO_4^{2-}] \cong [Na^+] = \text{const}, \tag{10}$$

where c[$NaH_2PO_4$] represents the concentration of supplemented $NaH_2PO_4$ to the equilibrium system $H_2O$–$(CO_2)_W$–$CaCO_3$.

To calculate the concentrations of $[CO_2]_W$, $[CO_3^{2-}]$, $[H_2CO_3]$, $[HCO_3^-]$, $[H^+]$, $[OH^-]$, $[Ca^{2+}]$, $[H_2PO_4^-]$ and $[H_2PO_4^{2-}]$ in the final equilibrium system, it is necessary to solve nine equations (1–9). To reduce the number of equations, the composite constant $K_{a1}$ is utilized. The first pseudo-acid ionization constant $K_{a1}$ [11] is expressed as the product of the constants $K_h$ and $K'_{a1}$:

$$K_{a1} = K_h \times K'_{a1} = 4.44 \times 10^{-7}\,\mathrm{mol \cdot L^{-1}}. \tag{11}$$

Based on Eqs (6) and (10), the following dependencies were developed:

$$[H_2PO_4^-] = [Na^+] \times \frac{[H^+]}{[H^+] + K_{a2,P}} \tag{12}$$

and

$$[HPO_4^{2-}] = [Na^+] \times \frac{K_{a2,P}}{[H^+] + K_{a2,P}}. \tag{13}$$

Replacing the variables from Eqs (3), (4), (5), (11), (12), and (13), Eqs (8) and (9) can be expressed as follows:

$$2 \times \frac{K_{SP}}{K_{a2}} \times \frac{[H^+]}{[HCO_3^-]} + [H^+] = 2 \times K_{a2} \times \frac{[HCO_3^-]}{[H^+]} + [HCO_3^-] + \frac{K_W}{[H^+]} + [Na^+] \times \frac{K_{a2,P}}{[H^+] + K_{a2,P}}, \tag{14}$$

$$\Sigma[CO_X]_{W0} + \frac{K_{SP}}{K_{a2}} \times \frac{[H^+]}{[HCO_3^-]} = K_{a2} \times \frac{[HCO_3^-]}{[H^+]} + [HCO_3^-] + [HCO_3^-] \times \frac{[H^+]}{K_{a1}}. \tag{15}$$

As a result of replacing variables, the system is characterized by two equations with two unknown concentrations $[HCO_3^-]$ and $[H^+]$. Equations (14) and (15) are converted to the following forms:

$$\left(\frac{2 \times K_{a2}}{[H^+]} + 1\right) \times [HCO_3^-]^2 + \left(\frac{K_W}{[H^+]} - [H^+] + [Na^+] \times \frac{K_{a2,P}}{[H^+] + K_{a2,P}}\right) \times [HCO_3^-] - \frac{2 \times K_{SP}}{K_{a2}} \times [H^+] = 0, \tag{16}$$

$$\left(\frac{K_{a2}}{[H^+]} + 1 + \frac{[H^+]}{K_{a1}}\right) \times [HCO_3^-]^2 - \Sigma[CO_X]_{W0} \times [HCO_3^-] - \frac{K_{SP}}{K_{a2}} \times [H^+] = 0. \tag{17}$$

Now, we have two quadratic equations with two unknown concentrations ($[HCO_3^-]$ and $[H^+]$). The concentration of $[HCO_3^-]$ is a function of the concentration of protons $[HCO_3^-] = f([H^+])$, containing only one unknown variable, and the concentration of $[H^+]$ must satisfy the conditions of the charge (8) and mass balance (9) equations. The equilibrium concentrations of the $[HCO_3^-]$ and $[H^+]$ ions are calculated iteratively using various values of the $[H^+]$ concentration [24]. The approach for the qualitative and quantitative description of the equilibrium system $H_2O$–$CO_2$–$CaCO_3$–$NaH_2PO_4$ is based on the systematic method for solving multiple equilibrium discrepancies as presented in Skoog et al. [22].

The final equilibrium concentrations of $[Ca^{2+}]$, $[H_2PO_4^-]$, $[H_2PO_4^{2-}]$, $\sum[CO_x]_W$, and pH are calculated based on the equilibrium concentrations $[HCO_3^-]$ and $[H^+]$. The concentration of $H^+$ ions taken up by $CO_3^{2-}$ ions ($\Delta[H^+]_{CO_3^{2-}}$) and the concentration of $H^+$ ions released comes from the dissociation of water ($\Delta[H^+]_{H_2O}$), $H_2CO_3$ ($\Delta[H^+]_{H_2CO_3}$), and ($\Delta[H_2PO_4^-]$ ($\Delta[H^+]_{H_2PO_4^-}$)).

The carbonate equilibrium system $H_2O$–$[CO_2]_{W0}$–$CaCO_3$ was established by adding 100 mg solid $CaCO_3$ to 1 L MilliQ water with a known initial concentration of dissolved $[CO_2]_{W0}$. Excess $CaCO_3$ was added so that some solid $CaCO_3$ remained undissolved in the system at equilibrium. After stabilizing the pH, $NaH_2PO_4$ was added in concentrations corresponding to 5 $\mathrm{mg \cdot L^{-1}}$, 10 $\mathrm{mg \cdot L^{-1}}$, 25 $\mathrm{mg \cdot L^{-1}}$, 50 $\mathrm{mg \cdot L^{-1}}$, and 100 $\mathrm{mg \cdot L^{-1}}$ of phosphorus, respectively, with molar concentrations of phosphorus ranging from 0.161 to 3.23 $\mathrm{mmol \cdot L^{-1}}$.

Initially, water was purged with pure $N_2$ gas to reduce the $[CO_2]_{W0}$ concentration to practically zero. pH values were measured using a Jenway type 3520 pH meter and analysed with Dataway software. A one-litre closed reaction cell was maintained at 25.0 ± 0.1 °C using a water bath thermostat equipped with pH and temperature sensors (Mettler Toledo InLab® Routine and Jenway model 027500 sensors, respectively). The experiments were conducted with 1000 mL of water containing 100 mg $CaCO_3$ (CAS No. 471-34-1, 99.95% Sigma-Aldrich) and $NaH_2PO_4$ (CAS No. 7558-80-7, 99.5% Acros Organics, US) concentrations ranging from 5–100 $mmol·L^{-1}$.

Salts were added to the reaction cell after purging with a specific concentration of $[CO_2]$ using gas bags. At the end of the experiment, samples were filtered through a 0.45 µm membrane filter. $[Ca^{2+}]$ ion concentrations were determined by titration using a 1 mM EDTA solution, while the concentrations of dissolved phosphate species were measured using a Hach-Lange DR2800 spectrophotometer and LCK388 cuvettes.

## 3. Results and discussion

Observations of pH changes in the studied system revealed a 2–4 unit increase in $pH_{W0}$ when $CaCO_3$ was added to the equilibrium system. This was observed across a concentration range of $[CO_2]_{W0}$ from approximately $3.39 \times 10^{-5}$ $mmol·L^{-1}$ to 33.9 $mmol·L^{-1}$, as shown in Table 2.

Within the given range of $[NaH_2PO_4]$, adding this salt to the initial closed system $H_2O–[CO_2]_{W0}–CaCO_3$ ($[CO_2]_{W0} \cong 1.32 \times 10^{-2}$ $mmol·L^{-1}$) resulted in a reduction in pH in the final equilibrium system of $H_2O–[CO_2]_{W0}–CaCO_3–NaH_2PO_4$, as presented in Table 2. The concentration of protons released from the dissociation of $H_2CO_3$ decreases when the initial concentration of $[CO_2]_{W0}$ is lower. The majority of $H^+$ ions, which will react with $CO_3^{2-}$, are derived from the dissociation of $[H_2PO_4^-]$.

The difference between $\Delta[H^+]_{H_2PO_4^-}$ and $\Delta[H^+]_{CO_3^{2-}}$ corresponds to the negative proton transfer value of $\Delta[H^+]_{H_2CO_3}$, which results from the reversible dehydration of $H_2CO_3$ occurring when $[CO_2]_{W0} \geq 3.39 \times 10^{-7}$ $mmol·L^{-1}$. In this scenario, the equilibrium in the system is governed by the dissociation-dehydration processes of $H_2CO_3$ and the dissolution of $CaCO_3$.

The concentration of $H^+$ ions released from the dissociation of $H_2PO_4^-$ ions ($\Delta[H^+]_{H_2PO_4^-}$) is equal to $[HPO_4^-]$. In the closed system under investigation, when $[CO_2]_{W0} \geq 2.45$ $mmol·L^{-1}$, the dissociation of $H_2CO_3$ predominates and produces more protons than the dissociation of $H_2PO_4^-$, causing the pH to decrease below seven. After the addition of $NaH_2PO_4$, the range where $\Delta[H^+]_{H_2CO_3}$ has negative values extends to higher values of $[CO_2]_{W0}$. When $[CO_2]_{W0} \cong 2.15$ $mmol·L^{-1}$ and $c[NaH_2PO_4] \cong 3.23$ $mmol·L^{-1}$, the corresponding pH value is seven. When $[CO_2]_{W0} \geq 2.45$ $mmol·L^{-1}$, the values of $\Delta[H^+]_{H_2O}$ become negative because the dissociation of water is suppressed.

The $CO_3^{2-}$ ions released during the dissolution of $CaCO_3$ will accept protons ($\Delta[H^+]_{CO_3^{2-}}$) from two sources: either the reversible dissociation of water ($\Delta[H^+]_{H_2O}$) or $H_2CO_3$ ($\Delta[H^+]_{H_2CO_3}$). A higher dose of $[CO_2]_W$ increases the solubility of $Ca^{2+}$ ions, lowers pH, and reduces the ratio of $[H_2PO_4^-]_W$ to $[HPO_4^-]$, illustrating the interdependence of carbon and phosphorus equilibria.

**Table 2.** Equilibrium parameters after adding $NaH_2PO_4$ (0.161, 0.323, 0.807, 1.61, 3.23 mmol P $L^{-1}$) to the closed initial system of $H_2O–(CO_2)_{W0}–CaCO_3$, containing $[CO_2]_{W0} \cong 1.32 \times 10^{-2}$ $mmol·L^{-1}$ at T = 25 °C

| Parameter (ions and molecules in $mmol·L^{-1}$) | Water purged with $1.32 \times 10^{-2}$ $mmol·L^{-1}$ $CO_2$* | [Phosphate–P] with $CaCO_3$ 100 mg (1 $mmol·L^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0 | 0.161 | 0.323 | 0.807 | 1.61 | 3.23 |
| $[Ca^{2+}]$ | 0 | 0.1044 | 0.2029 | 0.3405 | 0.7162 | 1.1577 | 1.7214 |
| $[CO_3^{2-}]$ | 0.0025 | 0.0268 | 0.0138 | 0.0092 | 0.0039 | 0.0024 | 0.0016 |
| $[CO_2]_W$ $[CO_3^-]$ | 0.0132 | 0.0932 | 0.2045 | 0.3465 | 0.7146 | 1.1180 | 1.5783 |
| $\sum[CO_X]_W$ | 0.0157 | 0 | 0.0003 | 0.0015 | 0.0134 | 0.0529 | 0.1567 |
| $[H_2PO_4^-]$ | 0 | 0.1201 | 0.2186 | 0.3563 | 0.7319 | 1.1734 | 1.7371 |
| $[H_2PO_4^{2-}]$ | 0 | 0 | 0.0018 | 0.0100 | 0.0982 | 0.4179 | 1.3689 |
| pH | 5.61 | 0 | 0.159 | 0.3130 | 0.7087 | 1.1922 | 1.8611 |
| | | 9.79 | 9.16 | 8.70 | 8.07 | 7.66 | 7.34 |

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* tests without $CaCO_3$ and $NaH_2PO_4$

**Table 3.** Proton balance in the $H_2O–[CO_2]_W–CaCO_3–NaH_2PO_4$ system for various dissolved phosphorus concentrations

| $[PO_4^{3-}]$ mmol·L$^{-1}$ | $\Delta[H^+]_{H_2O}$ mmol·L$^{-1}$ | $\Delta[H^+]_{H_2CO_3}$ mmol·L$^{-1}$ | $\Delta[H^+]_{CO_3^{2-}}$ mmol·L$^{-1}$ | $\Delta[H^+]_{H_2PO_4^-}$ mmol·L$^{-1}$ | Theoretical pH | Actual pH |
|---|---|---|---|---|---|---|
| 0 | $6.18 \times 10^{-2}$ | $1.59 \times 10^{-2}$ | $-7.75 \times 10^{-2}$ | 0 | 9.79 | 9.79 |
| 0.161 | $1.45 \times 10^{-2}$ | $1.54 \times 10^{-2}$ | $-1.89 \times 10^{-1}$ | $1.59 \times 10^{-1}$ | 9.16 | 9.18 |
| 0.323 | $5.10 \times 10^{-3}$ | $1.42 \times 10^{-2}$ | $-3.32 \times 10^{-1}$ | $3.13 \times 10^{-1}$ | 8.70 | 8.74 |
| 0.807 | $1.17 \times 10^{-3}$ | $2.31 \times 10^{-2}$ | $-7.12 \times 10^{-1}$ | $7.09 \times 10^{-1}$ | 8.07 | 8.08 |
| 1.61 | $4.43 \times 10^{-4}$ | $3.73 \times 10^{-2}$ | –1.16 | 1.61 | 7.66 | 7.64 |
| 3.23 | $1.76 \times 10^{-4}$ | $1.41 \times 10^{-1}$ | –1.72 | 1.86 | 7.34 | 7.22 |

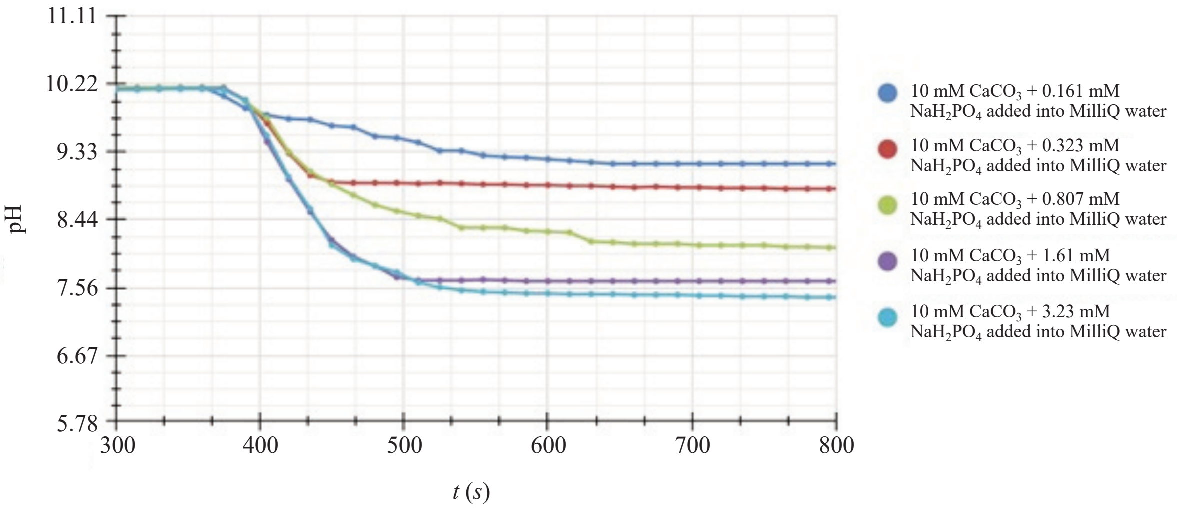

**Fig. 2.** Experimentally measured pH values of the closed equilibrium system $H_2O–[CO_2]_W–CaCO_3–NaH_2PO_4$ at a concentration range of $[CO_2]_{W0} \cong 3.39 \times 10^{-5}$ to $3.39 \times 10^{1}$ mmol·L$^{-1}$ at T = 25 °C.

Consequently, protons bind to $CO_3^{2-}$ ions, increasing the concentration of $OH^-$ ions and raising pH to a theoretical maximum of 9.79. The experimentally measured maximum pH of $9.79 \pm 0.03$ occurred at $[CO_2]_{W0} \cong 3.39 \times 10^{-5}$ mmol·L$^{-1}$, aligning closely with the theoretically calculated value.

After stabilizing the pH of the equilibrium system $H_2O–[CO_2]_{W0}$, following the addition of $CaCO_3$, we added $NaH_2PO_4$ at concentrations of 5 mg P L$^{-1}$, 10 mg P L$^{-1}$, 25 mg P L$^{-1}$, 50 mg P L$^{-1}$, and 100 mg P L$^{-1}$ to 1 L of liquid phase, which approximates the concentration range of phosphate phosphorus typically found in reject water [25–27].

In Fig. 2, at an initial concentration of $[CO_2]_{W0} \cong 3.39 \times 10^{-5}$ mmol·L$^{-1}$, the pH decreased from $9.79 \pm 0.03$ to $7.22 \pm 0.02$ upon adding $NaH_2PO_4$ to the system $H_2O–(CO_2)_{W0}–CaCO_3$, indicating a pH decline of $2.57 \pm 0.02$ units.

Table 3 shows that the experimentally measured final stabilized pH values of the closed equilibrium system $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$ closely approximated the theoretical values, with slight differences possibly attributable to the accuracy of the gas flow control system. This methodology can be extended to more intricate systems involving multiple acid-base equilibria, such as those with phosphoric acid. Thus, the reliability of our developed theoretical model was confirmed through the outcomes of this experimental study.

## 4. Conclusions

In this study of modelling the closed system $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$, we based our analysis on the system $H_2O–(CO_2)_W–CaCO_3$ and enhanced it using principles of proton transfer. The developed model calculated proton transfer parameters, pH, and equilibrium concentrations of ions and molecules in the liquid phase.

In forming the equilibrium system $H_2O–(CO_2)_W–CaCO_3$ through the dissolution of $CaCO_3$, $CO_3^{2-}$ ions release and accept protons ($\Delta[H^+]_{CO_3^{2-}}$) from two sources: the dissociation of water ($\Delta[H^+]_{H_2O}$) or $H_2CO_3$ ($\Delta[H^+]_{H_2CO_3}$). A lower initial concentration of $[CO_2]_{W0}$ results in fewer protons produced through the dissociation of $H_2CO_3$. Therefore, water dissociation predominates at the studied

$[CO_2]_{W0}$ concentrations, contributing the majority of protons to the equilibrium system. Consequently, protons bind to $CO_3^{2-}$ ions, leading to an increase in the pH of the formed equilibrium system.

In the system $H_2O–[CO_2]_W–CaCO_3–NaH_2PO_4$, at studied initial concentrations of $[CO_2]_{W0}$, $H_2PO_4^-$ ions served as the primary source of protons. The experimentally measured data closely matched the theoretically calculated values.

An equilibrium model is applicable when reactions occur rapidly or have sufficient time to achieve equilibrium. The developed model for the closed equilibrium system $H_2O–(CO_2)_{W0}–CaCO_3–NaH_2PO_4$ enables determination of component concentrations in the water phase across a wide range of natural and industrial conditions, utilizing the known concentration of $[CO_2]_{W0}$. This model facilitates the assessment of anthropogenic impacts on the environment and can be utilized by environmental technologists in water and wastewater treatment. The model is instrumental in advancing innovative methods for measuring $[CO_2]_W$ and $[HPO_4^{2-}]$ concentrations in water, supporting the development of new environmental technologies.

The theoretical and practical aspects of this study are fundamentally congruent, indicating the successful development of a functional model. Given the significant interest and demand for modelling ecological, chemical, and biological systems, there is ample opportunity to explore and construct more intricate models that can enhance wastewater treatment methodologies.

### Data Availability Statement

All research data are contained within the article and can be shared upon request from the authors.

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# Prootoni ülekandel põhinev uudne mudel suletud tasakaalulise süsteemi $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$ modelleerimiseks

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Uurimistöös käsitletakse uudset prootoni ülekandel põhinevat täiendatud mudelit suletud tasakaalulise süsteemi $H_2O–CO_2–CaCO_3–NaH_2PO_4$ modelleerimiseks matemaatilise iteratsiooni abil, mille aluseks on võetud varasemates uurimustes analüüsitud tasakaaluline süsteem $H_2O–(CO_2)_W–CaCO_3$. Loodud mudel võimaldab arvutada vees teadaolevate $CO_2$ ja $NaH_2PO_4$ kontsentratsioonide põhjal kõigi süsteemis moodustuvate ioonide ja molekulide sisalduse ning määrata vastava pH väärtuse. Väljatöötatud mudeli abil saab hinnata inimtegevuse mõju looduslikele veekogudele, optimeerida tööstuslikke protsesse ja modelleerida teisi analoogseid süsteeme.