

pH Control during the Struvite Precipitation Process of Wastewaters

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Abstract

The high concentration of phosphorus and nitrogen in wastewater and sludge could be lowered to a certain level by struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) crystallization. One of the main factors for struvite formation is the solution pH. It can be adjusted by non-reagent carbon (CO_2) dioxide stripping through the process of aeration. The intensity of the mass transfer between the air and the supernatant of dewatering sludge obtained from wastewater treatment plant is characterized by the volumetric liquid-side mass transfer coefficient, which can be estimated theoretically. It is found that the rate of pH increase depends strongly on the sparging area of the air distribution system while the air flow rate does not influence considerably the Dissolved Oxygen (DO) level which governs the CO_2 stripping process. The theoretical calculated values of the volumetric mass transfer coefficient have been compared with those obtained experimentally. Based on the data obtained, relationships of $\text{pH}/k_L a$ (mass transfer coefficient) were developed. These correlations serve as a tool for prediction of pH during the struvite precipitation process.

Keywords

Wastewater Treatment, pH, Carbon Dioxide Stripping, Mass Transfer

1. Introduction

Nitrogen and phosphorus are beneficial nutrients to many ecosystems in small amounts. In excessive, however, they cause a type of pollution called eutrophication (process causing reduction of oxygen concentration in water bodies due to significant growth of algae). The wastewaters are characterized by a high level of ammonia and phosphorus contents [1], therefore the effluents must be treated before discharging into water bodies [2] [3]. Conventional nitrogen removal from wastewater is carried out by biological nitrification and denitrification [4], or

other methods as ion exchange [5], microwave irradiation [6] and struvite precipitation [7]. Phosphorus can be removed from wastewaters by incorporation of phosphate into Total suspended solids (TSS) and the subsequent removal from these solids. Alternative method for P and N recovery is struvite precipitation. The product could be used as a slow release fertilizer [8] [9]. This is the reason why struvite precipitation is to be widely investigated. Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, magnesium ammonium phosphate hexahydrate—MAP) usually precipitates as a white orthorhombic crystals in a molar ratio $\text{Mg}:\text{MH}_4:\text{PO}_4 = 1:1:1$. MAP precipitation is a function of pH and molar ratios among ammonia, magnesium ions and phosphorus [10]. The solubility of the product can be defined by K_{sp} (solubility product constant), and struvite formation occurs when the concentration product exceeds struvite's solubility product (supersaturation). The constant can be described by following equation [11]:

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}]$$

Controlled MAP precipitation has been reported in treatment of digested sludge as source of phosphorus and ammonia. pH is a crucial variable that needs to be controlled in order to maximize the product production. Many authors have reported that the range of pH for MAP precipitation is from 8 to 11 [12]. According to the diagram showing concentration of species depending on pH (Figure 1), the optimal value of pH is about 9.6 [13].

Chemically pH can be controlled by using alkaline solutions as sodium hydroxide. High phosphorus and ammonia removal level were achieved at increased pH [14] [15]. NaOH is generally used for pH adjustment, but its addition rapidly increases pH value. Also the addition of NaOH will sharply increase the saturations of other magnesium precipitations, *i.e.* bobierrite and magnesite [16]. Alternative of addition of NaOH is the CO_2 stripping process. Willams (1999) has used CO_2 stripping for pH elevation [17]. Advantage is that pH increases slowly, which gives the optimum conditions for struvite crystal growth and crystallization process [18]. CO_2 stripping is non-reagent process for increasing of pH by dissolved carbon dioxide release using aeration of liquid [19]. It is a technique where dissolved CO_2 produced from an aerobic digestion process is removed from wastewater resulting in reduction of the total carbonate carbon concentration. The high concentration of CO_2 in wastewater is due to the relatively low specific exchange rates which do not allow the removal of substantial quantities of CO_2 . Therefore, an effective CO_2 control requires aeration for stripping process. When atmospheric air is placed in contact with wastewater, there is a tendency for a dissolved gas to come to equilibrium at saturation: undersaturated gas such as oxygen is transferred from the air to the wastewater, and supersaturated gas such as CO_2 is transferred to the air [20].

The gas—liquid equilibrium influences the transfer of CO_2 between air and wastewater. The carbonate species, H_2CO_3 , HCO_3^- , and CO_3^{2-} , are involved in instantaneous equilibrium among each other, as shown in Figure 1. In summary, dissolved CO_2 exists in the wastewater as part of the carbonate acid—base system. Therefore, the concentration of total dissolved CO_2 can be altered by change of the total amount of carbonate carbon in the solution. The intensity of this process is characterized by the volumetric liquid-side mass transfer

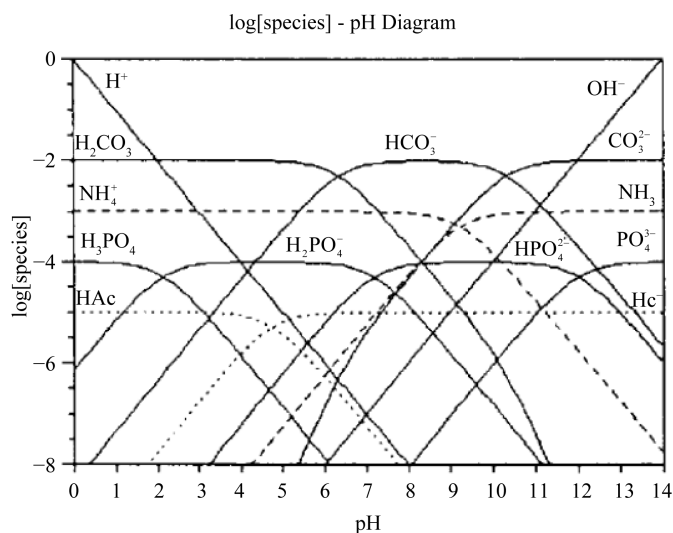


Figure 1. Concentration of species with pH.

coefficient, $k_L a$. If we estimate the volumetric liquid-side mass transfer coefficient, then we can predict pH solution by the following equation [21]:

$$r_T = \pm k_L \cdot a (\alpha_{oL} \cdot C_{TL} - \alpha_{oL.Eq} \cdot C_{TL.Eq})$$

where r_T , C_{TL} , $C_{TL.Eq}$, α_{oL} and $\alpha_{oL.Eq}$ are the CO_2 transfer reaction rate, total carbonates concentration in the liquid phase, equilibrium concentration of total carbonates in the liquid phase, H_2CO_3 fraction of the total carbonates in the liquid phase and equilibrium concentration of H_2CO_3 fraction of the total carbonates in the liquid phase, respectively.

In gas-liquid reactors, mass transfer from the gas phase to the liquid phase is a key parameter of the process. The $k_L a$ value in gas-liquid contacting equipment has mostly been determined by the oxygen physical absorption or desorption technique (classical method). In the actual large-scale aeration system, the application of the existing method for $k_L a$ determination can be limited by various factors such as absorption rate from air, complicated operating conditions, measuring equipment quality and cost, and also operator skills. Therefore, a simple theoretical way to predict the volumetric liquid-side mass transfer coefficient would be appreciated. These values can be predicted theoretically if we know how to estimate the liquid-side mass transfer coefficient k_L and the specific interfacial area, separately [22]-[25]. In order to improve the accuracy of the theoretical model for calculating the volumetric mass transfer coefficient for pH adjustment using air stripping, experimental data were needed for comparison.

2. Materials and Methods

The digested sludge was taken from one of the digesters of wastewater treatment plant (WWTP) (Pomorie, Bulgaria). The sludge contains 9310 mg $\text{PO}_4\text{-P/kg}$ solids and dry matter of 26 g/l as TSS. Principle scheme of WWTP-Pomorie and sampling point (digested sludge after digester) is shown in Figure 2. $\text{Al}_2(\text{SO}_4)_3$ is dosed before aeration tank.

The sludge was centrifuged in lab scale and the obtained supernatant was aerated in an up-flow reactor aiming pH elevation. Analytical measurement for chemical oxygen demand (COD, mgO_2/L), $\text{NH}_4\text{-N}$ (mg/L) and PO_4 (mg/L) were determined by Spectrophotometer (HACH LANGE DR 3900) using cuvette test (Cuvette test-

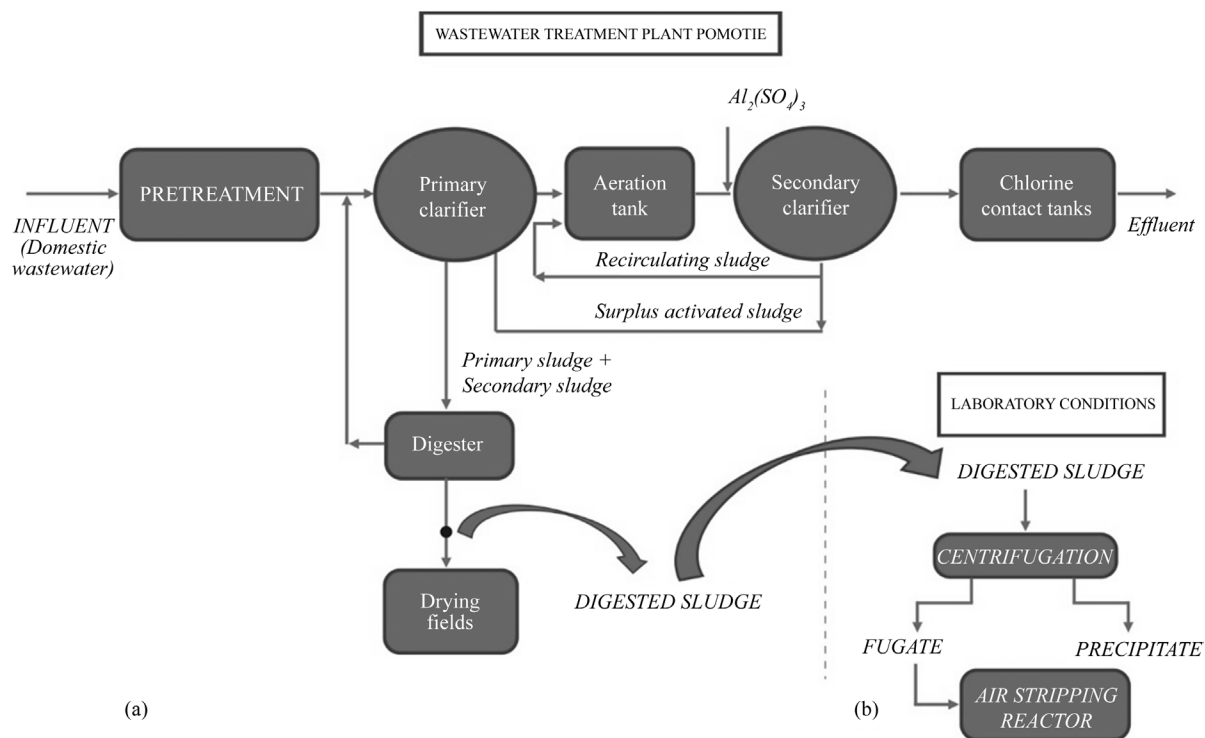


Figure 2. (a) Scheme of WWTP Pomorie and sampling point of digested sludge; (b) Sludge treatment in lab scale.

range 5 - 90 mg/L PO₄; range 100 - 2000 mgO₂/L COD; range 2.5 - 60 mg/L NH₄-N) and the obtained data is listed in **Table 1**. The samples were tested for magnesium and calcium content by the Ethylenediaminetetraacetic acid (EDTA) complexometric method [26]. The preliminary obtained information related to the concentrations of ammonia and phosphorous (o-PO₄) shows that the liquid phase following the dewatering of sludge from conventional WWTP contains significant concentration of these constituents for MAP precipitation. The concentrations of the dissolved oxygen and solution pH were measured by Multi-Parameter Meter (HQ40d Portable).

Plastic cylindrical column with diameter of 0.05 m was used as reactor for the CO₂ stripping process (**Figure 3**). Plastic perforated plate was installed at the bottom of the reactor and served as a gas sparger. Supernatant of 1000 ml was placed in the reactor. Air compressor was run and air flow was passing through the plastic perforated plate and the supernatant was aerated. The first series of experiments were carried out at different air volumetric flow rates (0.067 m/s; 0.134 m/s; 0.201 m/s) using large specific area yield by plate with number of orifices 132 and a diameter of each orifice 2 mm. For the second series of experiments was used a plate with a single orifice and airflow rate of 0.067 m/s. Dissolved oxygen and pH level were measured in both sets of experiments. Dissolved oxygen and pH level were measured in both sets of experiments aiming determination influence of organic matter on pH elevation. For this purpose the supernatant was diluted 2, 3 and 4 times using distilled water and COD levels in the diluted samples were 650 mgO₂/L, 400 mgO₂/L, and 320 mgO₂/L, respectively. The measurement of oxygen concentration was needed for the experimental calculation of the volumetric mass transfer coefficient, $k_L a_{exp}$. Sodium sulfite (Na₂SO₃) was added in order to deoxygenate the supernatant to an essentially zero concentration of dissolved oxygen. To increase the rate of the reaction copper sulfate (CuSO₄) was used as catalyst. After deoxygenation, the supernatant was aerated and the increasing concentration of the oxygen was recorded in order to calculate the mass transfer rate by the following equation:

$$\frac{dC_L}{dt} = k_L \frac{F}{V} (C_s - C_L) = k_L a (C_s - C_L)$$

where: C_s , C_L , a and V are the saturation concentration of oxygen, concentration of oxygen in the body of the liquid, the specific interfacial area and the volume of the liquid, respectively.

$k_L a_{exp}$ was obtained after integration of the above equation:

Table 1. Values of ammonia (mg/L), phosphate (mg/L), COD (mgO₂/L), calcium ions (mg/L) and magnesium ions (mg/L) in the supernatant.

Sample	Concentration of PO ₄ , mg/L	Concentration of NH ₄ , mg/L	COD, mgO ₂ /L	Concentration of Mg ²⁺ , mg/L	Concentration of Ca ²⁺ , mg/L
Supernatant	130	380	1260	102.1	108.2

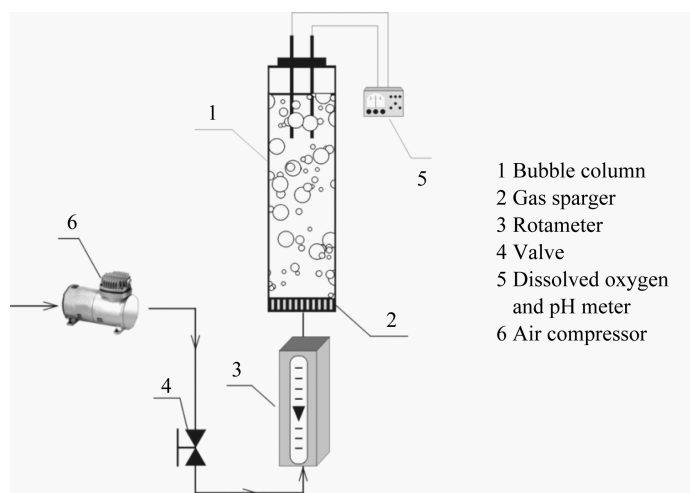


Figure 3. Experimental setup.

$$k_L a_{\text{exp}} = \frac{1}{t} \ln \frac{(C_s - C_{L_1})}{(C_s - C_{L_2})}$$

For the theoretical prediction of the volumetric liquid-side mass transfer coefficient $k_L \cdot a_{\text{theor}}$, we need to calculate some hydrodynamic (d_s , f_B , u_B) and mass transfer parameters [27]-[29]. Once we have calculated the liquid-side mass transfer coefficient k_L and the specific interfacial area a , some correction is needed due to the ellipsoidal shape of the bubble. Miller has introduced the following correction factor [30]:

$$f_c = 683d_s^{1.376}$$

The $k_L \cdot a_{\text{theor}}$ values should be multiplied by this correction factor for optimal prediction [31] [32]:

$$k_L a_{\text{theor}} = f_c \sqrt{\frac{4D_L}{\pi t_c}} \frac{N_B S_B}{(AH + N_B V_B)}$$

3. Results and Discussion

3.1. Influence of Different Air Flow Rates

pH elevation and oxygen concentrations at different air flow rates were observed (Figure 4 and Figure 5). The results show evidently that within the volumetric air rate applied the effect of pH increase follows a similar mode

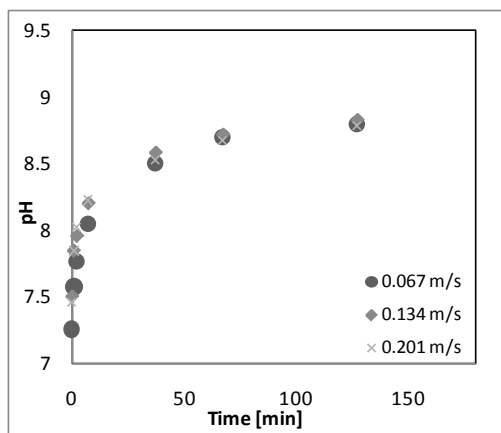


Figure 4. pH elevation by air stripping column applying different volumetric air rates.

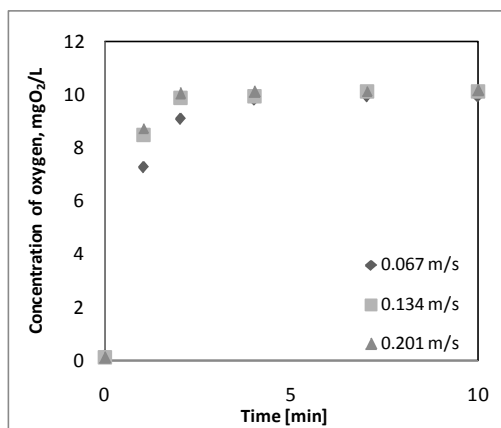


Figure 5. Concentration of oxygen applying different volumetric air rates.

of change. More rapidly oxygen saturation of the supernatant within the first 5 minutes of aeration was observed. pH increases from 7.5 to 8.4 were achieved by air stripping within 20 minutes, while pH values were increased up to 9 after 250 minutes of aeration. Actually, pH values from 8.3 to 8.5 are enough for MAP precipitation by CO₂ stripping process. But many studies are showing that the optimal pH is in the range of 9 to 9.5 [33] [34]. The targeted pH of 9 was achieved after 4 hours of aeration. The slow change of pH after the 20th minute of aeration is an advantage of the CO₂ stripping process because it restricts the rapid increase of solution saturation. As such conditions the struvite crystallization process predominates [16].

3.2. Influence of Different Sparging Area

Although the curves follow similar mode of change (Figure 6 and Figure 7), the rate of pH elevation and oxygen concentration is higher at larger developed sparging area compared to the rate of pH elevation and oxygen concentration using gas sparger with single orifice. When gas sparger with 1 orifice was used for aeration, pH was increased to 8.4 within 120 minutes. For the same period of aeration but different gas sparger with 132 orifices pH achieved value of 8.8. The result is demonstrating that larger developed surface area lead in rapidly pH increasing because of faster oxygen saturation of solution and carbon dioxide stripping.

3.3. Influence of Organic Contain

The dependence of pH elevation on organic contain was determined (Figure 8). pH values of 8.7 and 9 (starting of pH = 8.1) were achieved within 250 minutes of aeration at COD = 650 mgO₂/L, COD = 400 mgO₂/L and COD = 320 mgO₂/L, respectively. The experiment indicated that higher organic contain in the supernatant

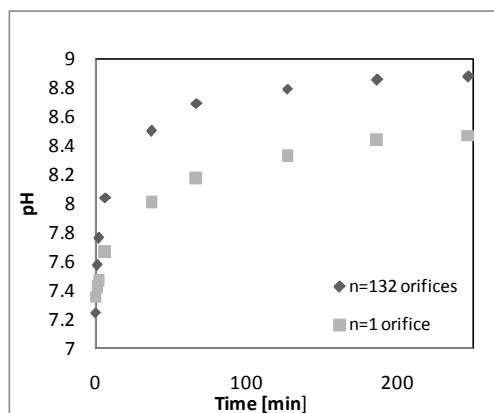


Figure 6. pH elevation applying different gas spargers.

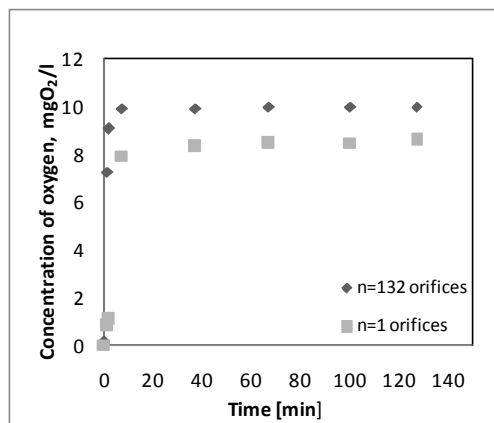


Figure 7. Concentration of oxygen applying different gas spargers.

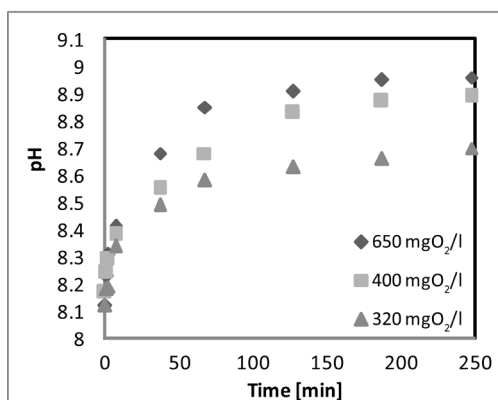


Figure 8. pH elevation applying different organic contain.

resulting in higher increase of pH value.

3.4. Mass Transfer Coefficients

The predicted of experimental data are plotted in Figure 9. The figure shows that there is relative agreement between the predicted and the experimental coefficients. The data obtained show that the experimental data are within the range of -25% $+25\%$ of the theoretical trend (the central continuous line).

The theoretical and experimentally obtained mass transfer coefficients are also compared at different air volumetric rates (w , m/s) (Figure 10). These results show at higher air volumetric rates the experimental coefficients are close to the theoretical values.

Aiming to find relationships between pH, w [m/s] and K_{La} [s^{-1}], a logarithmic function was applied. Actually, three functions were followed, namely $pH = f(w)$, $K_{La} = f(w)$ and $pH = f(k_{La})$ at constant time of aeration. We choose time of aeration two minutes. The pH/w and k_{La}/w functions are presented in Figure 11. Evidently, at higher air velocity k_{La} and pH are increased. However, at the values of air velocity higher than 0.2 m/s the influence of air velocity is negligible. The direct relation between pH and k_{La} is given in Figure 12. For the three curves shown in Figure 11 and Figure 12 the correlation coefficients over 0.98 (Figure 11 and Figure 12). Such relationships could serve as a prediction tool for pH in struvite precipitation reactor.

For the specific case of struvite precipitation of supernatant of digested sludge (parameters: $[PO_4^{3-}] = 130$ mg/L, $[NH_4^+] = 380$ mg/L, COD = 1260 mgO₂/L) aerated by air flow supplied through plate (number of orifices 132 and diameter of each orifice 2 mm), three logarithmic functions were elaborated:

$$K_{La} = 0.0142 \cdot \ln(W) + 0.0571$$

$$pH = 0.2431 \cdot \ln(W) + 8.4214$$

$$pH = 0.451 \cdot \ln(K_{La}) + 9.5426$$

These functions describe the interactions between the pH, w (m/s) and k_{La} .

4. Conclusions

CO₂ stripping was applied as an alternative method for pH elevation of supernatant taken from digested sludge. It was found that the rate of increase of pH depended strongly on the sparging area of the air distribution system while the air flow rate did not influence considerably DO level which governed the CO₂ stripping process. Based on the data obtained, relationships of pH/k_{La} (mass transfer coefficient) were developed. These correlations served as a tool for prediction of pH during the struvite precipitation process.

Relationships among pH, w [m/s] and K_{La} [s^{-1}] were determined for the specific case of struvite precipitation using supernatant of digested sludge.

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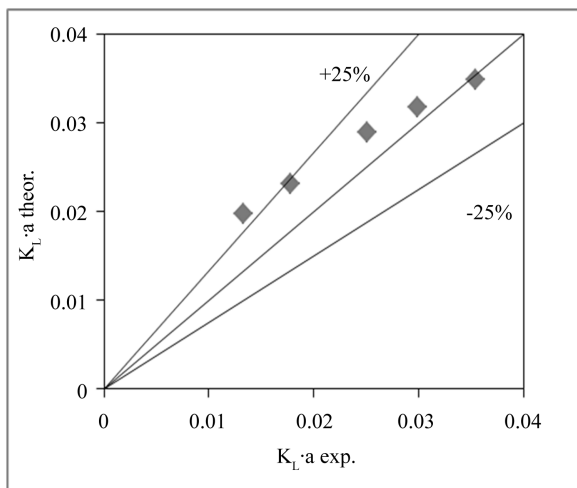


Figure 9. Comparison between the theoretical and the experimental volumetric liquid-side mass transfer coefficients (◆: experimental data).

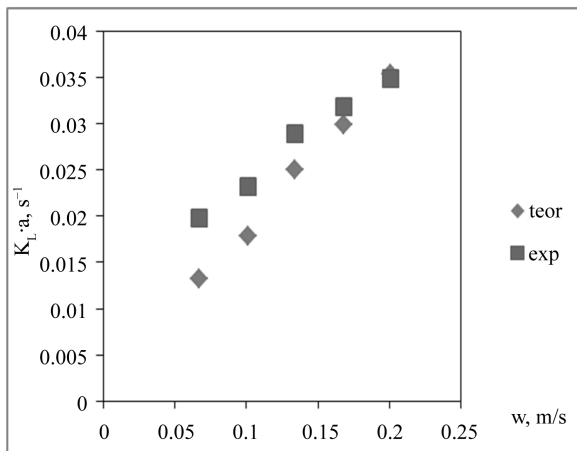


Figure 10. Volumetric liquid-side mass transfer coefficient as a function of gas velocity.

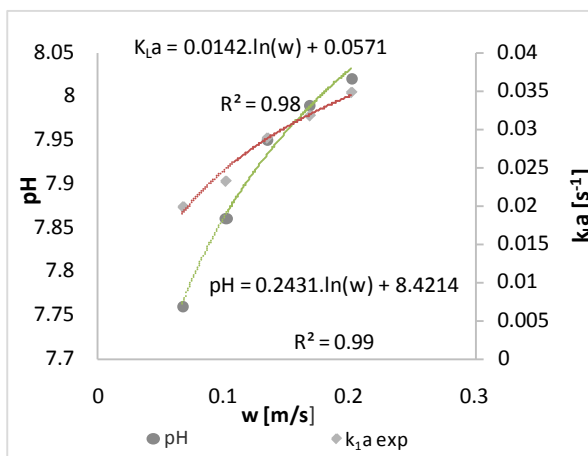


Figure 11. Relation between pH and w (m/s), and $K_L a$ and w (m/s).

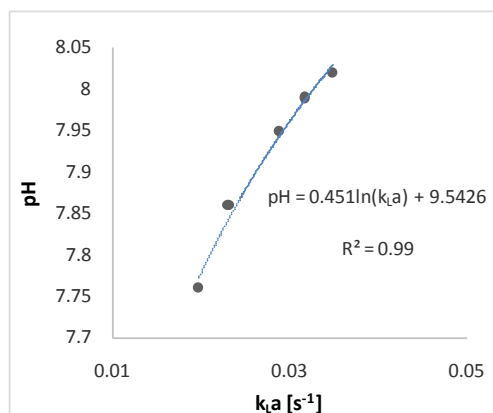


Figure 12. Relation between pH and K_{La} .

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