Mathematical Modelling of Alkaline Sludge Disintegration

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Abstract

The disintegration of waste activated sludge (WAS) by alkaline pre-treatment (alkalization) was carried out in batch reactors in this study. The influences of operating conditions (sludge concentration, NaOH dosage and pre-treatment time) on the sludge disintegration, the release of extracellular polymeric substances (EPS) and the dewatering and settling properties of sludge were investigated at room temperature. The alkalization was determined to be an effective disintegration method. Optimum operational conditions were found as 0.10 N NaOH, 0.5 h pre-treatment time and 1.0% total solid (TS) content of the sludge. It was also observed that the alkaline sludge disintegration occurred in two stages: the rapid disintegration stage in the first 0.5 h and the subsequent slow disintegration stage in the remaining part of the pre-treatment time. Therefore, the alkalization process was simulated via a two-phase kinetic mathematical model in order to predict the process performance. The suggested mathematical model was proven to be a useful tool for predetermining the efficiency of alkalization process and for designing the process.

Keywords: Alkalization, mathematical modelling, sludge disintegration, waste activated sludge

Alkali Çamur Parçalamanın Matematiksel Modellemesi

Özet

Bu çalışmada, kesikli reaktörlerde atık aktif çamurun (AAÇ) alkali ön arıtma (alkalizasyon) ile parçalanması çalışılmıştır. İşletme şartlarının (çamur konsantrasyonu, NaOH dozu ve ön arıtma süresi) çamur parçalamaya, hücrelerarası polimerik maddelerin salınımına ve çamurun su verme ve çökelebilme özelliğine etkileri oda sıcaklığında araştırılmıştır. Alkalizasyonun etkili bir parçalama metodu olduğu belirlenmiştir. % 1.0 katı madde (KM) içeren çamurun 0.10 N NaOH dozunda 0.5 sa ön arıtımı, optimum işletme şartları olarak belirlenmiştir. Ayrıca, alkalizasyon ile çamurun parçalanmasının iki aşamada gerçekleştiği görülmüştür: ilk 0.5 sa'de gerçekleşen hızlı parçalama aşamadı ve onu takip eden yavaş parçalama aşaması. Böylece, alkalizasyon süreci, prosesin çamur parçalama verimini tahmin edebilmek için iki aşamalı bir matematiksel model ile simule edilmiştir. Önerilen matematiksel modelin, alkalizasyon sürecinin tasarımı ve parçalama verimini tahmin edebilmek için kullanışlılığı kanıtlanmıştır.

Anahtar Kelimeler: Alkalizasyon, atık aktif çamur, matematiksel modelleme, çamur parçalama

1. Introduction

Biological wastewater treatment results in the production of huge amounts of excess biological sludge which is called as "waste activated sludge (WAS)". Since WAS includes pathogenic organisms, readily degradable organic substances, refractory organic compounds and inorganic components; its treatment is necessary prior to final disposal. In addition, the mandatory legislations for the disposal are becoming increasingly stringent in many countries. However, the sludge management is one of the most

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complex problems limiting the operation of wastewater treatment plants. Besides, the treatment and disposal of sludge cost up to about 50 % of total cost of treatment plants [1].

To reduce the treatment cost and to improve the sludge treatment efficiency, alkaline sludge pre-treatment (alkalization) can be applied before the sludge digestion process. Alkalization is a harsh chemical pre-treatment method with advantages such as easy operation, simple device and high efficiency [2]. Its disintegration mechanism is briefly based on the disintegration of sludge flocs, the destruction of cell walls and membranes and the transfer of extracellular and intracellular substances into the aqueous phase by hydroxyl anions (OH^-) [3].

In the present study, since NaOH is one of the most effective alkaline agents to disintegrate the WAS [3 – 5], it was used as the alkaline source. Most of the studies in the literature have been focused on the optimization of process parameters, based on soluble chemical oxygen demand (COD) parameter [1, 2, 6, 7]. However, in the present study, the operating parameters were optimized depended on the increase in carbohydrate and protein in addition to COD in soluble form. Besides, the modeling of alkaline sludge pre-treatment had been scarcely investigated so far. Therefore, the mathematical modelling of alkaline sludge disintegration was examined by a two-phase kinetic mathematical model. After the optimization of sludge concentration, NaOH dosage and pre-treatment time were studied in detail, an experimental mathematical model was developed, which can predict easily the process performance under the varying operational conditions. Besides, changes in the dewatering and settling properties of the sludge were also investigated.

2. Materials and Methods

2.1. Sample collection

The WAS used in this study was collected from Başarakavak domestic wastewater treatment plant in Konya, Turkey. The sludge sample was taken from the return activated sludge line and was stored at + 4℃ before its usage. The sludge sample had a water content of 99.5%, pH of 7.5, total chemical oxygen demand (tCOD) of 4200 mg/L, soluble chemical oxygen demand (sCOD) of 65 mg/L, total solid (TS) of 4990 mg/L, volatile solid (VS) of 3300 mg/L, suspended solid (SS) of 4300 mg/L, volatile suspended solid (VSS) of 1105 mg/L, capillary suction time (CST) of 10.7 s and settled sludge volume (SSV_{30}) of 98%. Before the alkalization experiments, TS content of the raw sludge was adjusted to the desired value by gravitational settling and diluting with ultrapure water.

2.2. The set up of alkalization process

The sludge disintegration experiments were performed with a jar test apparatus (Velp, Italy) equipped with six 500 beakers containing 250 mL of sludge sample. The experimental run was carried out under rapid mixing condition (90 rpm) at room temperature. Alkalization was conducted by adding 5 N into the WAS to reach the desired NaOH dosages in the range of 0.01 – 0.50 N. The pre-treatment times were 0.5, 1.5 and 24 h. After the alkaline pre-treatment, pH of the alkalized sludge was adjusted to about 7.5 by using 5 N H_2SO_4 solutions. After the neutralization, the sludge at room temperature was used for the analysis.

2.3. Analysis

The measurements of SS, TS, tCOD and CST were performed according to Standard Methods [8]. After the samples were centrifuged at 3000 rpm for 10 min, the supernatant was removed, filtered through a membrane with a mesh diameter of 0.45 μm (Sartorius, Germany), and then filtrate was used for the analysis of COD, protein and carbohydrate in soluble phase. The soluble carbohydrate and protein were measured according to the phenol sulphuric acid method [9] and the modified Lowry method (Pierce test kit) [10], respectively. The measurements of VSS and TVS were conducted according to the procedure defined by Tiehm et al. [11]. The sludge pH was determined using a pH meter (WTW, Germany). Turbidity was measured by using a turbidimeter (Hach Lange, Germany). The settling ability of sludge was represented by the settling volume of 100 mL sludge in a measuring cylinder in 30 min (SSV_{30}) [12]. Despite the fact that the settling ability measurement is not a standard method; it was used to observe the changes in the settled sludge volume after the pre-treatment. The dewatering capacity of WAS samples was determined by CST test and measured via a CST meter (Venture, USA). In addition, the microscopic examination of the disintegrated sludge samples was performed by using a light microscope (Olympus, Germany) to determine the chemical and physical effects of alkalization on the sludge.

In order to evaluate the disintegration performance, the disintegration degree (DD_{COD}) was calculated as the ratio of the sCOD increase by alkalization to the maximum possible sCOD increase, as given in Eq. (1) [13],

$$DD_{COD}\ (\%) = \left[\frac{(sCOD - sCOD_0)}{(tCOD - sCOD_0)} \right] \cdot 100 \qquad (1)$$

where, $sCOD_0$ is the initial soluble COD in the raw WAS (mg/L), tCOD is the total COD in the raw WAS (mg/L) and sCOD is the soluble COD in the pre-treated WAS (mg/L).

3. Results and Discussion

3.1. Effect of TS content on the sludge disintegration

The effect of sludge concentration on the sludge disintegration was experienced with three different TS content (0.5, 1.0 and 2.0% TS) at a fixed NaOH dosage (0.05 N) for a constant pre-treatment time (0.5 h). As shown in Figure 1, the thickening of sludge from 0.5 to 1.0% TS content resulted in a sharp increase in sCOD concentration from 450 mg/L to 1300 mg/L. Further raise in TS content of sludge to 2.0% gradually increased the sCOD concentration to 1865 mg/L. However, the thickening of WAS to 2.0% TS caused a decrease in DD_{COD}. Because the applied NaOH dosage was not enough to disintegrate the thickened WAS. Hence, an increase in the applied NaOH dosage was needed to improve the disintegration of concentrated sludge. Besides, as it was seen from Figure 1, there was no correlation between the sludge concentration and the increases in sCOD and DD_{COD}. Consequently, since the highest DD_{COD} was achieved at 1.0% TS content; the optimal TS content was found to be as 1.0% TS.

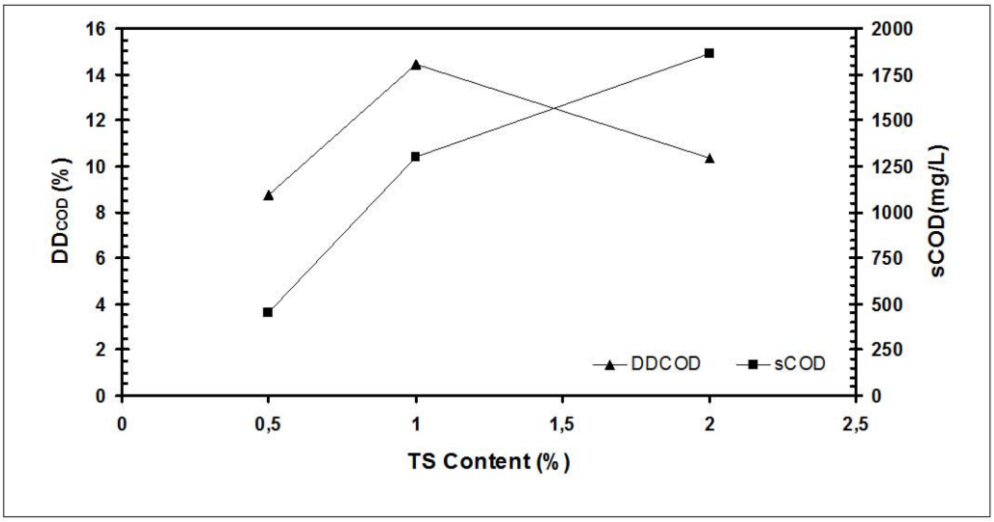

Figure 1. Effect of the sludge concentration on sCOD and DD_{COD}

3.2. Effect of alkalization on the release of EPS

The main components of the microbial cells are carbohydrate and protein. Their releases are due to the disintegration of sludge flocs and the break-up of cells. Thus, the effects of alkalization on sludge disintegration were investigated based on soluble carbohydrate and protein, in addition to sCOD. Changes in the concentrations of soluble carbohydrate, protein and COD at different base dosages are shown in Figure 2.

The pH values of the alkalized sludge samples at 0.01, 0.03, 0.05, 0.08, 0.10, 0.30 and 0.50 N NaOH dosages were measured as 8.7, 9.7, 12.1, 12.4, 12.6, 12.7 and 12.9, respectively. NaOH dosage of 0.10 N resulted in an extreme increase in pH value (equal to 12.6). However, higher dosages did not raise the sludge pH significantly. As shown in Figure 2, since the sludge disintegration efficiency of alkalization is depended on the sludge pH, NaOH dosage has an important effect on sludge disintegration up to reaching pH of 12.6 (at 0.10 N NaOH).

When compared the increase in soluble carbohydrate, protein and COD concentrations with the alkaline dosages applied, 0.30 and 0.50 N NaOH dosages have a limited impact on the sludge disintegration. In addition, some of the carbohydrates, transferred to soluble phase, were hydrolyzed and so, the soluble carbohydrate concentration was decreased at extremely high NaOH dosages (0.30 and 0.50 N) for 24 h pre-treatment time. Since the alkaline dosage and pre-treatment time significantly influence the sludge disintegration efficiency and the main cost of pre-treatment process, optimization of the base dosage is very important.

3.3. Effects of alkaline dosage and pre-treatment time on the sludge disintegration

The DD_{COD} values showed a rising trend with an increase in NaOH dosage and prolongation of alkalization (Figure 3). When NaOH dosages were 0.01 and 0.03 N, DD_{COD} was 3.9% and 7.5% for 0.5 h and 4.4% and 8.2% for 1.5 h, respectively. However, DD_{COD} increased to 16.1% and 19.0% at 0.10 N for pre-treatment times of 0.5 and 1.5 h, respectively. When NaOH dosage increased to 0.50 N, DD_{COD} increased negligibly to 16.3% and 17.4% for 0.5 and 1.5 h. The application of base at 0.10 N dosage resulted in an increment in DD_{COD} to 40% and to 46.6% at 0.50 N NaOH with alkalization of 24 h.

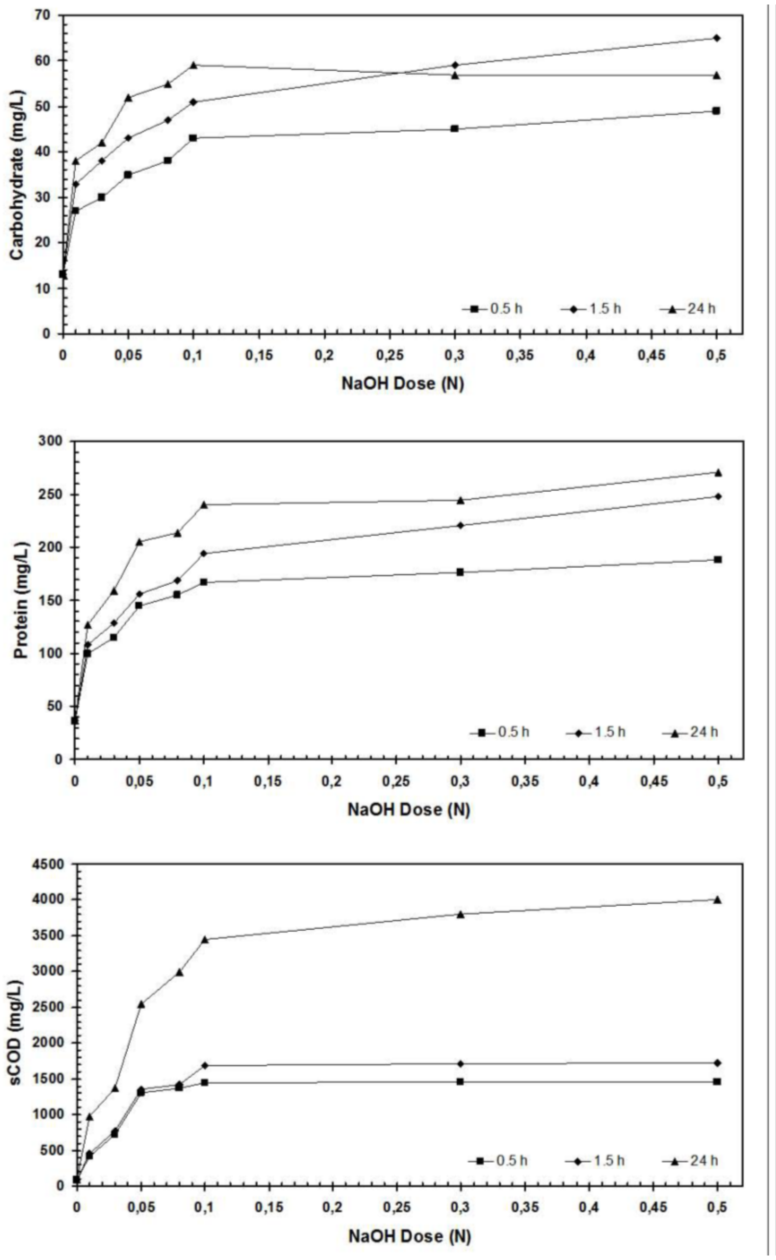

Figure 2. Effects of NaOH dosage and pre-treatment time on soluble carbohydrate, protein and COD

Therefore, sludge disintegration was improved depending on the increase in NaOH dosage applied into the WAS. Similarly, Li et al. [1], Lin et al. [14] and Vlyssides and Karlis [15] reported that the sludge disintegration was steadily enhanced with increase in the applied base dosage. In addition, it was determined that the waste sludge was rapidly disintegrated during the first 0.5 h of alkalization. Then, the disintegration rate was relatively slowed down in the remaining part of the alkalization time, as shown in Figure 3. The solubilization quantity in the first 0.5 h was 36.4 – 52.0% of the total solubilized organic matters in 24 h at different NaOH dosages. Similar results were reported in the study of Li et al. [1]. Since NaOH dosage and pre-treatment time are the most important operating parameters which significantly affect the overall performance and the total cost of the pre-treatment method, the optimal pre-treatment conditions were determined as NaOH dosage of 0.10 N and pre-treatment time of 0.5 h. Differently from our results, Li et al. [1] found optimum conditions as NaOH dosage of 0.05 N for 0.5 h, based on only the

DD_{COD} parameter. However, in this work, releases of carbohydrate and protein were taken into consideration to determine the optimal base dosage, in addition to the increase in sCOD.

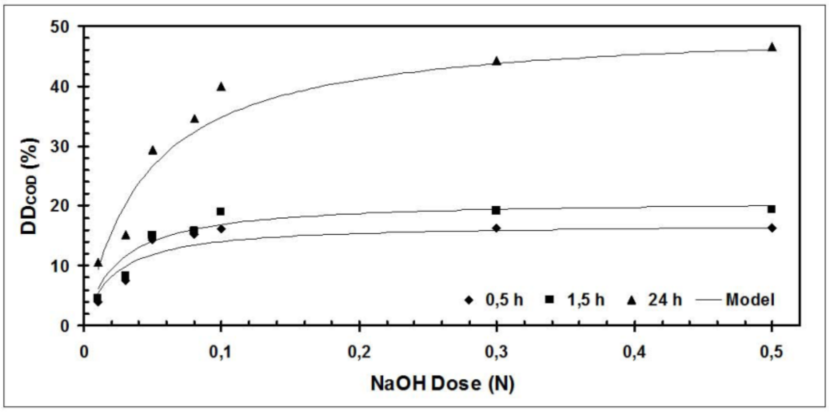

Figure 3. Effects of NaOH dosage and pre-treatment time on DD_{COD}.

3.4. The mathematical modelling of alkalization

The sludge disintegration is a complex process due to the involvement of many side reactions. Hence, the modelling of alkalization process was performed by using the DD_{COD} parameter which indicates the sludge disintegration efficiency [16]. Since the disintegration of sludge was occurred in rapid and slow stages, the overall disintegration process could not be explained by simple reaction kinetics. Based on DD_{COD}, new mathematical model approach (Eq. (2)) [13] was therefore implemented for the predetermination of alkalization performance. Simple equation of the model is given in Eq. (2);

$$Y = \frac{X}{a + b \cdot X} \quad \text{or} \quad \left(\frac{X}{Y}\right) = a + b \cdot X \tag{2}$$

For modelling of alkaline sludge disintegration, Eq. (2) was first modified and a new relationship among the applied NaOH dosage (D_{NaOH}) and disintegration degree (DD_{COD}) has been developed for each pre-treatment time (t) applied (Eq. (3)).

$$\left(\frac{D_{NaOH}}{DD_{COD}}\right) = a + b \cdot D_{NaOH} \tag{3}$$

where, D_{NaOH} is the applied NaOH dosage (N), DD_{COD} is the disintegration degree of WAS (%) for any alkalization time and thus, (D_{NaOH} / DD_{COD}) is the specific NaOH dosage. a and b are the model constants showing the initial disintegration rate ($1/a$) and theoretical maximum sludge disintegration capacity ($1/b$), respectively.

The experimental DD_{COD} data obtained was linearized by using Eq. (3). The relationship between applied and specific NaOH dosages for different pre-treatment times is represented in Figure 4. The correlations resulted in very high determination coefficient (R^2) values indicating that the suggested model could accurately predict the process performance under the different experimental conditions.

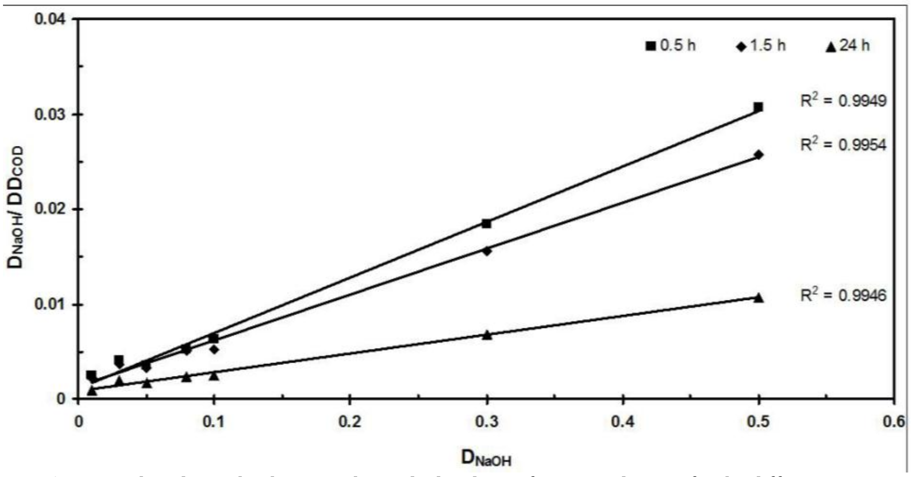

Figure 4. The relationship between the applied and specific NaOH dosages for the different times

In order to calculate the two model constants, slope (*a*) and intercept (*b*) were correlated to the pre-treatment times (*t*), by plotting *a* and *b* values versus ln *t*. Thus, the correlations were formulated in the following equations:

$$a = -0.0100 \cdot \ln t + 0.0517 \qquad R^2 = 0.9994 \qquad (4)$$

$$b = -0.0001 \cdot \ln t + 0.0012 \qquad R^2 = 0.7659 \qquad (5)$$

By substituting the slope of line (*a*) (Eq. 4) and the intercept (*b*) (Eq. 5) into Eq. (3), Eq. (6) is produced as below,

$$DD_{COD}(\%) = \frac{D_{NaOH}}{(0.0517 \cdot D_{NaOH} - 0.01 \cdot D_{NaOH} \cdot \ln t - 0.0001 \cdot \ln t + 0.0012)} \qquad (6)$$

The obtained model equation (Eq. 6) can be used simply by inputting the alkalization time and dosage for the WAS with a fixed TS content. A comparison between experimental and simulated DD_{COD} data was made and the modelling performance was shown in Figure 3. The results obtained from the proposed model were in good agreement with the experimental data in all conditions.

The proposed mathematical model was also implemented on the results of alkaline pre-treatment studies of some researchers [1, 5, 12, 14], as described above. The data needed for the model was read from the graphics in their studies. While Li et al. [1] and Jin et al. [12] experienced the alkaline pre-treatment of WAS taken from municipal wastewater treatment plants using anaerobic-anoxic-aerobic process, the waste biological sludge samples were supplied from industrial wastewater treatment plants in the studies of Lin et al. [1] and Navia et al. [5]. Therefore, we tried to prove the accuracy of the mathematical model by using the results of those studies performed for different sludge samples under different alkaline pre-treatment conditions, in addition to our empirical results. As seen from Figure 5, the simulated data was good agreement with experimental data and the R^2 values were found as quite high (> 0.80). However, the R^2 values determined for the studies of Navia et al. [5] and Jin et al. [12] was lower than those of data of other two studies. The lower R^2 values might be resulted from application of the model on less number of data. On the other hand, difference in the experimental results might be arisen from the different nature of waste biological sludge samples. Consequently, it was determined that the proposed model gives satisfactory results for both municipal and industrial waste biological sludge and thus, it can be utilized in order to predetermine easily the process performance and to design the process in the wastewater treatment plants.

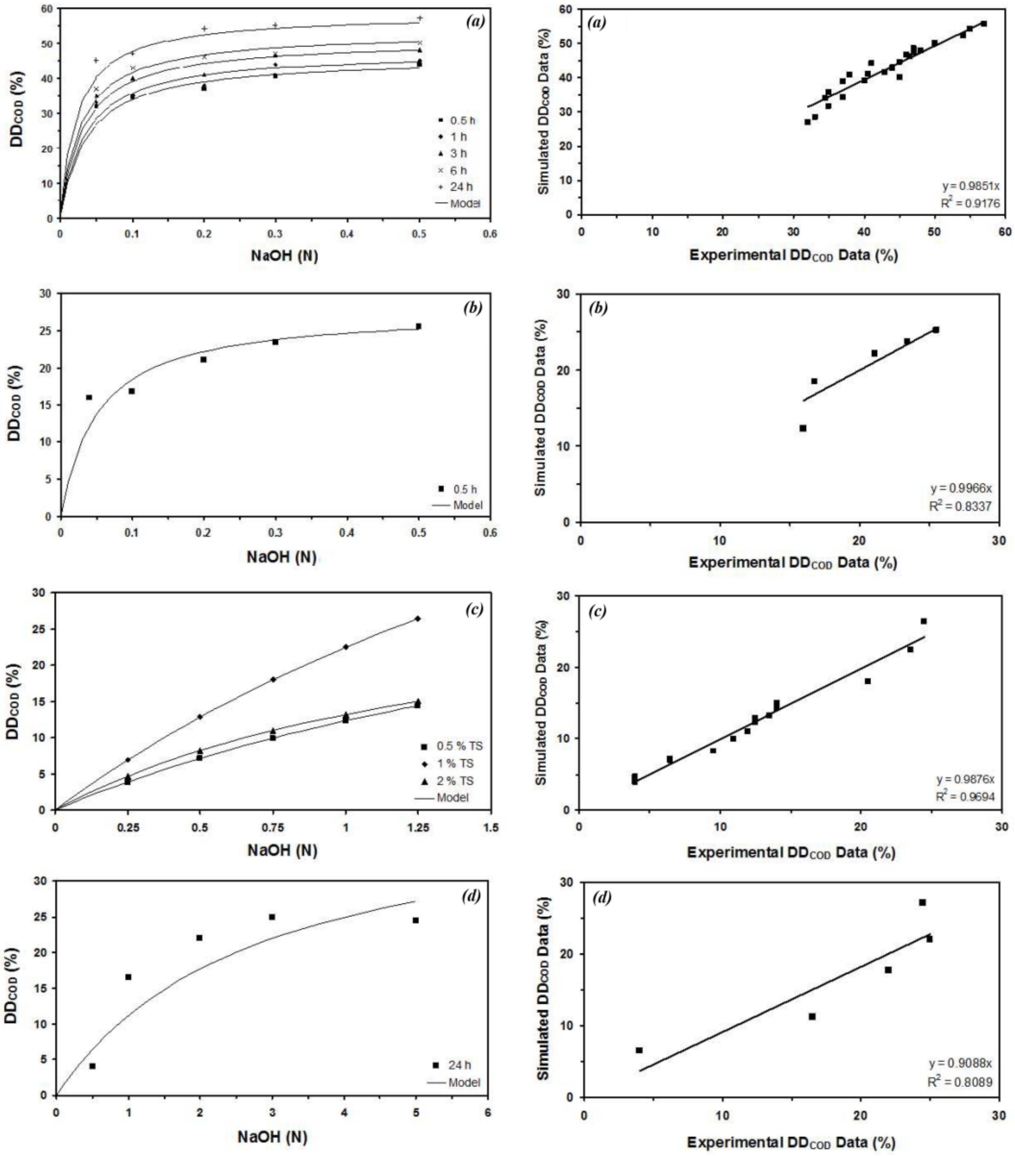

Figure 5. Correlation between simulated and experimental DD_{COD} data for the results of studies of Li et al. (2008) (a), Navia et al. (2002) (b), Jin et al. (2009) (c) and Lin et al. (1998) (d).

3.5. Effects of alkalization on the dewaterability and settleability of WAS

Turbidity is an important parameter indicating the changes in particle size, which has a critical influence on the dewatering ability of the sludge. Hereby, turbidity and dewaterability were evaluated together in this section. The effects of alkalization on the turbidity and dewaterability of the WAS is represented in Figure 6.

Since the sludge flocs had become smaller after alkalization (Figure 5), the alkalization in the range of 0.01 and 0.08 N NaOH for 0.5 and 1.5 h pre-treatment times resulted in a rise in turbidity. In spite of the increase in turbidity with increasing NaOH dosage, turbidity decreased at 0.08 and 0.10 N NaOH dosages for 24 h pre-treatment due to re-flocculation of the solubilized organic matters by the formation of gel-like material [17]. Turbidity of the pretreated WAS with 0.08 and 0.50 N NaOH for 0.5

and 1.5 h decreased because of the re-flocculation of the particles. Because, the solubilized organic matters composes a gel-like material containing a large amount of water and some fine particles, and this gel-like material holds the fine particles together [1]. Therefore, since the particle size increased by forming gel-like material, turbidity decreased. But, the turbidity of the pretreated WAS at 0.30 and 0.50 N dosages for 24 h increased due to both the decrease in particle size as a result of the solubilization of gel-like material and the enhancement in sludge disintegration.

As seen from Figure 6, the CST indicating the dewatering characteristic of sludge changed similarly to turbidity of the alkalized sludge. Dewaterability of the pretreated sludge deteriorated in the range of 0.01 – 0.10 N NaOH for 0.5 and 1.5 h (Figure 6). Similar to turbidity, the CST values raised due to the decrease in the particle size [17]. However, sludge dewatering property improved with alkalization at 0.03 – 0.10 N for 24 h due to the re-flocculation of fine particles in the gel-like material. Additionally, the dewaterability enhanced by alkaline pre-treatment at 0.30 and 0.50 N NaOH for 0.5 and 1.5 h because of the re-flocculation of the particles, compared to the sludge treated at lower NaOH dosages (Figure 5). However, alkalization at extremely high pH for 24 h resulted in the solubilization of gel-like material which causes the reduction of particle size and the release of EPS. The dewatering ability deteriorated with increasing the concentration of EPS which has an important affinity to water [18]. Besides, since smaller flocs supply more absorbing surface area for water, a part of the water was absorbed on the surface of particles [18]. Therefore, the dewatering property became worse.

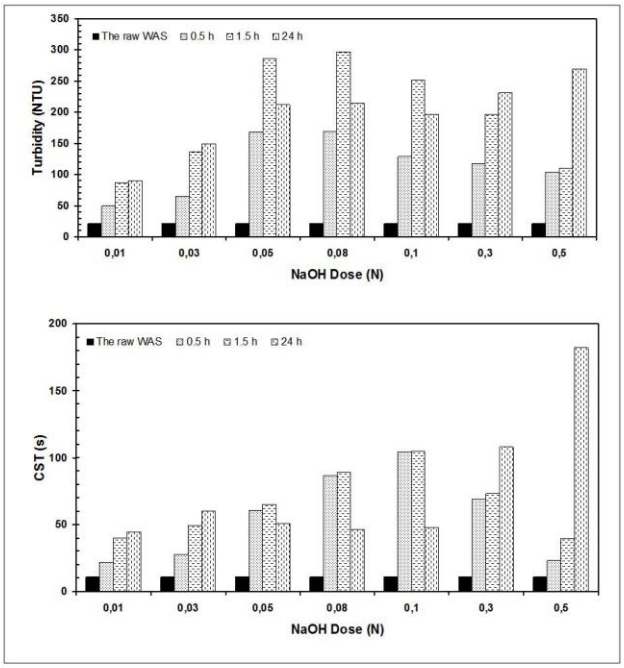

Figure 6. Effects of NaOH dosage and pre-treatment on turbidity and CST.

The alkalization had a positive effect on the sludge settleability, as shown in Figure 7. The improvement in the settleability of the alkalized sludge may have been resulted from two reasons: (1) the effect of EPS on reducing the surface charge and bridging the cells physically and (2) the disintegration of filamentous microorganisms. Neyens and Baeyens [19] reported that the main factor in bio-flocculation is the bio-polymers, which bridge cells physically. The sludge settleability might be therefore improved steadily (Figs. 2 and 7), as the EPS concentration was risen.

Besides, although filamentous organisms are desired in adequate numbers to form floc, excessive amount of filamentous organisms results in the buoyancy of sludge flocs. It was observed via microscopic examination that the disintegration of filamentous organisms improved by prolonging the pre-treatment time and increasing the alkaline dosage. In addition to these reasons, the rise of temperature during the neutralization of WAS after the pre-treatment might contribute the improvement in the sludge settleability by thermal conditioning [20, 21]. Therefore, the settling property of the pretreated sludge was improved steadily, as seen from Figure 7.

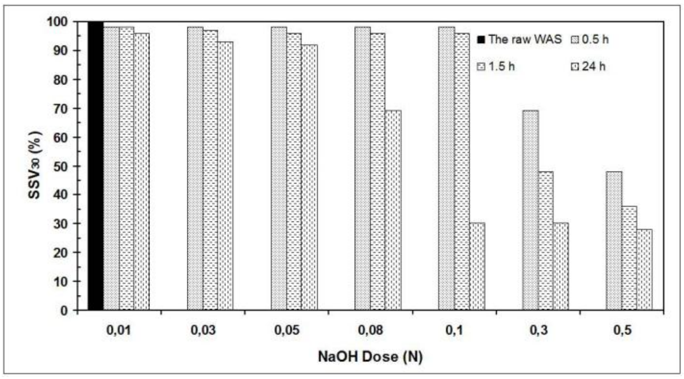

Figure 7. Effects of NaOH dosage and pre-treatment on SSV_{30}.

4. Conclusion

In this study, the effects and modelling of alkaline sludge pre-treatment were examined. Based on the experimental work, the obtained results can be summarized as follows:

- The waste biological sludge was effectively disintegrated by the alkalization method. Therefore, before the sludge digestion, the alkalization can be applied for the sludge pre-treatment.
- The applied NaOH dosage, pre-treatment time and sludge concentration have a significant impact on the process performance and pre-treatment cost of alkalization. The optimal operating conditions were determined as 0.10 N NaOH for 0.5 h pre-treatment time using the WAS of 1.0% TS content. Among these parameters, while the sludge concentration is the most effective parameter, the pre-treatment time is the least effective one.
- The alkaline sludge disintegration was occurred rapidly in the first 0.5 h. Later on, the disintegration rate was slowed down in the remaining part of the total pre-treatment time.
- The suggested experimental mathematical model was proven as a good tool in order to predetermine the process performance under different conditions. Thus, the two-phase kinetic mathematical model, which made the process design simpler and more accurate, can be used for the alkalization process in the full scale industrial and municipal wastewater treatment plants.
- The sludge dewaterability deteriorated compared to raw sludge, whereas the sludge settleability improved by alkalization.

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