Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25755

192 (2020) 166–175
July

Determination of the effect of multi-walled carbon nanotube on the treatment efficiency and design parameters in the activated sludge systems

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Received 21 August 2019; Accepted 24 February 2020

ABSTRACT

In recent years, carbon nanotubes (CNTs) have been spreading around in various ways and can be involved in biological wastewater treatment processes. Their effect on treatment facilities is unknown. Therefore, when multi-walled carbon nanotube (MWCNT) is found in activated sludge processes, it is important to define the treatment performance and to show the changes of the process design determined with biokinetic coefficients. In this paper, the potential effect of MWCNT on the activated sludge process was evaluated through the continuous flow tank reactor (CSTR). CSTR was exposed to wastewater contained 0, 10, 20, and 30 mg/L MWCNT. Addition of 10, 20, and 30 mg/L MWCNT provided 65.66%, 66.14%, and 74.77% total nitrogen removal, respectively. At the same time, these MWCNT amounts decreased the NH_4^+ concentration by 71.81%, 52.34%, and 77.08%, respectively. Increasing of the MWCNT concentration causes a decrease in the rate of chemical oxygen demand (COD) removal. The COD removal rates were 49.9%, 48.3%, and 35.08%, respectively. The experimental results showed that the increase of the MWCNT amount decreases K_d-value (from 6.36 to 2.63 d^{-1}). Besides, as the amount of added MWCNT increased, a significant change of Y value did not occur and K_d increased from 0.9687 to 0.128 d^{-1}.

Keywords: MWCNT; Activated sludge; Total nitrogen; Ammonium; Chemical oxygen demand

1. Introduction

Activated sludge is the most widely used biological wastewater treatment process [1]. Especially, the quality assessment of the sludge produced in wastewater treatment plants (WWTP) is essential prior to its application for the improvement of agricultural lands in recent years [2]. It is based on the biological degradation of both soluble organic and inorganic components and particulate matter carried out by microbial flocs [3], which are traditionally separated from the liquid stream through gravity sedimentation. Mixed liquor suspended solids (MLSS) concentration calls typically varying from 1,000 to 3,000 mg/L in the conventional systems [4]. The suspended solids concentration of activated sludge ranges from 0.4% to 1.5% by weight of dry solids with a pH of 6.5 to 8.0. Due to the low solids concentration and high volume, the process of thickening the activated sludge is very crucial [5]. Flocculation (part of solid–liquid separation processes) is, therefore, one of the most important mechanisms occurring in the activated sludge process [6,7].

Activated sludge floc has a multilevel configuration, which is formed by macroflocs specified by such factors as endogen Hydrophobicity, the extracellular polymeric substances (EPS) formation, and polyvalent cation bridge [6]. Microorganisms have an important role in the formation of EPS consisting of polysaccharides, uronic acids, proteins, gelatinous matrix excreted during their growth [6,8]. EPS is the main constituent of the organic fraction of activated sludge [9].

EPS consists of apolar regions which are groups with hydrogen-bonding potential, anionic groups (in uronic acids and proteins), and cationic groups (e.g. in amino sugars). The cohesion of flocs and biofilms provides a crucial role in the stability of several processes including flocculation, settling, and dewatering during the treatment of wastewater. EPS protects organisms against some antibiotics and metallic cations because it can behave as a molecular sieve that releases sequestering cations, anions, apolar compounds, and particles from the water phase. Due to the stickiness of the matrix, particles and nanoparticles can be captured and accumulated [10].

Since the operation of activated sludge processes can be inhibited by the presence of recalcitrant organic compounds, tertiary treatment is needed in the treatment of wastewater [11]. Many studies have been carried out with activated sludge combined with powdered activated carbon (PACT process). It has been reported that the PACT process provided in higher quality treated wastewater, a more stable system, and reusable water production, improved sludge settling and dewatering [12].

Carbon nanotubes (CNTs) are a new material in growing commercial applications due to their special electronic and mechanical properties [13,14] and find new applications as absorbent and adsorbent for organic contaminants and heavy metal removal [14,15]. As a result of the increase in their production and application, CNTs inevitably spread from industrial discharges, stormwater runoff, and landfill and eventually enter WWTP [16]. The concentration of CNT in water and soil in Switzerland was estimated to vary between 0.0005–0.0008 μg/L and 0.01–0.02 μg/L, respectively [17]. Gottschalk et al. [18] calculated and compared predicted environmental concentrations (lower and upper) of CNT for Europe, Switzerland, and the U.S. They found that highest CNT concentration of surface water in Europe, U.S., and Switzerland was 0.021, 0.004, and 0.025 ng/L, respectively [18]. Therefore, concerns about risks related to biological processes and systems are increasing [12].

In recent years, there are various studies on the use of multi-walled carbon nanotube (MWCNT) as an adsorbent in wastewater treatment. The adsorption capacity of MWCNTs and MWCNT-COOH removing reactive blue 29 dye (RB29) from aqueous solutions were 49 and 34 mg/g, respectively [19]. Dehghani et al. [20] reported that it was removed 100% of diazinon from water sources with MWCNTs under 0.1 g/L adsorbent dose, and 0.3 mg/L initial concentration of diazinon. Dehghani et al. [21], the overall results confirmed that MWCNTs usable adsorbent material for THMs removal from aqueous solutions. In other studies, it showed that the highest removal efficiency was obtained of fluoride using single-walled carbon nanotube (SWCNT) with 0.5 g/L concentration, as 58% [22]. In another study by Dehghani et al. [23], MWCNT was used to remove phenol from wastewater.

It is reported that CNTs have a natural affinity for proteins and carbohydrates. Pure carbon nanotubes are hydrophobic in pure water. However, CNTs can be dissolved in water by the interaction between CNTs and soluble protein and carbohydrates [15]. To date, several studies have been carried out on the impact of CNTs on the physical properties of flocs, the removal of chemical oxygen demand (COD) and biological nutrients (biological phosphorus and nitrogen) in activated sludge systems fed with synthetic wastewater and real wastewater. In these studies, it was determined that SWCNT and MWCNT have no negative effect on the activated sludge treatment performance. Moreover, SWCNT and MWCNT contributed to the removal of COD, ammonium (NH_4^+), and phosphate (PO_4^{3-}) and improved sludge settling, flocculation properties and relative hydrophobicity [13–16,24,25]. Luongo and Zhang [14] reported that EPS has played an important role in protecting microorganisms from the toxic effects of MWCNT.

When it is considered that MWCNT has a positive effect on biological treatment and EPS contributes to the prevention of toxicity, CNTs can be used to support treatment in activated sludge processes. However, the effect of MWCNTs on the biokinetic coefficients used in the activated sludge process design is unclear. The objective of this paper was to evaluate the impacts of MWCNT on biokinetic coefficient and removal of COD, NH_4^+, and total nitrogen (tN).

2. Materials and methods

2.1. Preparation of MWCNT suspensions

Over 90% of the purified MWCNT used in this study were obtained from Sigma-Aldrich Inc., (Merck KGaA, Darmstadt, Germany). Properties of MWCNT are powdered, 110–170 nm diameter, 5–9 μm length, 1.7 g/mL density (25°C), and it is produced by carbon vapor deposition method.

In previous studies, MWCNT was used in concentrations of 0.64–3.24 g/L, 1, 10, 20, and 100 mg/L to investigate the toxicity and treatment efficiency of MWCNTs. Therefore, 10, 20, and 30 mg/L MWCNT stock solutions were prepared depending on the reactor usage volume. MWCNT stock solution (MWCNT) was mixed in a 1 h sonicator (Bandalin HD 2070, Berlin, Germany, Frequency-20 kHz). To ensure homogeneous dissolution in an activated sludge system, the sonicator was operated with a 50% amplitude.

2.2. Operation of continuous flow stirred reactor

In this study, all experimental studies were carried out using a laboratory-scale activated sludge reactor. The activated sludge used in the reactor was supplied from the aerobic reactor at the Ordu-Giresun Airport Package Wastewater Treatment Plant in Turkey.

A continuous flow stirred tank reactor (CSTR) without recycle was used during experiments (Fig. 1). It is usually used to determine the biokinetic coefficient by the reason of the ease of operating conditions. Hydraulic retention time (θ) and mean-cell residence time (θ_c) are equal in CSTR [26]. The microorganism cultivation of CSTR is frequently called as chemostat [27]. In this configuration, the mixing (fluid dilution) is so vigorous that the substrate concentration and dissolved oxygen are uniform through the reactor [28]. It is an ideal reactor based on this assumption.

The laboratory-scale reactors were made of acrylic glass. In the experimental setup, reactor outer diameter is 15 cm, depth is 23 cm and operation volume is 2.5 L. Reactor hydraulic retention time is 6 h and it was fed with synthetic wastewater at a flow rate of 6.94 mL/min. Two peristaltic pumps, whose brands are Heidolph (Schwabach, Germany),

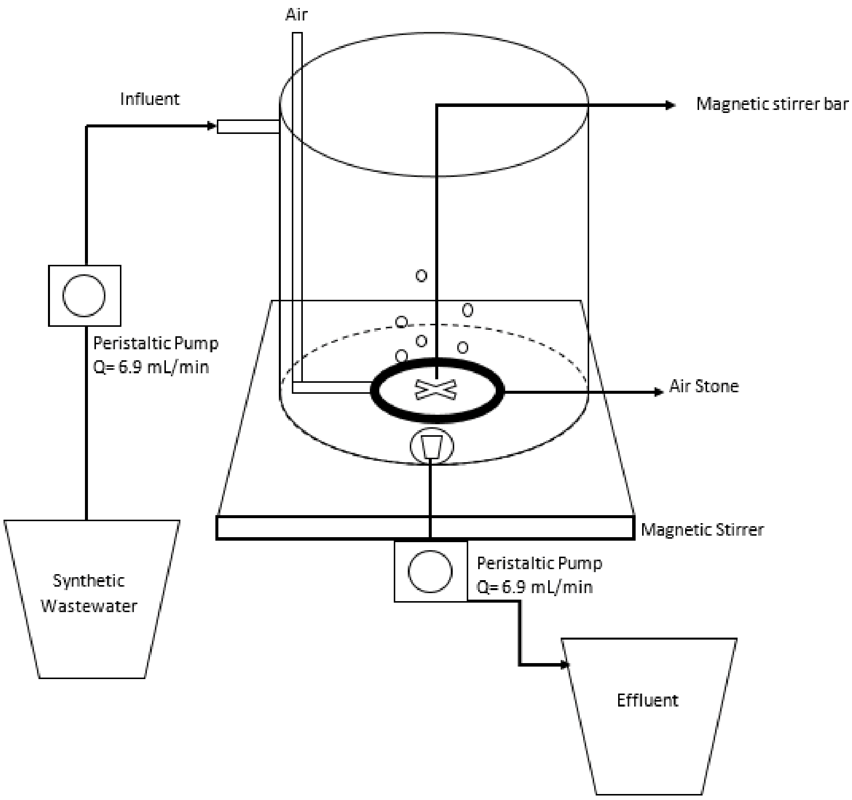

Fig. 1. Schematic diagram of a completely mixed continuous flow reactor.

were used to regulate the influent and effluent flow rate being 6.94 mL/min. Aeration of the mixture liquid containing microorganisms in the reactor was provided by aquarium stone in circular form and aquarium pump. The temperature of the experimental set-up was kept constant at 25°C ± 3°C, pH 7–8, and dissolved oxygen at 2–4 mg/L. The schematic drawing of the system and experimental setup are as shown in Figs. 1 and 2. The composition of synthetic wastewater used in the activated sludge system is given in Table 1.

Before starting the experiment, the activated sludge taken from the WWTP was aerated to ensure that microorganisms are acclimatized. Activated sludge/synthetic wastewater mixture (1/2 ratio) was kept under aerobic conditions (9 h/1 d) by stirring with a magnetic stirrer at 300 rpm for 4 d.

At the end of each day, mixing in the reactor was terminated and mixed liquor was settled. 1 L of water was withdrawn, and the same amount of synthetic wastewater was added to the reactor. On the 2nd day, Merck Millipore 8 g of "nutrient broth (5 g/L peptone and 3 g/L meat extract)" (Merck KGaA, Darmstadt, Germany) was added to the synthetic wastewater. Then, on the 5th day, the MWCNT-stock solution at different concentrations was added to the reactor. Immediately, the reactor was fed with synthetic wastewater and samples were taken at every 1 h (at 0, 1, 2, 3, 4, 5, and 6 h) and analyzed. The reactors were tested once for each concentration. Analyzes were performed in triplicate.

Table 1
Composition of synthetic wastewater [29]

Composition	Concentration (g/L)
$C_6H_{12}O_6$	2.55
$(NH_4)_2HPO_4$	0.563
K_2HPO_4	1.875
NaCl	0.075
$CaCl_2H_2O$	0.075
$MgSO_4{\cdot}7H_2O$	0.075
$FeCl_3$	0.015

2.3. Analytical method and calculation of biokinetic coefficients

40 mL samples were taken from the effluent wastewater and allowed to settle for 10 min, and COD, NH_4^+ (ammonium), and tN were analyzed in clear portions of the samples. Concentrations of COD, NH_4^+, and tN were measured by the Merck Cell test and reagent test (Merck KGaA, Darmstadt, Germany) according to Standard Methods. Spectroscopic measurements were made with the Merck Nova 60 photometer (Merck KGaA, Darmstadt, Germany). Besides, MLSS measuring was carried out to determine biokinetic coefficients.

For the steady-state CSTR, the substrate concentration of the reactor should be constant. Therefore, *dS*/*dt* is equal to zero [30].

Monod equation is widely used in determining the biokinetic coefficients in the activated sludge process [1–31].

$$\mu = \mu_m \frac{S}{K_s + S} \tag{1}$$

Fig. 2. Lab-scale completely mixed continuous flow reactor.

Biokinetic coefficients have a great influence on the design of the bioreactor in biological treatment [32].

Biokinetic coefficients;

μ is the specific growth rate, time^{-1}, μ_m is the maximum specific growth rate, time^{-1}, K_s is the half of velocity constant, mass/unit volume, k is the maximum rate of substrate utilization per unit mass of microorganism, time^{-1} are described [31–34].

The values of k, K_s, Y, and K_d are found using the linearized Eqs. (2) and (3) [35].

$$\frac{\theta X}{S_0 - S} = \frac{K_s}{k}\frac{1}{S} + \frac{1}{k} \quad (2)$$

$$\frac{1}{\theta} = Y\frac{S_0 - S}{X\theta} - K_d \quad (3)$$

These coefficients are calculated with the aid of substrate concentration, biomass concentration, and hydraulic retention time [31].

In Eqs. (2) and (3), θ is the hydraulic retention time (d); X is the biomass concentration (mg SS/L); S_0 is the influent substrate concentration (COD) (mg/L); S is the effluent substrate concentration (COD) (mg/L); Y is the maximum cell yield (cell mass/substrate mass); K_d is the endogenous decay coefficient (time^{-1}).

By the aid of Eq. (2), a graph is plotted by writing $X\theta/S_0–S$ values on the y-axis and $1/S$ x-axis. In the graph, the intercept on the y-axis is $1/k$ and the slope is K_s/k. Using Eq. (3), a graph is plotted by $1/\theta$ on the y-axis and $S_0–S/X\theta$ on the x-axis. K_d and Y values are intercept and slope of the best fit line [35].

3. Result and discussion

3.1. Removal effects of MWCNT on tN, NH_4^+ and COD

The time-dependent tN removal performance for each cycle at different MWCNT concentrations is given in Fig. 3. In the control reactor, tN concentration at t = 0 was 148 mg/L and the tN % removal was calculated by varying the tN concentration in the reactor from the initial moment to the end of 6 h. In the control reactor (CR) and MWCNT-added reactors, tN concentration decreased over time. While the tN removal in CR was 51.35%, the tN removal increased in the reactor exposed to MWCNT. The use of 10, 20, and 30 mg/L MWCNT resulted in removal of tN 65.66%, 66.14%, and 74.18%, respectively. The nutrient the removal efficiencies provided by the addition of MWCNT in each active sludge cycle are summarized in Table 2.

Fig. 4 shows the effect of MWCNT at different concentrations on NH_4^+ removal. A change of about 39% occurred in the control reactor. In addition, NH_4^+ removal was achieved at 71.81%, 52.34%, and 77.08%, respectively, in the treatment cycle of 10–20–30 mg/L MWCNT-added reactors. The use of limited oxygen led to a slight reduction in NH_4^+ concentration for the control reactor. It is thought that the reduction in ammonia concentration is due to the conversion of ammonia to nitrate in the control reactor.

Nitrifying bacteria oxidize nitrogen compounds by two-step cooperation between the ammonia-oxidizing bacteria

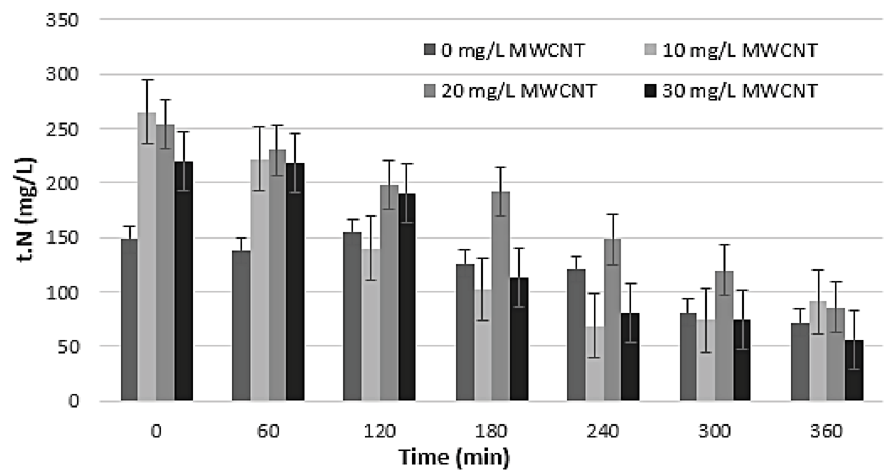

Fig. 3. Effects of MWCNT on tN removal.

and nitrite-oxidizing bacteria in the nitrification process, but these organisms also strive for common resources (especially oxygen) [36]. The basic organisms involved in the nitrification process are the genus *Nitrosomonas* and *Nitrobacter*. Yin et al. [13] reported that the abundance of nitrifying bacteria influenced by MWCNT. Studies showed that there were no significant differences in the oxidation of NH_4^+ in short-term exposure [16,25]. 10, 20, and 30 mg/L MWCNTs, in contrast, to the control reactor promoted the removal of ammonium, yet the performance in 10 and 30 mg/L reactor with MWCNT is higher than 20 mg/L used MWCNT. It should be considered that NH_4^+ adsorption affected the ammonium removal in the reactor using 20 mg/L MWCNT. Adsorption mechanism is important in the stabilization of MWCNTs with a natural organic substance found in waterways [13]. In the studies carried out complex microbial systems, it is reported that MWCNTs (500–875 mg/L NH_4^+) did not show antimicrobial activity after short term exposure [16]. Thus, in this study, the addition of MWCNT (10, 20, and 30 mg/L) provided getting the better performance of the activated sludge process.

In the studies on the effect of MWCNT on complex microbial systems, after a shock exposure of SWCNT (250–270 mg/L), Yin et al. [13] found that the addition of SWCNT did not adversely affect the performance of the continuous reactor. Moreover, it was also determined that SWCNT by adsorbing contributed to the removal of COD [24]. It can be said that the addition of CNT has a major role in the adsorption mechanism and nitrification and denitrification process in the COD and nutrient removal.

Table 2
Nutrient removal efficiencies

	Removal (%)		
MWCNT (mg/L)	tN	NH_4^+	COD
0	51.35	38.55	83.27
10	65.66	71.81	65.24
20	66.14	52.34	73.55
30	74.77	77.08	64.88

After, the control reactor and MWCNT-added reactors were fed with synthetic wastewater at constant flow and concentration, the change in COD removal was determined from the time t = 0. The COD concentration at the time t = 0 in the reactor was used as initial COD concentration to calculate the COD % removal efficiency. The change of the COD concentration for each reactor at the end of treatment is shown (Fig. 5). While the COD removal rate in the control reactor was about 83.27%, the efficiency of COD removal decreased with the increase of the exposed MWCNT. Addition of 10, 20, and 30 mg/L MWCNT resulted in 65.24%, 73.55%, and 64.88% COD removal, respectively. The reason for the high COD removal in the control recycle can be explained as follows: The interaction of MWCNT and EPS protects the activated sludge process from the toxic effect of MWCNTs [14]. Also, the MWCNT-EPS complex is more readily separated and flocculated from wastewater.

However, the sheared mixed liquor causes decreasing in activated sludge flocks and hence microbial population. The activated sludge process uses organic material for the production of new microorganisms. Because of the hydrophobicity of the MWCNT-EPS complex, it is considered that organic matter the removal is lower than control reactors. It is possible that the removal of organic and inorganic substances via adsorption achieved approximately 70% of COD removal in the reactors with MWCNT. Nevertheless, the MWCNT-EPS complex has a significant effect on the removal of dissolved and inert organic materials with absorption and adsorption mechanisms [14,15]. Unlike the studies to date [13,15,16,24], this study shows that the adsorption mechanism is important for the removal of tN and NH_4^+ while biodegradation mechanisms of the microbial population are important in the removal of soluble organic matter (COD). The increase in COD removal in the reactor with 20 mg/L MWCNT can be explained by the fact that the input COD concentration in this reactor is lower than the 10 mg/L MWCNT-added reactor.

3.2. Effect of MWCNT on activated sludge biokinetic

In the experimental setup, after the microorganisms allowed to acclimatize for 4 d, feeding with synthetic

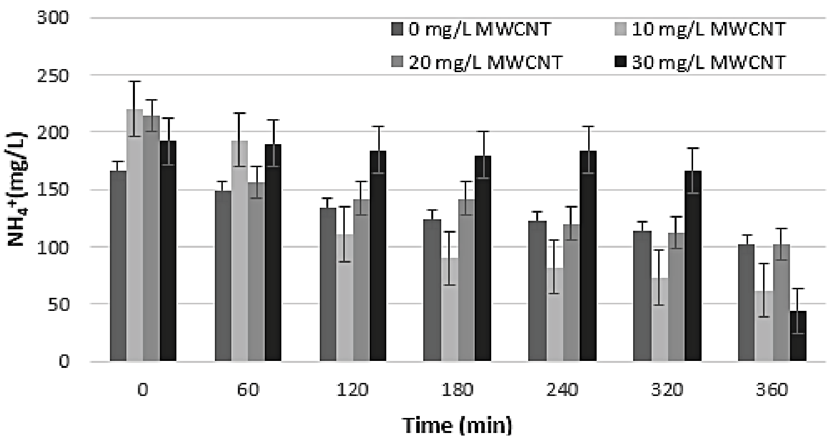

Fig. 4. Effect of MWCNT on NH_4^+ change.

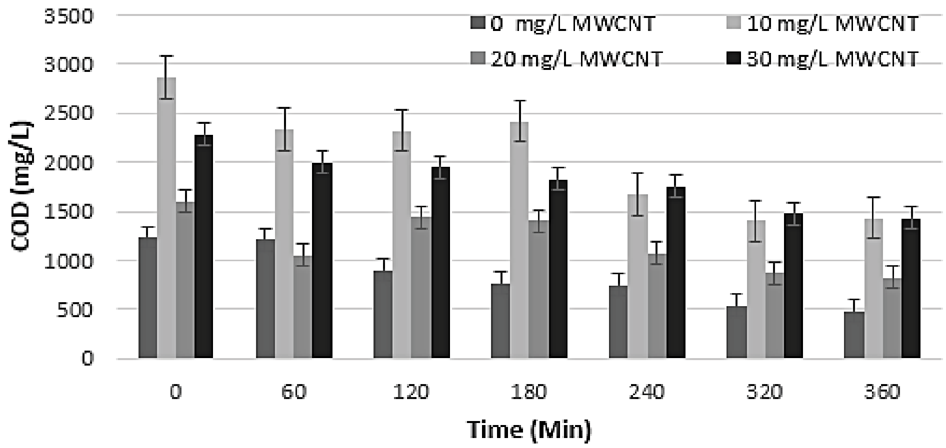

Fig. 5. Effect of MWCNT on COD change.

wastewater started. It was assumed that the process reached steady-state conditions. Analyzes were carried out in the sample of treated effluent. The initial MLSS concentration in the control reactor is 1,700 mg/L. To determine the biokinetic coefficients of the control reactor and MWCNT-added reactors, the graphs obtained from Eqs. (2) and (3) are given in Figs. 6–9.

According to Fig. 6, biokinetic coefficients of control reactor are k = 6.36 d^{-1}, K_s = 1,406 mg/L, μ_m d^{-1} = 6.16, Y = 0.9687 mg SS/mg COD, K_d = 0.0957 d^{-1}. A comparison of the biokinetic coefficients of the MWCNT added reactors are also given in Table 3. The coefficients obtained in this study are compared with other studies related to the activated sludge process in Table 4.

3.2.1. Maximum substrate utilization rate (k)

In this study, k value (COD based) for a control reactor was determined to be 6.36 d^{-1}. This value increased with the addition of 10 mg/L MWCNT to the reactor. The decrease in k value was observed with increasing MWCNT by 10 mg/L. In a study by Lateef et al. [32], it was stated that the value of k affects the reactor volume. The reactor volume is reduced with increasing k value. The high rate of substrate utilization is explained by the high ratio of glucose in the wastewater [37]. In this study, the decrease in k value after the addition of 20 and 30 mg/L MWCNT is likely to lead to an increase in reactor volume.

3.2.2. Half of the velocity constant (K_s)

K_s is named as half of the velocity constant. It is numerically equal to the substrate concentration giving one-half the maximum specific substrate utilization rate at the growth limiting substrate [4,32]. In this study, the K_s value was determined to be 1,406 mg/L for the control reactor. The addition of MWCNT at the concentration of 10 mg/L of the reaction resulted in a very large increase in K_s and it was determined to be 4,078 mg/L. Once the addition of 20 mg/L MWCNT, the K_s value decreased to 1,907 mg/L. The K_s value at the addition of 30 mg/L MWCNT is 2,355 mg/L. These values are consistent with other literature data according to Table 4.

High values for K_s indicate the maximum specific yield of bacteria found in the high substrate concentration resulting from the dairy industry and other industrial wastewaters [32]. If K_s value is greater, the growth rate of cells will be lower in the wastewater [37]. The increase in K_s indicates the decrease in specific growth rate. Although normally K_s is determined as a coefficient, there is no direct application in process design. K_s only gives an idea of a change in

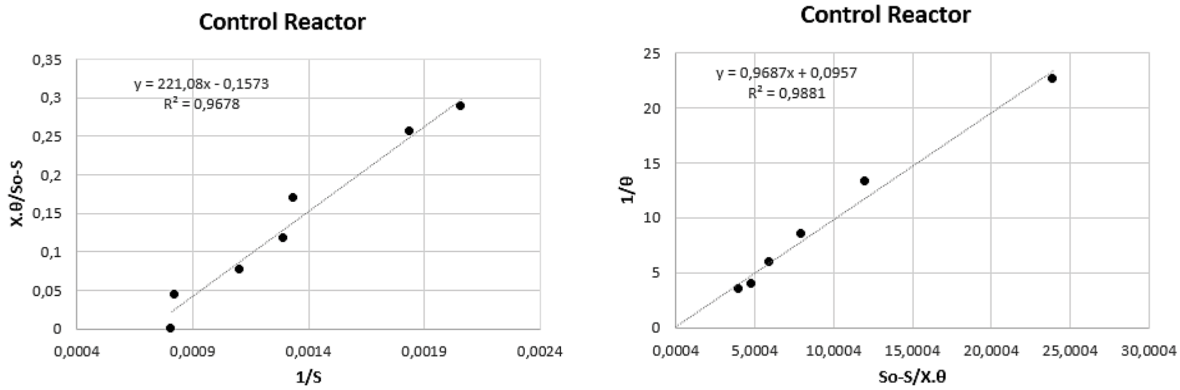

Fig. 6. Determination of K_s, k, K_d and Y values for the control reactor.

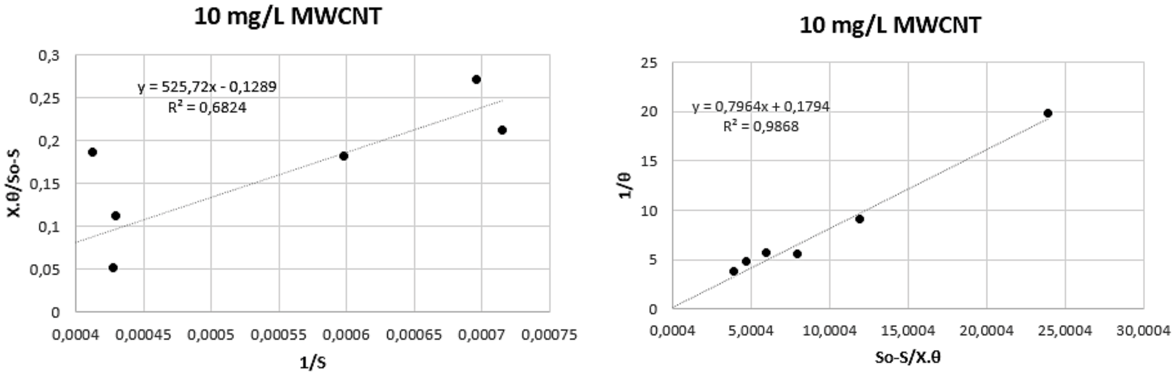

Fig. 7. Determination of K_s, k, K_d and Y values for the reactor added 10 mg/L MWCNT.

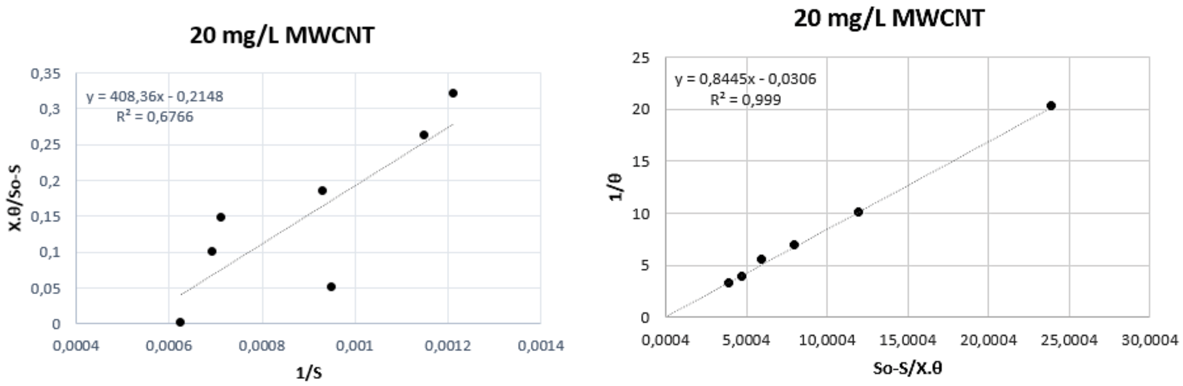

Fig. 8. Determination of K_s, k, K_d and Y values for the reactor added 20 mg/L MWCNT.

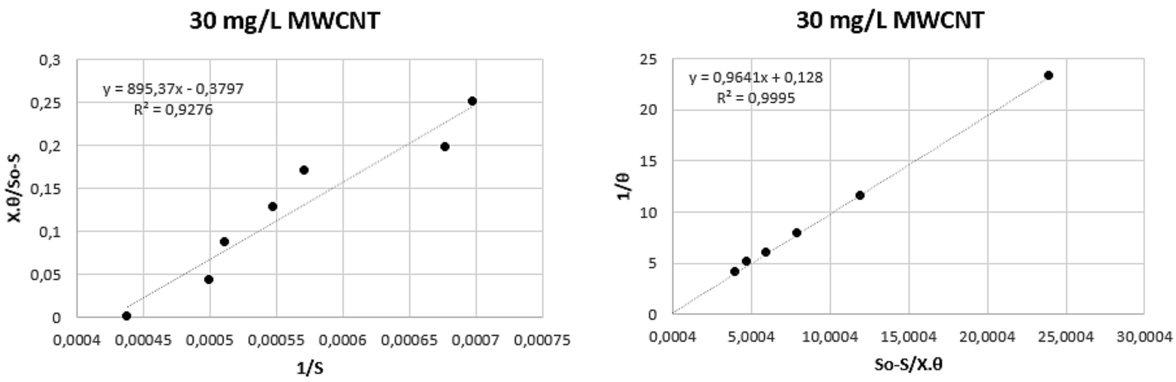

Fig. 9. Determination of K_s, k, K_d and Y values for the reactor added 30 mg/L MWCNT.

growth-limited substrate concentration and a change in the rate of specific bacterial growth [38].

3.2.3. Maximum growth efficiency (Y)

Y is referred as the biomass yield, in other words, it represents how the biomass is produced by substrate use. According to the results, the Y value was obtained as 0.9687 mg SS/mg COD from the highest control reactor. Firstly, the addition of 10 mg/L MWCNT resulted in a decrease in Y-value. Then, with increasing MWCNT concentration, the Y-value increased and reached the same value as the control reactor (about 0.96 mg SS/mg COD). The Y-value for 10, 20, and 30 mg/L MWCNT is about 0.79, 0.84, and 0.96 mg SS/mg COD, respectively.

In the process design, Y gives an estimate of the sludge production as a result of the wastewater treatment. The higher value of Y will cause an increase in the amount of sludge and sludge handling facility. The initial investment cost for sludge handling facility is determined when the size is known [32]. It is understood that the addition of MWCNT to the activated sludge process increases the

Y value and increases the amount of sludge. Yin et al. [13] reported that SWCNTs particles became better dispersed and adsorbed by the activated sludge (influenced by EPS composition) with the increase in reaction time. Thus CNT-activated sludge interaction is likely to result in the formation of larger activated sludge flocs.

3.2.4. Endogenous death coefficient (K_d)

K_d value is expressed as the biomass of endogenous respiratory loss per unit biomass per unit time, and its dimension is time^{-1} [32]. The endogenous death coefficient obtained for each reactor is in the range of values given for different types of wastewater in Table 4. The K_d value in the control reactor is 0.0957 d^{-1}. The endogenous death coefficients were determined as 0.1794, 0.0306, and 0.128 d^{-1}, respectively, by the addition of 10, 20, and 30 mg/L MWCNT.

K_d is a significant design parameter used to evaluate net sludge production in the treatment plant. Higher K_d value reduces net sludge production. Although its effect is minimal, due to its some economic benefits in reducing cost, it can be used to fine-tune the size of sludge handling facilities [32].

3.2.5. Maximum specific growth rate (μ_m)

The growth rate (μ) depends on the substrate concentration (S) and the K_s coefficient, and as the K_s value increases, the curve of the microorganism growth curve becomes flat. At the limited nutrient concentration, μ approaches to the maximum value (μ_m) [42]. The maximum growth rate in the study was 6.16 d^{-1} in CR. The addition of 10 mg/L MWCNT showed no significant change in μ_m which is 6.18 d^{-1}. The increase in the amount of MWCNT resulted in a decrease in the maximum specific growth rate, which was 3.94 and 2.54 d^{-1} for 20 and 30 mg/L MWCNT, respectively.

3.2.6. Mixed liquor suspended solids

It is observed that amount of MLSS increased and the concentration of COD decreased in control and MWCNT-added reactor (Fig. 10). However, the addition of MWCNT resulted in a lower increase in MLSS concentration. MLSS increase was 38.76% in the control reactor. When 10 mg/L MWCNT added to the reactor, the MLSS increase was 25.1%. Similarly, the addition of 20 and 30 mg/L MWCNT resulted in an increase of 22.3% and 23.8% in MLSS concentration, respectively. Yin et al. [13] reported that SWCNT addition to the activated sludge reactor increased the MLSS concentration and sludge settleability in the activated sludge reactor.

It is understood that the addition of MWCNT contributes to the sludge settling and therefore the MLSS increase is lower than in the control reactor. In activated sludge flocs, bacteria are embedded in EPSs, which typically protect them from biocides and harmful conditions. Thus, unlike pure cultures (microorganisms directly exposed to

Table 3
Biokinetic coefficients for control reactor and MWCNT added reactors

Reactor	Biokinetic coefficients						
	k (d^{-1})	K_s (mg/L)	R^2	Y (mg SS/mg COD)	K_d (d^{-1})	R^2	μ_m (d^{-1})
Control reactor	6.36	1,406	0.9678	0.9687	0.0957	0.9881	6.16
10 mg/L MWCNT	7.76	4,078	0.6824	0.7964	0.1794	0.9868	6.18
20 mg/L MWCNT	4.67	1,907	0.6766	0.8445	0.0306	0.999	3.94
30 mg/L MWCNT	2.63	2,355	0.9276	0.9641	0.128	0.9995	2.54

Table 4
Biokinetic coefficients of other COD based studies (activated sludge and PACT process)

Reference	k (d^{-1})	K_s (mg/L COD)	Y (mg SS/mg COD)	K_d (d^{-1})	μ_m (d^{-1})	Type of wastewater
[1]	2–10	15–70	0.4–0.8	0.025–0.075	–	Domestic
[39]	–	3–30	0.5–0.70	0.1–0.2	4.0–8	Municipal and domestic
[33]	–	289–2,933	0.49–0.58	0.037–0.151	1.28–6.46	Synthetic
[33]	–	250–3,720	0.46–0.60	0.05–0.16	5.6–8.1	Municipal
[33]	–	11–181	0.5–0.62	0.025–0.48	7.4–18.5	Glucose
[40]	–	343	0.70	0.053	1.13	Domestic
[26]	3.125	488	0.64	0.035	–	Tannery
[31]	–	311.7–508	0.62–1.25	0.02–0.031	1.96–3.17	Municipal
[34]	–	3.34	0.74–1.34	0.12–0.17	2.78–71.94	Municipal
[41]	–	4.6–345	0.39–0.67	0.0029–0.0071	0.16–0.8	Synthetic, municipal, glycerine
[43]	0.75	7.4				Synthetic
This study	2.63–7.76	1,406–4,078	0.79–0.97	0.0306–0.179	2.54–6.18	Synthetic

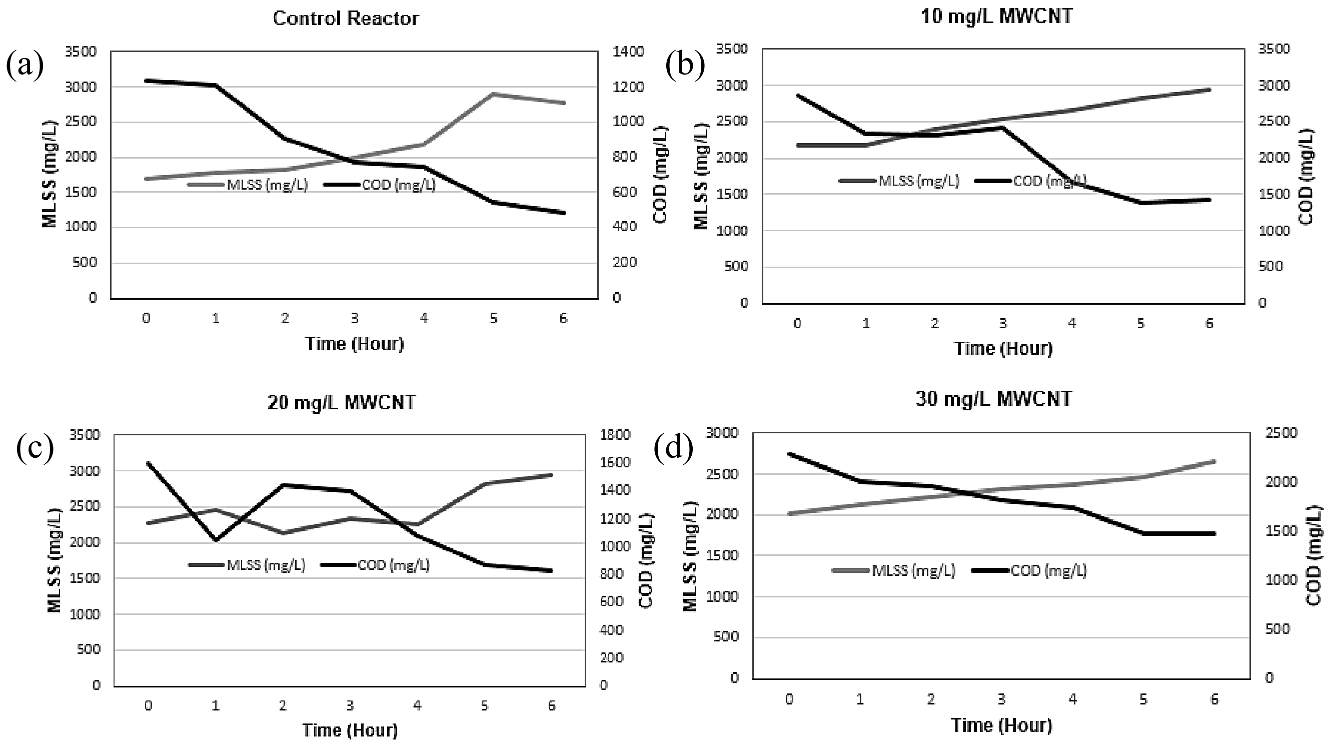

Fig. 10. Change of MLSS and nutrient (COD) (a) control reactor, (b) 10 mg/L MWCNT-added reactor, (c) 20 mg/L MWCNT-added reactor, and (d) 30 mg/L MWCNT-added reactor.

SWCNT), Luongo and Zhang [14] reported that direct interaction between bacterial cells and SWCNT bundles is not possible in activated sludge reactors. In this study, it can be said that MWCNT added to the activated sludge reactor has no negative effect on bacteria due to microorganism-EPS interaction.

4. Conclusion

In this study, it is investigated that effect of MWCNT on the activated sludge performance. Conclusions of this paper are summarized as follows:

- Usage of MWCNT with 10, 20, and 30 mg/L dosages was found to have a positive effect on the removal of NH_4^+ and tN. An inverse relationship was found between the increase in the amount of MWCNT and COD removal. As in many studies carried out on activated sludge reactors except pure culture, the use of MWCNT does not have a negative effect on activated sludge microorganisms and reactor yield.
- Biokinetic coefficients have importance for the activated sludge design. As the amount of MWCNT in the reactor increased, a decrease in *k* observed relative to the control reactor. As a result, the increase in the amount of MWCNT in the reactor will cause the reactor volume to be affected by the value of *k*. The concentrations of MWCNT used in this study lead to an increase in K_s, which is due to the decrease in the specific growth rate.
- When the concentration of MWCNT in the reactor increases, at first, the value of *Y* decreased, then increased and reached the *Y*-value in the control reactor. Also, the increase in the amount of MWCNT caused a higher K_d value. Since the greater *Y* value will determine the quantity of sludge, the initial investment cost of sludge handling facilities will increase with higher MWCNT concentration.
- While MWCNT addition contributes to the treatment efficiency, it causes an increase in the facility investment and operation cost due to an increase in reactor volume and handling facilities.
- As in the PACT process, MWCNT can be integrated into the activated sludge process to protect biological treatment from shock loads and toxic effects and improve treatment efficiency.

Acknowledgment

This work supported by Giresun University, Scientific Research Project Funding (GRU BAP) [Project number: FEN-BAP-A-20051585].

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