International Research Journal of Pure & Applied Chemistry

22(1): 22-37, 2021; Article no.IRJPAC.65576
ISSN: 2231-3443, NLM ID: 101647669

Pollutants Removal in Sewage Wastewater Efficiency and Kinetic of Ammonia Nitrogen Removal through Subsurface Vertical Flow Constructed Wetlands (SSVFCW)

Dègninou Houndedjihou[1,2], Tomkouani Kodom[1*], Delmira Beatriz Wolff[2], Luis Gustavo Marchioro[2], Thiago Augusto Formentini[2,3], Limam Moctar Bawa[1], and Gbandi Djaneye-Boundjou[1]

[1]*Laboratoire d'Hydrologie Appliquée et Environnement, Faculté Des Sciences, Universités de Lomé, BP: 1515 Lomé, Togo.*
[2]*Laboratório de Engenharia do Meio Ambiente, Universidade Federal de Santa Maria, 97105-900 Santa Maria, Brazil.*
[3]*Department of Soil and Environment, Swedish University of Agricultural Sciences, P.O. Box 7014, SE-750 07 Uppsala, Sweden.*

Authors' contributions

This work was carried out in collaboration among all authors. Authors DBW and TK designed and supervised the study. Authors LMB and GDB supervised the manuscript writing. Author DH performed the research and managed the analyses of the study with a strong help of authors LGM and TAF. All the authors contributed in writing the manuscript and all authors read and approved the final manuscript submitted for publication.

Article Information

DOI: 10.9734/IRJPAC/2021/v22i130365
Editor(s):
(1) Dr. Farzaneh Mohamadpour, University of Sistan and Baluchestan, Iran.
Reviewers:
(1) Sheikh Ahmad Izaddin Sheikh Mohd Ghazali, Universiti Teknologi MARA (UiTM), Malaysia.
(2) Festus Sunday Fabiyi, Bowen University, Nigeria.
(3) Wael Abdalla Aziz Elhelece, Egyptian Nuclear and Radiological Regulatory Authority (ENRRA), Egypt.
Complete Peer review History: http://www.sdiarticle4.com/review-history/65576

Original Research Article

Received 01 December 2020
Accepted 05 February 2021
Published 25 February 2021

ABSTRACT

Aims: The removal of some pollutants such as ammonia nitrogen, Total Kjeldahl Nitrogen (TKN), chemical oxygen demand (COD), biological oxygen demand (BOD_5), phosphate and some solids (total (TS), fixed (TFS) and volatile (TVS)) from sewage wastewater was investigated in vertical subsurface flow constructed wetlands (SSVFCW).

**Corresponding author: E-mail: tchakodotom@yahoo.fr, tomkouani.kodom@gmail.com, tkodom@univ-lome.tg;*

Study Design: The bed of the constructed wetland is composed of gravel and *Canna indica* is used as vegetation.
Place and Duration of Study: The study was conducted at the Federal University of Santa Maria, southern Brazil, under subtropical climate from June to September 2019.
Methodology: Three kinds of samples of water collected (Raw, septic tank and outlet from the wetland) one time per week were analyzed according to American standards. Anions were analyzed by gas chromatography using 930 compact IC Flex Metrohm. Statistical analysis performed using ANOVA and U test of Mann-Whitneyto investigate the statistical difference were performed by STATISTICA and Origin software.
Results: A total of 10 samples of each kind of water were collected and analyzed. In the conditions of this study, the removal percentage is 89.88, 88.00, 84.93, 84.62, 84.31, 72.94, 41.71, 15.63 respectively for COD, TKN, NH_4^+-N, TVS, BOD_5, TS, TFS and PO_4^{3-}-P. Environment temperature, hydraulic retention time have an effect on the performance of the wetlands system. The effect of the contact time shows that adsorption process is a partway of ammonia nitrogen removal in the wetland. Among the three models of kinetic studied to describe the removal of ammonia nitrogen, Stover-Kincannon and second order models showed a better fit than the first order model.
Conclusion: The nitrification and adsorption are the principal process of ammonia removal in the wetland. The plant has been found to be very efficient on the removal of ammonia nitrogen, TKN, COD, BOD5 while phosphate removal has been found too weak.

Keywords:Constructed wetlands; subsurface vertical flow; wastewater; ammonia and kinetic.

1. INTRODUCTION

Water is a precious and vital commodity for all processing. Unfortunately, the increasing growth of world population and economic growth through industries have increased the pollution of freshwater due to the inadequate discharge of wastewater that contained several organic and inorganic compounds, especially in developing countries [1]. Domestic sewage is considered to be one of the most important sources of aquatic pollution and is the cause of public health, predominantly in many rural areas of developing countries [2]. Overcome these environmental problems and public health caused by sewage wastewater become crucial and a global environmental concern. Several efficient and economical approaches such as aerobic activated sludge method, anaerobic method, constructed wetlands treatment etc. have been developed. However, these methods based on activated sludge or fixed microorganisms are not suitable in rural areas or small cities due to their cost[3]. The main problems encountered in the common methods of wastewater treatment are high energy consumption, high construction and operation costs, requirement for complex operations, requirement for sludge disposal and the use of mechanized systems which are necessary for a treatment method using high-tech [4]. So, it is necessary to develop new cost-effective and easy technologies method such as constructed wetlands (CWs) technology that fits well the developing countries. Constructed wetlands (CWs) are engineered systems that utilize natural systems including wetland vegetations, soils, and their associated microbial assemblages to assist in treating wastewater [5]. These technologies are low costs economically to operate [6], easy and require low external energy operation [7] and are technically feasible solution to environmental problem caused by wastewaters [8]. They are ecologically friendly compared to the conventional treatment systems of wastewaters [9]. The constructed wetland technology has been stimulated in 1960 by Käthe Seidel and by Reinhold Kickuth in 1970 [7]. Constructed wetlands are classified into two principal groups: surface flow and subsurface flow. Among the two groups, the subsurface flow that gained worldwide interest because of its performance in the pollutant’s removal, is divided into horizontal and vertical subsurface flow [10], [11,12]. The vertical flow constructed wetland (VFCW) demands small area, has good oxygen supply, good nitrification, better organic and suspended solids removal but poor in denitrification and low nitrate removal while the horizontal flow is good in suspended solids and organics removal but poor in denitrification, high area demand, clogging problem, low ammonium oxidation [11]. To enhance the pollutants removal efficiency by this technology, numbers of strategies have been developed: combination of horizontal subsurface flow and vertical subsurface flow constructed wetlands [13], combination of submerged membrane reactor and integrated vertical constructed wetland [14].

So, several researches are conducted in lab-scale and pilot - scale to evaluate the efficiency of this technology on different kinds of wastewaters (food - processing industry wastewater [15], domestic wastewater [6,16,17], slaughterhouse wastewater [18]. In the last decades, constructed wetland technology for wastewater treatment induced worldwide a lot of interests due to its efficiency in removal of pollutants from water[19]and research in this field has been increasing since these technologies are a feasible treatment alternative to conventional wastewater treatment[20]. However, although the performance of this system in the wastewater treatment and its best fit to tropical and subtropical climate, it remains under known and under applicated because of the lack of generally adopted design criteria for tropical and subtropical climates [21]. Biological, physical and chemical process are combined in this technology when the microorganisms, soil, atmosphere, plants and water interact [1].

The aim of this research is to investigate domestic sewage wastewater treatment through reliable and feasible constructed wetland by removing some pollutants and on the kinetic model of ammonia (NH_4^+-N) removal in domestic sewage wastewater in order to understand its behavior and the its performance removal in subsurface vertical flow constructed wetland (SSVFCW).

2. MATERIALS AND METHODS

The domestic wastewater treatment plant was installed in 2015 in Santa Maria, southern Brazil, under subtropical climate (latitude: -29.7175; longitude: -53.7132). The plant (Fig. 1) was composed by a septic tank (working volume of 4.7 m^3) operating as primary treatment followed by a vertical flow constructed wetland VFCW (Fig. 2). The SSVFCW was 7.0 m long, 3.5 m wide (surface area = 24.5 m^2), total depth of 1.15 m and 0.75 m bed depth. Hydraulic residence time (HRT) calculated according to the formula: $HRT = \frac{Ahe}{Q}$ (1) where (A) is the wetland area (m^2), (Q) is the inflow rate (m^3/d) and (e) is the porosity of the packed media [22] was 3 days. The hydraulic loading rate (HLR) defined as the rainfall equivalent of whatever flow is under consideration and calculated by: $HRL = 86.4Q \times A^{-1}$ (2) where HLR is hydraulic loading rate (m/d), A is the wetland area (m^2), Q is inflow rate (m^3/d) [23] was 0.1225 m d^{-1}.

The bed of the SSVFCW was composed of three layers of two kinds of gravel. From the top to the bottom (Fig.1) 0.05 m of gravel n. 2 (25 mm); 0.50 m of gravel n. 1 (19 mm); and 0.20 m of gravel n. 2 (25 mm). The overall average porosity was 49% [24]. *Canna indica* was used as macrophyte in the SSVFCW since the beginning of its operation in 2015.

The VFCW was scaled for treating the domestic wastewater produced by 10 habitants living in the student accommodation in the campus of Federal University of Santa Maria (UFSM, Brazil), with a mean daily flow of 3 m^3 d^{-1}. Three sampling points were installed along the wastewater treatment plant: (i) the raw wastewater (influent), (ii) the wastewater at the septic tank and (iii) the wastewater out from the SSVFCW (effluent). Samples were collected once per week, between 8:30h and 10:30h. From June to August 2019, 10 samplings were performed.

Fourteen physico-chemical parameters were analyzed on each sample: pH, temperature, conductivity, oxidation-reduction potential (ORP), total solid (TS), total fixed solid (TFS), total volatile solid (TVS), ammonia nitrogen (NH_4^+-N), Total Kjeldahl Nitrogen (TKN), chemical oxygen demand (COD), biological oxygen demand (BOD_5), (NO_3^--N), nitrite (NO_2^--N)and phosphate (PO_4^{3-}-P). All parameters were analyzed in the same day except TKN or COD that was analyzed sometimes the second day of sampling. So, for the parameters we were not able to analyze the same day, a given volume of 100 ml of the sample with 2 ml of concentrated sulfuric acid was preserved in a fridge at temperature around 4°C and analyzed the next day of sampling. All parameters were analyzed (and preserved, when necessary) according toAPHA, [25]

Temperature, pH and ORP were measured using a Thermo Scientific ORION STAR A211 benchtop meter. Conductivity was measured using a conductivity meter scientifica. BOD_5 was measured using a BODmeterOxitop WTW 208210. COD was analyzed after digestion (Dry-Block SL-25/16, Solab) using a spectrophotometer. Solid determination (TS, TFS and TVS) was performed by measuring 100 mL of sample in a crucible, all was in oven at 105°C for total water evaporation and after in muffle furnace at 550°C for 30 min, digester TE-041/25 and distiller for nitrogen TE-0364 were used for TKN and NH_4^+-N; NO_3^--N, NO_2^--Nand PO_4^{3-}-P were determined by gas chromatography using 930 compact IC Flex Metrohm and IC conductivity Metrohm as detector monitored by MagIC Net.3-2 software. All the parameters analyzed in this work are triplicated and the average has been used.

The efficiency of the wastewater treatment plant was evaluated by analyzing the same physico-chemical parameters in the influent and the effluent. The removal percentage was calculated by equation 3:

$$\text{Re}\,moval\ efficiency(\%) = (\frac{C_i - C_e}{C_i}) \times 100 \quad (3)$$

where C_i and C_e are respectively the concentration of the raw wastewater (influent) and the wastewater out from wetland (effluent) for each parameter.

The environment temperature was measured during each wastewater sampling to evaluate its effect on BOD_5, COD, TKN and NH_4^+-N. To study the effect of the hydraulic residence time, the daily influent flow (Q) was varied. This allowed us to vary the retention time between 0 -6days.And then, NH_4^+-N concentration was analyzed at different residence time. The ammonia nitrogen concentration in the effluent was determined at different ratioCOD/TKN in the influent to evaluate its effect on the removal of ammonia nitrogen. Relation between this ratio and ammonia concentration in the effluent was investigated by plotting four different kind of function (Linear, Logarithmic, Polynomial, Exponential). Statistical analysis was performed using ANOVA and U test of Mann-Whitneyto investigate the statistical difference in the parameters between influent and effluent. The difference was considered significant when Pvaluesare less than 0.05 and all statistical analyses were performed by STATISTICA and Origin software.

Three of the commonly encountered kinetic models of organic removal in bioreactors have been used to study the behavior and the performance of NH_4^+-N removal in the wetland: Stover-Kincannon model, First-order with plug-flow assumption and second-order pollutant removal model [26]. They were used to evaluate the suitable model that fits well the present study.

2.1 Stover-Kincannon Model

The Stover–Kincannon model is described by equation 2 [22]:

$$(\frac{dC}{dt})^{-1} = \frac{V}{Q(C_i - C_e)} = \frac{K_B}{U_{\max}}(\frac{V}{QC_i}) + \frac{1}{U_{\max}} \quad (4)$$

In this equation, C_i and C_e are respectively influent and effluent concentration (g L^{-1}); $U_{max}$is the maximum speed of substrate removal (g L^{-1} d^{-1}); K_B is the saturation constant (g L^{-1} d^{-1}); Q is the flow rate (m^3 d^{-1}), and V is the volume of the reactor (m^3). The parameters $K_B/U_{max}$and $1/U_{max}$ were calculated as the slope and the intercept of the plotting of $\frac{V}{Q(C_i - C_e)}$ versus $\frac{V}{QC_i}$

According to Jin and Zheng[26],the concentration of ammonia nitrogen in the effluent and the efficiency (E) or the removal (%) prediction of the system for ammonia removal can be obtained as:

$$C_e = C_i(1 - \frac{U_{\max}}{K_B + \frac{QC_i}{V}}) \quad (5)$$

$$E = \frac{U_{\max}}{K_B + \frac{QC_i}{V}} \quad (6)$$

2.2 First-order Kinetic Equation

The First-order with plug-flow pollutant removal equation can be written as follows [27,28]: $\frac{C_e}{C_i} = e^{-K_1 t}$ (7)

Where C_e and C_i represent effluent and influent pollutant concentration, t is the hydraulic retention time (d) and K_1 is the first-order kinetic area-based constant.

The plot of $\ln(\frac{C_e}{C_i})$ against t was used to determine the value of K_1 as the slope

2.3 Second-order Kinetic Equation

The second-order kinetic can be expressed as [29]:

$$\frac{C_i \times HRT}{C_i - C_e} = n \times HRT + m \quad (8)$$

By plotting $\frac{C_i \times HRT}{C_i - C_e}$ against HRT, the values of n and m (d^{-1}) were calculated as the slope and the intercept of the plot of Eq. 8.

According to Abyar et al. [30], the effluent nitrogen concentration and the efficiency prediction of the system for nutrient removal were obtained by the following equations:

$$C_e = C_i\left(1 - \frac{HRT}{m + n \times HRT}\right) \quad (9);$$

$$E = \frac{HRT}{m + n \times HRT} \quad (10)$$

3. RESULTS AND DISCUSSION

3.1 Characteristics of the Influent and Effluent

The characteristics of influent (raw wastewater) and the effluent were summarized in Table 1. In the raw wastewater, average concentrations from the 10 samplings were 1328.52 mg/L (COD), 356.00 mg/L (BOD_5), 133.72 mg/L (TKN), 77.15 mg/L (NH_4^+-N), 25.46 mg/L (PO_4^{3-}-P). In the effluent, the concentrations were 134.47 mg/L (COD), 55.85 mg/L (BOD_5), 16.24 mg/L (TKN), 11.63 mg/L (NH_4^+-N), 21.48 mg/L (PO_4^{3-}-P). The comparison of the characteristics of influent and effluent shows removal of ammonia nitrogen (84.93%), COD (89.88%) and BOD_5 (84.3%), while the nitrate concentration increased 40-fold in the effluent as compared to the influent. This observation highlights the conversion of the ammonia nitrogen in the wetland. One can conclude good nitrification and poor denitrification in the system indicating that the system was highly oxygenated [10,12].Indeed, nitrogen removal follows three steps: nitrification of ammonia to nitrite, (nitritation), oxidation of nitrite to nitrate (nitratation) and the subsequent direct reduction of nitrite or nitrate to N_2 gas, denitritation/ denitratation. High oxygenated media will then favor the first two steps while the third step will be put at disadvantage leading to nitrate increasing. There was big differencebetween the maximum and the minimum concentration of most of the parameters analyzed (COD, TKN, NH_4^+-N, TVS, BOD_5, TS, TFS, PO_4^{3-}-P…) in the influent as well in the effluent. The plot of the concentration of pollutant versus time showed the weekly distribution of pollutant content in the influent. Almost of the parameters showed maximum concentration the sixth week. This observation can be probably due to the return of the students on the campus (student residence) and to a high stock of sludge because of clogging of the pipe. All these phenomena could be explained by high dynamic activity in constructed wetlands (CWs) which are engineered systems designed and constructed to utilize the natural processes involving wetland vegetation, soils, and the associated microbial assemblages needed to treat wastewater. Also, domestic wastewaters vary in concentration depending to people activities in houses.

3.2 Efficiency of the Wastewater Treatment Plant

The removal percentage of some parameters (BOD_5, COD, KTN, NH_4^+-N, TS, TVS, TFS) was calculated to bring out the efficiency of the system in the sewage wastewater treatment. The removal percentage of all other parameters (COD, TKN, NH_4^+-N, TVS, BOD5, TS) was higher than 80% (Fig.4), except for phosphate (PO_4^{3-}-P) and total fixed solid (TFS), which presented removal percentages below 50%. This reinforced that the wastewater treatment plant (SSVFCW) presented good oxygen supply.

Indeed, it has been demonstrated, in the same SSVFCW here studied, that the oxygen supply was sufficient for organic matter removal and nitrification [31]. Then, aerobic degradation of organic compounds via aerobic chemoheterotrophs with fast metabolic rate is very favorable [11]. Furthermore, the presence of plants in the system can stimulate microorganisms' activities in the rhizosphere, which could increase the mineralization of the carbon in the water [32]. However, the removal of phosphate in the artificial system was weak (15.63%). The same observation has been reported by other studies on phosphorus removal [4,8,33].Gao et al. [34] reported that Phosphorus is removed through interaction among substrate, plants, and microorganisms in CWs. Adsorption and precipitation are the main factors in phosphorus removal. The phosphate present will be probably enough assimilable for the plants in the SSVFCW or the time the influent stay in contact with the bed is insufficient for the plants assimilation. The solid removal (TS, TVS, TFS) from the SSVFCW can be attributed mainly to sedimentation, filtration, adsorption onto biofilm and flocculation/precipitation [35].

The mean values of temperature and pH of the effluent are not significantly different (*P = .07*) from the influent while the ORP values are significantly different (*P =.01*) (Table 1) based on the U test of Mann-Whitney. The mean pH value of the raw wastewater 7.0 -7.5, is very favorable for high rate of nitrification [11]. Furthermore, pH can play an important role in the anaerobic degradation of organics. Alkalinity is consumed by nitrification. So, significant nitrification can cause an important drop of the pH in the wastewater hindering denitrification [11] and also affecting the methane-formers bacteria causing odorous compounds production from the wetland [13].

3.3 Ammonia Nitrogen

3.3.1 Ammonia nitrogen removal

The removal percentage of NH_4^+-N and NO_3^--N was 85% and – 3924%, respectively. The comparison of the results on nitrogen concentration in the influent and effluent shows a decreasing of the ammonia concentration and an increasing of NO_3^--N in the effluent, justifying the negative removal percentage (Table 1). Similar trend has been reported by Zhai et al. [36] and Yang et al. [37] on nitrogen removal in constructed wetlands system. The increasing of nitrate in the effluent is mainly related to the microbial-assisted oxidation of ammonia into nitrate (nitrification) [37]. The subsurface vertical flow has good oxygen supply. So, nitrification of ammonia nitrogen (NH_4^+-N) into nitrate nitrogen (NO_3^--N) is typically aerobic chemo-autotropic microbial process in which oxygen is provided to the nitrifying bacteria through the plant rhizosphere [38].

3.3.2 Effect of temperature on BOD_5, COD, TKN and NH_4^+-N removal

The effect of the environment temperature on the efficiency of the wastewater treatment plant has been evaluated on the removal of some of the most important global pollutant indicators in wastewater: BOD_5, COD, TKN and NH_4^+-N. The results (Fig. 5) show a significant (*P=.04*) effect of the environment temperature on the removal performance of NH_4^+-N, COD and TKN in the wetland with 93%, 93,5%, 91% and 84%; 90%, 75% respectively at highest and lowest environment temperature. Redmond et al. [39] have reported the effect of environment temperature on the removal of ammonia and total nitrogen concentrations. The highest removal has been obtained for the highest temperatures. In the range of temperature of our study, the BOD_5 is more sensible to the effect of the environment temperature with 75% and 91% of removal percentage respectively at lowest and highest temperatures. Indeed, nutrient removal is general limited in low temperature periods because plants fad due to cold weather and the performance of CWs usually deteriorates.

3.3.3 Effect of the ratio COD/TKN on NH_4^+-N removal

The concentration of NH_4^+-N in the effluent was measured at different ratios of COD/TKN in the influent (Table 2). There was positive correlation for all sample between the ratio COD/TKN and NH_4^+-N with correlation coefficient of r = 0. 77.. The removal percentage of ammonia increased when the ratio increased to 7 and decreased slightly to ratio 9 (Fig. 6). Above ratio 9 there is no significant variation of ammonia nitrogen removal with ratio COD/TKN. These results are in accordance with those of Wang et al.[40]. In fact, Wang et al. [40] found a positive correlation between the ratio COD/TKN and nitrogen removal rate and negative correlation between the ratio COD/TKN and ammonia nitrogen concentration in the effluent. Those increase of ammonia removal rate with the ratio when COD/TKN increased to 3 and above 3 there is no significant variation of ammonia nitrogen removal with ratio COD/TKN.

The plot of different kind of function has been used to find the best equation between the ratio COD/TKN and NH_4^+-N concentration in the effluent (Table 3). The comparison of the R squared of the different functions confirms that the correlation between COD/TKN and NH_4^+-N was second degree polynomial function. So, the polynomial second-degree equation $Y = 0.294X^2 - 3.5492X + 17.335$ where Y is the NH_4^+-N concentration in the effluent and X the ratio COD/TKN was the best equation to determine the NH_4^+-N concentration in the effluent showing that the effect of COD/TKN ratio is nonlinear on the ammonia nitrogen removal.

However, the lower the ratio, the lower is the removal efficiency of ammonia nitrogen [38]. The ratio COD/TKN in the present study is high leading to good process of ammonia nitrogen removal.

3.3.4 Effect of the hydraulic retention time on ammonia removal

The study of effect of the hydraulic retention time (0-6 days) (Fig. 7) shows that the removal of ammonia was increased rapidly with the increasing of the hydraulic retention time from 0 to 3 days and then decelerates until reaching a steady state after 3 days. The maximum concentration of nitrogen removed was obtained for a retention time of 3 days. After this time, the increase of the residence time did not affect the removal percentage of ammonia in the system. The high removal of ammonia at small HRT shows adsorption process is then an important pathway for ammonia conversion in the constructed wetlands system [41]. Similar trend has been reported by Brooks et al. [41] who find linear and rapid phase the first 43h and equilibrium after this time. Adsorption process occurred in the system is an important part of the rapid phase observed [41]. In fact, the bed in the system is composed of porous materials (gravel) as an adsorbent. So, the rapid phase may be attributed to the availability of vacant surface sites during the preliminary stage of adsorption, and after a certain time period, the vacant sites get occupied by the adsorbate ($NH4^+$-N) which leads to the creation of a repulsive force between the adsorbate on the adsorbent (gravel) surface and in bulk phase [42].

3.3.5 Kinetic of ammonia removal

Kinetic modeling is an analytical approach to describe and predict the specific parameters used to monitor system performance [43]. The advantage of kinetic coefficient determination is that the model can be adjusted to fit data and then used for analyzing alternatives to improve the process [4].

Data of the three kinetic models (Kincannon, First-order kinetic and Second-order kinetic) studied are summarized in the Table 4. The first-order kinetic with plug-flow had correlation coefficient of R^2 = 0.4584 and weak root mean square error (RMSE) of 0.06579. The R^2 values which resulted from the linear plot (Fig. 8) of first-order model kinetic were weak showing that this model was not suitable to describe ammonia nitrogen removal in the constructed wetland system.

The linear plot (Fig. 8b) of Stover-Kincannon model had a high correlation coefficient of R^2 = 0.98 and also weak root mean square error (RMSE) of 0.0042.

The Stover-Kincannon model should be applied for calculating the removal of ammonia nitrogen. The saturation constant (K_B) and the feed consumption rate (U_{max}) calculated from this model were 87.4 and 85.62 mg/l.d respectively. Kermani et al. [29] found U_{max} value of 43.305 mg/l.d while Gholizadeh et al. [22] found U_{max} value of 3.64 mg/l.d for the same ammonia removal in a moving bed biofilm process for wastewater treatment. The comparison of those different U_{max} value to our present study reveals that the U_{max} in our present study was largely high for 3 days as retention time showing that the present SSVFCW was well designed. One can conclude that based on this U_{max} value, the loading rate, has good proportion to the system (bed volume) and that this treatment plant cannot receive more wastewater flow. The following equations were proposed to model the wastewater treatment plant for the prediction of ammonia nitrogen concentration in the effluent and the efficiency of our wetland in ammonia removal:

$$C_e = C_i\left(1 - \frac{85.62}{87.4 + \frac{QC_i}{V}}\right) \ (11)\ ;$$

$$E = \frac{85.62}{87.4 + \frac{QC_i}{V}} \ (12)$$

The second-order kinetic has a high correlation coefficient of R^2 = 0.99 and very weak root mean square error (RMSE) of 0.0002. The second-order kinetic with high value of the correlation coefficient obtained can be used to describe the transport behavior of ammonia in the wetland. The predicted effluent concentration and removal efficiency (%) using second-order kinetic were evaluated. The value of n and m calculated as the slope and the intercept from the equation 6 are 1.17 and 0.083 respectively. Similar value has been reported by Alavi et al. [43] on the removal of nitrogen. The second-order kinetic was found suitable to describe the ammonia nitrogen removal in our wastewater treatment plant. The effluent nitrogen concentration and the efficiency prediction of the wastewater treatment plant for ammonia removal will be obtained by the following equations:

$$C_e = C_i\left(1 - \frac{HRT}{0.083 + 1.17 \times HRT}\right) \ (13)\ ;$$

$$E = \frac{HRT}{0.083 + 1.17 \times HRT} \ (14)$$

The predicted value of ammonia concentration in the effluent and its removal percentage calculated using Stover-Kincannon model and second-order model are summarized in (Table

5). The R^2 value from the linear plot of Stover-Kincannon model was ≥ 0.98 with low value of RMSE. Also, the linear plot of second-order model presented R^2 value ≥ 0.98 and low value of RMSE. These observations indicate better fitness of the data for Stover-Kincannon and second-order model. Furthermore, the calculated values of ammonia concentration in the effluent and its removal percentage were close to the measured values showing that the Stover-Kincannon model (R^2 = 0.98) and second-order model (R^2 = 0.977) are then suitable to describe the nitrogen removal by predicting its concentration and percentage removal in the wastewater treatment plant. Some researchers as Jin and Zheng [26], Xu et al. [44] reported similar trend on the suitable models that describe the removal kinetic of nitrogen.

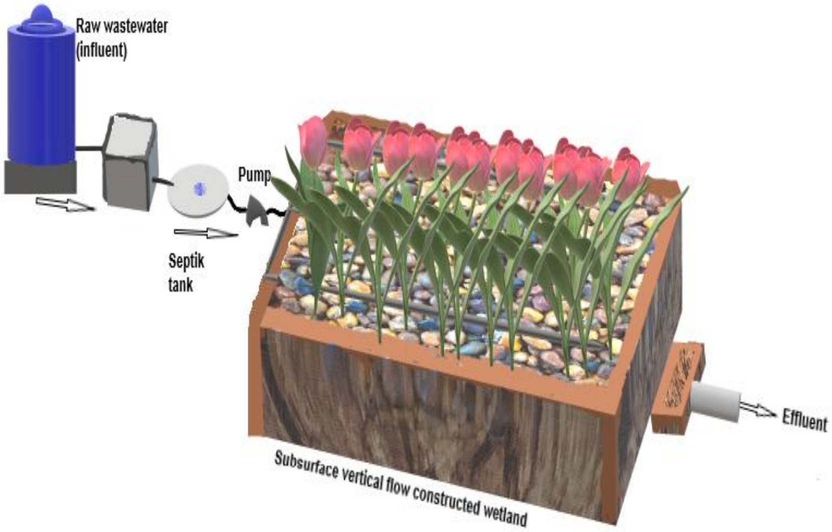

Fig. 1. Diagram of the wastewater treatment plant

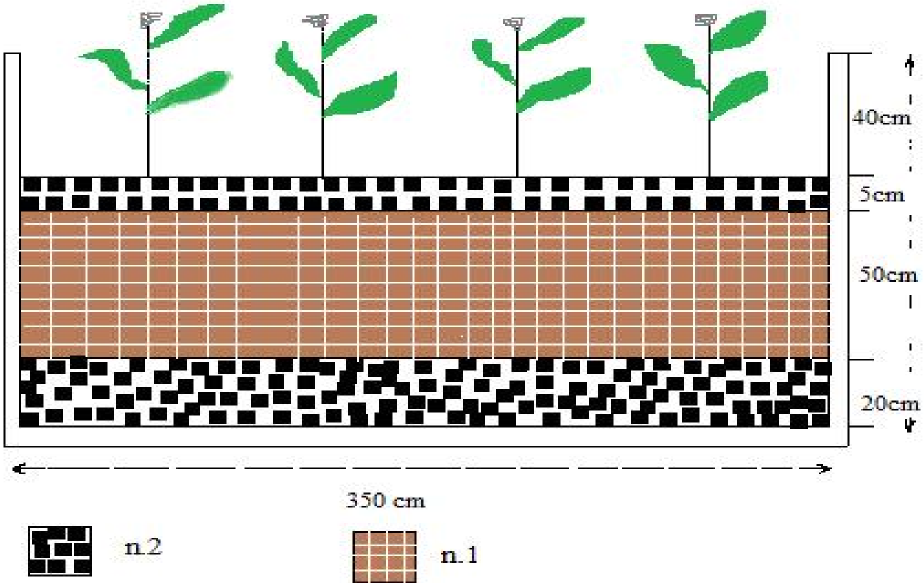

Fig. 2. Schematic description of the constructed wetland system

Table 1. Characteristics of the influent and the effluent (n = 10)

Parameters	**Influent**				**Effluent**			
	Min	**Max**	**Average**	**SD**	**Min**	**Max**	**Average**	**SD**
pH	6.86	7.89	7.42	0,29	6.44	7.31	6.89	0,30
T(°C)	14.10	21.80	16.57	2,89	13.80	22.90	16.83	2,75
ORP (mV)	-55.40	2.60	-29.07	0,65	-22.90	28.90	0.85	74,95
Cond. (µs/cm)	695.80	1183.00	935.47	129,16	490.80	731.40	577.43	6,47
COD (mg/L)	442.48	2735.90	1328.52	736,72	30.26	225.81	134.47	70,43
BOD_5(mg/L)	220.00	480.00	356.00	88,34	20.00	100.00	55.85	33,19
TKN (mg/L)	62.77	255.30	133.72	59,83	6.11	31.17	16.24	8,67
NH_4^+-N(mg/L)	47.84	144.19	77.15	30,57	3.43	27.86	11.63	7,77
NO_3^-N(mg/L)	0.93	2.88	1.78	0,65	30.96	141.59	71.62	39,50
NO_2^-N(mg/L)	ND	ND	ND	ND	0.33	1.76	0.915	0,45
PO_4^{3-}P(mg/L)	12.93	44.07	25.46	9,76	17.85	26.30	21.48	2,55
TS (mg/L)	219.00	5501.00	1970.35	1506,84	368.00	670.00	533.10	115,61
TVS (mg/L)	319	4149.50	1408.75	1193,95	103.00	328.00	216.65	69,58
TFS (mg/L)	206.00	1351.50	542.90	327.51	227.00	468.00	316.45	75,21

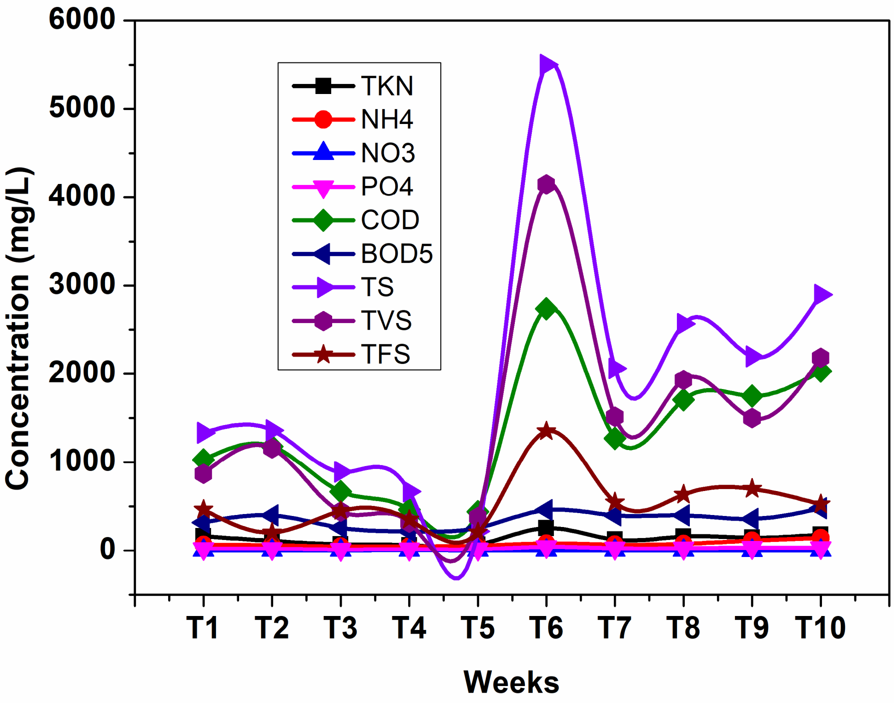

Fig. 3. Weekly distribution of pollutant content in the influent

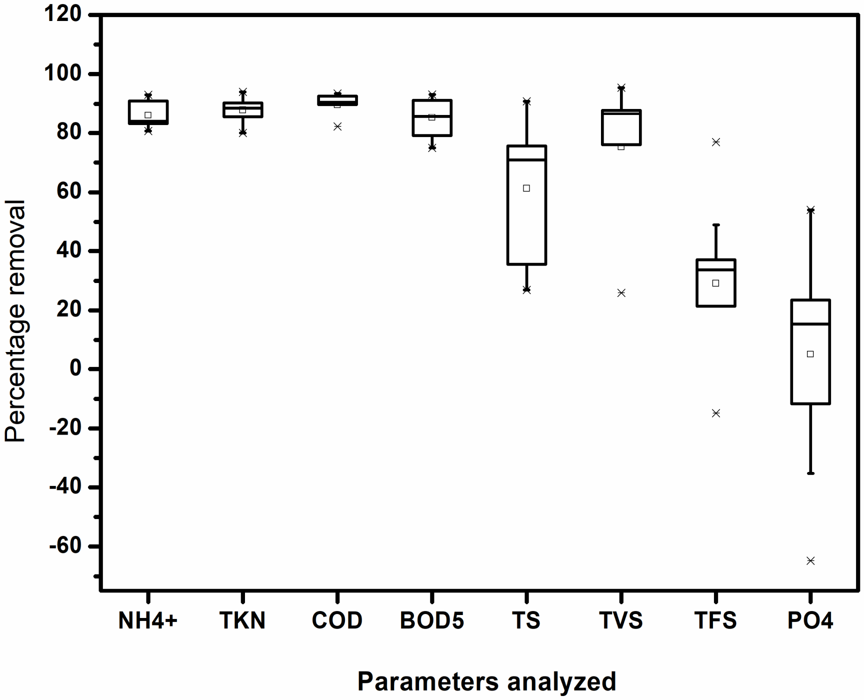

Fig. 4. Performance of the sewage wastewater treatment plant (n =10)

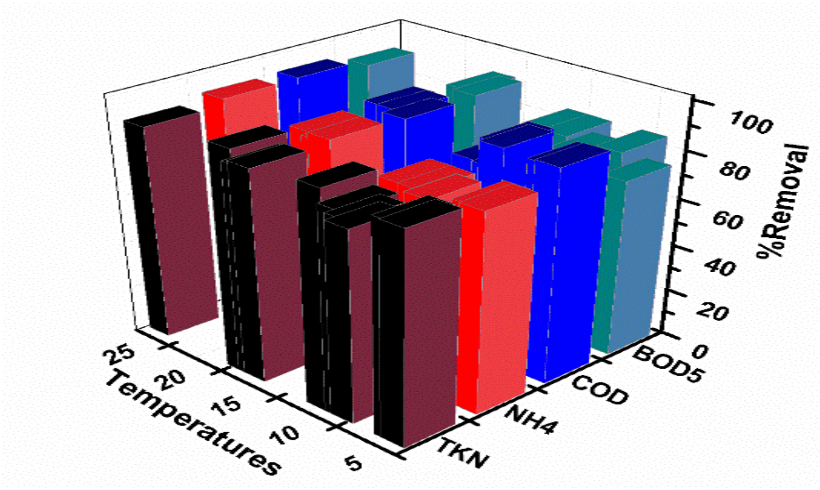

Fig. 5. Effect of the temperature on some nutrients removal in the SSVFCW

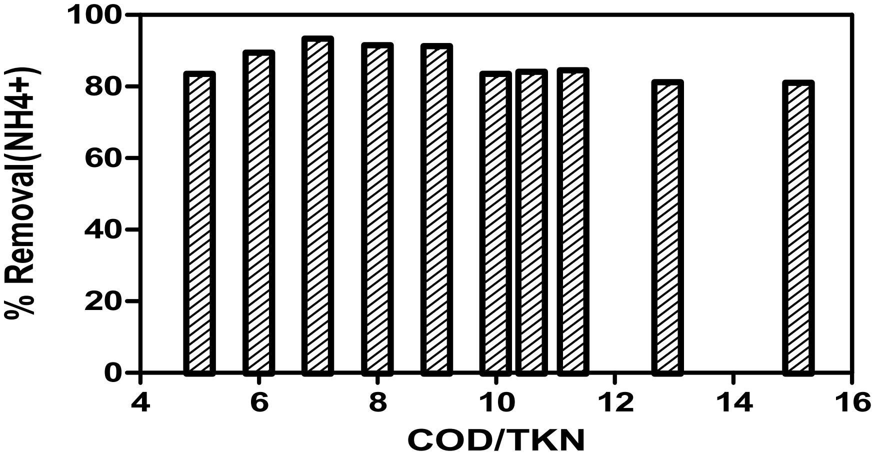

Fig. 6. Ammonia removal rate at different ration of COD/TKN

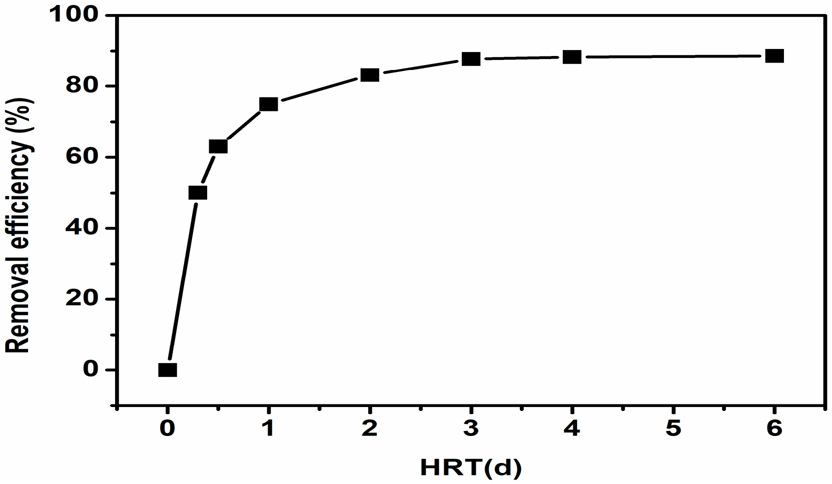

Fig. 7. Effect of hydraulic retention time on ammonia nitrogen removal

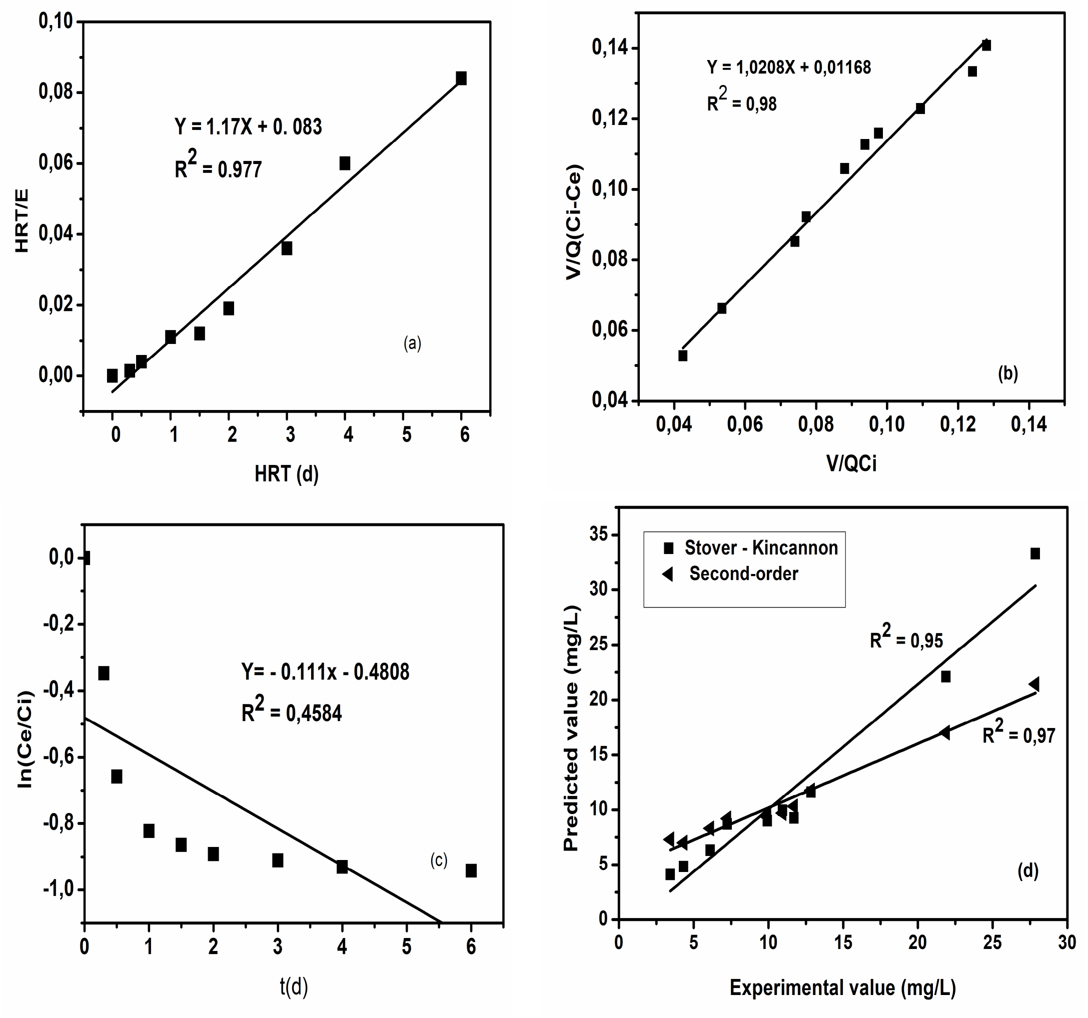

Fig. 8. Substrate removal kinetic plot for ammonia nitrogen removal in the SSVFCW: (a) second-order model; (b) Stover-Kincannon model; (c) First-order model; (d) The conformity between the predicted and experimental value in the two models

Table 2. Concentration of NH_4^+ in the effluent at different ratio of COD/TKN in the influent (n=10)

Influent				**Effluent**
TKN	COD	COD/TKN	NH_4^+-N	NH_4^+-N
182.8	1029.2	5.3	65,31	10.94
111.9	1180.8	10.5	62,77	9.92
73.8	668.3	9.1	47,84	4.32
62.8	464.2	7.4	49,36	3.43
69.1	442.5	6.4	55,98	6.11
255.3	2034	8.0	82,70	7.25
126.8	1270	10.0	69,55	11.71
161.2	1708.9	11.0	79,31	12.85
135.4	1751.3	13	114,51	21.88
181.9	2735.9	15.0	144,19	27.86

Table 3. Equation for ammonia nitrogen determination for different function and R^2 value

Correlation	**Equations**	**R^2**
Linear	Y = 2.4435X - 11685	0.7171
Logarithmic	Y = 21.986ln(X)-37.267	0.6175
polynomial	$Y = 0.294X^2 -3.5492X+17.335$	0.8145
Exponential	$Y = 1.632e^{0.1874X}$	0.5784

Table 4. Kinetic parameters of ammonia nitrogen removal with different kinetic models in the system

Stover-Kincannon model				
Regression equation	R^2	U_{max}	K_B	RMSE
Y = 1.0208x + 0.01168	0.98	85.62	87.4	0.0042
First-order kinetic				
Regression equation	R^2	K_1	RMSE	
Y = -0.111x - 0.4808	0.4584	0.111	0.06579	
Second-order kinetic				
Regression equation	R^2	n	m	RMSE
Y = 1.17x + 0.083	0.977	1.17	0.083	0.0002

Table 5. comparison of the predicted value and experimental value for ammonia nitrogen removal

Experimental Values	**Concentration (mg/L)**	**Efficiency (%)**
	11.63	84.93
Predicted Values	**Stover-Kincannon model**	
	11.13	85.5
	Second-order kinetic model	
	11.47	85.13

4. CONCLUSION

The removal study of some nutrients in sewage wastewater has been conducted using vertical flow constructed wetland system. The results show that the SSVFCW is efficient on the removal of COD, TKN, NH_4^+-N, BOD5 with a removal percentage higher than 80% while the removal rate is very weak for PO_4^{3-}-P (15.63%). The removal percentage of NO_3^{-}N has been found negative (-3924%) showing an increasing of nitrate concentration with a decreasing of ammonia nitrogen concentration in the SSVFCW. The nitrification and adsorption are the principal process of ammonia removal in the wetland. The study of contact effect showed that ammonia removal in wetland occurs mostly by adsorption. Among the three kinetic models studied to describe the ammonia nitrogen removal, Stover-Kincannon model (R^2 = 0.98) and second-order model (R^2 = 0.977) were found suitable to describe the nitrogen removal predicting its concentration and percentage removal in the wastewater treatment plant.

ACKNOWLEDGMENT

This work was supported by EXCEED Swindon project financial supported by DAAD and Federal Ministry for Economic cooperation and development of Germany, The World Academy for Sciences (TWAS, Grant N° 18-065 RG/CHE/AF/AC_I-FR3240303628).

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Bustillo-Lecompte CF, Mehrvar M. Slaughterhouse wastewater characteristics, treatment and management in the meat processing industry: A review on trends and advances. J Environ Manage Bd. 2015; 161:287–302. DOI: 10.1016/j.jenvman.2015.07.008.

2. S Lu UA. Nitrogen removal from agricultural runoff by full-scale constructed wetland in China. Hydrobiologia, BdMärz. 2009;621(1):115–126.
   DOI: 10.1007/s10750-008-9636-1.
3. Ye F, Li Y.Enhancement of nitrogen removal in towery hybrid constructed wetland to treat domestic wastewater for small rural communities. Ecol Eng Bd. 2009;35(7):1043–1050.
   DOI: 10.1016/j.ecoleng.2009.03.009.
4. M. Farzadkia U A. Investigating the efficiency and kinetic coefficients of nutria nt removal in the subsurface artificial wetland of Yazd wastewater treatment plant. 2015;8.
5. Zhu WL, Cui LH, Ouyang Y, Long CF, Tang XD.Kinetic adsorption of ammonium nitrogen by substrate materials for constructed wetlands. Pedosphere Bd. 2011;21(4):454–463.
   DOI: 10.1016/S1002-0160(11)60147-1.
6. Scholz M.Comparative study of domestic wastewater treatment by wetlands and ponds in sustainable water treatment, Elsevier. 2019;131–153.
7. Wu S, Kuschk P, Brix H, Vymazal J, Dong R. Development of constructed wetlands in performance intensifications for wastewater treatment: A nitrogen and organic matter targeted review, Water Res Bd. 2014;57:40–55.
   DOI: 10.1016/j.watres.2014.03.020.
8. Stefanakis AI, Tsihrintzis VA. Effect of outlet water level raising and effluent recirculation on removal efficiency of pilot-scale, horizontal subsurface flow constructed wetlands, Desalination, Bd. 2009;248(1-3):961-976.
   DOI: 10.1016/j.desal.2008.08.008.
9. Mustapha HI, Van Bruggen JJA, PNL Lens. Vertical subsurface flow constructed wetlands for polishing secondary Kaduna refinery wastewater in Nigeria. Ecol. Eng. 2015;8:588–595.
   DOI: 10.1016/j.ecoleng.2015.09.060.
10. GDotro UA. Treatment wetlands. London: IWA Publishing; 2017.
11. Saeed T, Sun G. A review on nitrogen and organics removal mechanisms in subsurface flow constructed wetlands: Dependency on environmental parameters, operating conditions and supporting media. J Environ Manage. 2012;112:429-448.
    DOI: 10.1016/j.jenvman.2012.08.011
12. Vymazal J, Removal of nutrients in various types of constructed wetlands, Sci. Total Environ. 2007;380(1-3):48-65.
    DOI: 10.1016/j.scitotenv.2006.09.014.
13. Vymazal J. Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment. EcolEng.2005;25(5):478-490.
    DOI: 10.1016/j.ecoleng.2005.07.010.
14. XiaoER., Liang W, He F, Cheng SP, Wu Zhen Bin. Performance of the combined SMBR–IVCW system for wastewater treatment, Desalination. 2010;250(2):781-786.
    DOI: 10.1016/j.desal.2008.11.041.
15. Paing J, Serdobbel V, Welschbillig M, Calvez M, Gagnon V, Chazarenc F. Treatment of high organic content wastewater from food-processing industry with the French vertical flow constructed wetland system, Water Sci. Technol. 2015;72:70.
    DOI: 10.2166/wst.2015.190.
16. Chan SY, Tsang YF, Cui LH,Chua H.Domestic wastewater treatment using batch-fed constructed wetland and predict tive model development for NH3-N removal, Process Biochem.2008;43(3):297-305.
    DOI: 10.1016/j.procbio.2007.12.009.
17. Sathe SM, Munavalli GR, Domestic wastewater treatment by modified bio-rack wetland system, J. Water Process Eng. 2019;28:240-249.
    DOI: 10.1016/j.jwpe.2019.02.010.
18. Soroko M. Treatment of wastewater from small slaughterhouse in hybrid constructed wetlands systems», Ecohydrol. Hydrobiol. 2007;7(3-4):339-343.
    DOI: 10.1016/S1642-3593(07)70117-9.
19. Chang J, Wu S, Dai Y, Liang W, and Wu Z. Treatment performance of integrated vertical-flow constructed wetland plots for domestic wastewater. Ecol Eng. 2012; 44:152-159.
    DOI: 10.1016/j.ecoleng.2012.03.019.
20. Bustillo Lecompte CF, Mehrvar M, Quiñones-Bolaños E,Castro-Faccetti CF.Modeling organic matter and nitrogen removal from domestic wastewater in a pilot-scale vertical subsurface flow constructed wetland. J Environ. Sci Health Part A.2016;51(5):414-424.
    DOI: 10.1080/10934529.2015.1120528.
21. Kantawanichkul S, Kladprasert S, Brix H, Treatment of high-strength wastewater in tropical vertical flow constructed wetlands

planted with *Typha angustifolia* and *Cyperus involucratus*. Ecol. Eng. 2009; 35(2):238-247.
DOI: 10.1016/j.ecoleng.2008.06.002.

22. Gholizadeh A, Gholami M, Davoudi R, Rastegar A, Miri M. Efficiency and kinetic modeling of removal of nutrients and organic matter from a full-scale constructed wetland in Qasr- e-Shirin, Iran. 2015;10.
23. Sindilariu PD, Brinker A, and Reiter R, Factors influencing the efficiency of constructed wetlands used for the treatment of intensive trout farm effluent. Ecol Eng. 2009;35(5):711-722.
DOI: 10.1016/j.ecoleng.2008.11.007.
24. Decezaro ST.Sistema de tanqueséptico e wetland construído vertical com recirculação para remoção de matériaorgânica enitrogênio de esgotodoméstico, Universidade Federal De Santa Maria; 2018.
25. American Public Health Association, Hrsg. Standard methods for the examination of water and wasterwater, 23rd edition. Washington, DC: American Public Health Association; 2017.
26. Jin RC, Zheng P, Kinetics of nitrogen removal in high rate anammox upflow filter. J. Hazard. Mater. 2009;170(2-3):652-656.
DOI: 10.1016/j.jhazmat.2009.05.016.
27. Gajewska M, Skrzypiec K, Kinetics of nitrogen removal processes in constructed wetlands, E3S Web Conf. 2018;26:00001.
DOI: 10.1051/e3sconf/20182600001.
28. Weerakoon GMPR, Jinadasa KBSN, Manatunge J, Wijesiri B, Goonetilleke A. Kinetic modelling and performance evaluation of vertical subsurface flow constructed wetlands in tropics, J. WaterProcess Eng. 2020;38:101539.
DOI: 10.1016/j.jwpe.2020.101539.
29. Kermani M, Bina B, Amin MM, Movahedian H, Nikaeen M. Performance and Modeling of Moving Bed Biofilm Process for Nutrient Removal from Wastewater.2010;12.
30. Abyar H, Younesi H, Bahramifar N, Zinatizadeh AA, Amini M. Kinetic evaluation and process analysis of COD and nitrogen removal in UAASB bioreactor. J. Taiwan Inst. Chem. Eng. 2017;78:272-281.
DOI: 10.1016/j.jtice.2017.06.014.
31. Decezaro UA ST. Influence of hydraulic loading rate and recirculation on oxygen transfer in a vertical flow constructed wetland Sci. Total Environ. 2019;668:988-995.
32. Xiang XM, Zhou XB, Wang XK, Zhou JT, and Wang R. Nutrients removal from secondary effluent by using different constructed wetland systems. Adv Mater Res.2012;(518-523):2155-2160.
DOI: 10.4028/www.scientific.net/AMR.518-523.2155.
33. El Hamouri B, Nazih J, Lahjouj J. Subsurface-horizontal flow constructed wetland for sewage treatment under Moroccan climate conditions. Desalination. 2007;215(1-3):153-158.
DOI: 10.1016/j.desal.2006.11.018.
34. Gao Y, Xie YW, Zhang Q, Wang AL, Yu YX,Yang LY, Intensified nitrate and phosphorus removal in an electrolysis – integrated horizontal subsurface-flow constructed wetland, Water Res. 2017;108:39-45.
DOI: 10.1016/j.watres.2016.10.033.
35. Keerthana K, Thivyatharsan R. Constructed wetland for slaughterhouse wastewater treatment, AGRIEAST. J Agric Sci. 2018;12(1):7.
DOI: 10.4038/agrieast.v12i1.47.
36. ZhaiUA J.New nitrogen removal pathways in a full-scale hybrid constructed wetland proposed from high-throughput sequencing and isotopic tracing results. Ecol. Eng.2016;97:434-443.
DOI: 10.1016/j.ecoleng.2016.10.045.
37. Yang Y, Wang ZM, Liu C, Guo XC. Enhanced PNC.Removal from domestic wastewater using constructed wetland employing construction solid waste (CSW) as main substrate», Water Sci. Technol. 2012;66(5):1022-1028.
DOI: 10.2166/wst.2012.277.
38. Yu G, Peng H, Fu Y, Yan X, Du C, Chen H. Enhanced nitrogen removal of low C/N wastewater in constructed wetlands with co-immobilizing solid carbon source and denitrifying bacteria. Bioresour Technol. 2019;280:337-344.
DOI: 10.1016/j.biortech.2019.02.043.
39. Redmond ED, Just CL, Parkin GF. Nitrogen removal from wastewater by an aerated subsurface-flow constructed wetland in cold climates. Water Environ. Res. 2014;86(4):305-313.
DOI:10.2175/106143013X13736496908591.
40. Wang X, Tian Y, Liu H, ZhaoX, Wu Q. Effects of influent COD/TN ratio on nitrogen removal in integrated constructed

wetland–microbial fuel cell systems. Bioresour. Technol. 2019;271:492-495.
DOI: 10.1016/j.ecoleng.2016.07.006.

41. Brooks AS, Rozenwald MN, Geohring LD, Lion LW, Steenhuis TS. Phosphorus removal by wollastonite: A constructed wetland substrate.Ecol. Eng. 2000;15(1-2):121-132.
DOI: 10.1016/S0925-8574(99)00056-7.
42. Vunain E, Houndedjihou D, Monjerezi M, Muleja AA, Kodom B. Correction to: Adsorption, kinetics and equilibrium studies on removal of catechol and resorcinol from aqueous solution using low-cost activated carbon prepared from sunflower (*Helianthus annuus*) seed hull residues water. Air. Soil Pollut. 2019; 230(2):46.
DOI: 10.1007/s11270-019-4099-8.
43. Xu F, Huang Z, Miao H, Ren H, Zhao M, Ruan W. Identical full-scale biogas-lift reactors (BLRs) with anaerobic granular sludge and residual activated sludge for brewery wastewater treatment and kinetic modeling. J Environ Sci. 2013;25(10): 2031-2040.
DOI: 10.1016/S1001-0742(12)60268-X.
44. Alavi N, Azadi R, Jaafarzadeh N, Babaei AA. Kinetics of nitrogen removal in an anammox up-flow anaerobic bioreactor for treating petrochemical industries wastewater (Ammonia Plant). 2011;23(12): 6.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sdiarticle4.com/review-history/65576