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Enhancing the nitrogen removal of vertical flow constructed wetland by using organic media

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ABSTRACT

A major constraint in vertical flow constructed wetlands (VFCWs) while treating low carbon sewage is poor removal of nitrogen. Lack of carbon sources causes low denitrification. In this research, four pilot-scale VFCWs (R1, R2, R3 and R4) were constructed and filled with sand and gravel at the top and bottom portions, respectively. The middle portion was filled with organic media: R2 - wood mulch, R3 - paddy straw, R4 - coir pith, respectively. Wetland R1 acted as a control system and was filled with gravel in the middle. All the wetlands were planted with *Canna indica* and were intermittently loaded with synthetic wastewater at a retention time of 72 h. Ammoniacal nitrogen (NH_4–N) removal efficiency of R1, R2, R3, R4 wetlands were 75%, 82%, 80% and 86%, respectively. Nitrate (NO_3–N) removal efficiency of R1, R2, R3, R4 wetlands were 57%, 83%, 86% and 82%, respectively. The mass balance study of nitrogen showed that the nitrogen removal in vertical flow (VF) wetlands is mainly by plant uptake and nitrogen loss by gasification (nitrification and denitrification process). Scanning electron microscope (SEM) and energy dispersive analysis of the organic media confirms the carbon leaching in the organic media.

Keywords: Constructed wetlands; *Canna indica*; Organic media; Carbon source; Nitrogen removal

1. Introduction

Constructed wetlands (CWs) are recognized as an efficient, sustainable treatment technology with low cost of construction, operation and maintenance [1]. A major ingredient of CWs is wetland media. It intercepts contaminant in wastewater through filtration, sedimentation and adsorption [2]. As an important wetland component, media provides attachment sites and elements for biofilm growth, additionally supporting wetland plant growth [3]. Microorganism attached to the media and roots of the plants can ultimately remove pollutants through biological degradation, nitrification and denitrification. These are the main conduits for organic carbon and nitrogen removal in CWs [4,5]. Due to these unique abilities of the media for aiding physico-chemical and biological removals, different types of materials were tried as wetland media. For example: wheat straw, apricot pit and walnut shell (i.e., agricultural biomass) [6], wood mulch and zeolite [7], sugarcane bagasse [8], rice husk [9], biochar [10], green waste (i.e., plant litter) [11] have been utilized as wetland media. These organic media were used especially to enhance the denitrification process by supplying organic carbon internally to the treatment process. Other waste materials such as cupola slag (by-product of iron melting process) [12], alum sludge (by-product of drinking water treatment process) [13], water treatment residuals [14], construction materials [3], construction solid waste [15], shell grits and plant biomass [16] and mineralized refuse [17] were also used as wetland media to enhance the treatment process. Satisfactory removal performances of these

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wetlands, as reported in these studies, indicate a prospective conversion of waste into resources.

However, the main constraint in VFCWs is inadequate nitrogen removal. Deficiency of carbon sources especially for treating low carbon sewage leads to low denitrification [6]. This deficiency can be resolved by bringing change in the wetland media. Not much research has been conducted in the nitrogen removal especially in tropical conditions such as in India. The role of organic material as a wetland media for enhancing pollutant removal, especially nitrogen removal needs to be identified.

A study was conducted using different agricultural waste as wetland media – wood mulch, paddy straw and coir pith. Wood mulch is a waste material from timber processing; paddy straw is a long hollow golden yellow color fiber. It is an agricultural by-product obtained from paddy field; and coir is the short fibres left behind after the industrially valuable long fibres of coir have been extracted from the coconut husk. All these media are agricultural waste which might be converted into resources. The main objective of this research was to investigate the efficiency of constructed wetland employing organic media such as wood mulch, paddy straw and coir pith as substrates in VFCWs to improve the nitrogen removal while treating low carbon sewage.

2. Materials and methods

2.1. Study area and wastewater

The present study was conducted in the sewage treatment plant (STP) located at Anna University, College of Engineering, Chennai, Tamil Nadu, India (13º00′39.19″ N, 80◦14′7.54″ E). The synthetic wastewater was prepared with COD/N = 5 (synthetic wastewater composed of 193.4 mg/L sucrose, 188 mg/L $(NH_4)_2SO_4$,17.5 mg/L KH_2PO_4, 10 mg/L $MgSO_4$, 10 mg/L $FeSO_4$, and 10 mg/L $CaCl_2$ was used in this study [18]. In every 70 L of the synthetic wastewater, 10 L of domestic wastewater was added. The domestic wastewater was collected from the sewage treatment plant and supplemented so as to feed a source of solids and coliforms.

Four pilot-scale VFCWs (labeled R1–R4) were constructed outdoors. The wetlands were cylindrical plastic tanks of diameter 0.55 m and height 0.75 m. The top 0.2 m and bottom 0.2 m portions of all the wetlands were filled with sand and gravel, respectively. The middle layer (0.2 m) of each wetland had different substrate materials (R1 - gravel, R2 - wood mulch, R3 - paddy straw and R4 - coir pith), respectively, as shown in Fig. 1. The wetland filled with gravel in the middle (R1) acted as the control wetland system. Sampling ports were provided at every 0.2 m depth and 0.15 m at the top was left as a freeboard. Bottom sampling port was used for the collection of effluents.

The wood mulch, of size 10–20 mm, was a mixture of wood chips and humus materials with a pack porosity of 53%. Paddy straw, size 20–80 mm, had a pack porosity of 52%. Coir pith, size 10–20 mm, with a pack porosity of 55%, sand of size 2–3 mm with a pack porosity of 35% and gravel of size 10–20 mm and pack porosity of 42% were used.

Each of the wetlands was planted with twenty rhizomes of *Canna indica* (15 cm height). The wetland plants (*Canna indica)* were collected from a waterway. After plantation all the wetland systems were filled with real domestic wastewater and kept flooded for 1 month. This was done to enable plant growth and acclimatisation adjustment to the bed environment. The initialisation of bacteria culture and biofilm occurred naturally without translocation of microorganism from an activated sludge system.

2.3. Operation of the constructed wetland system

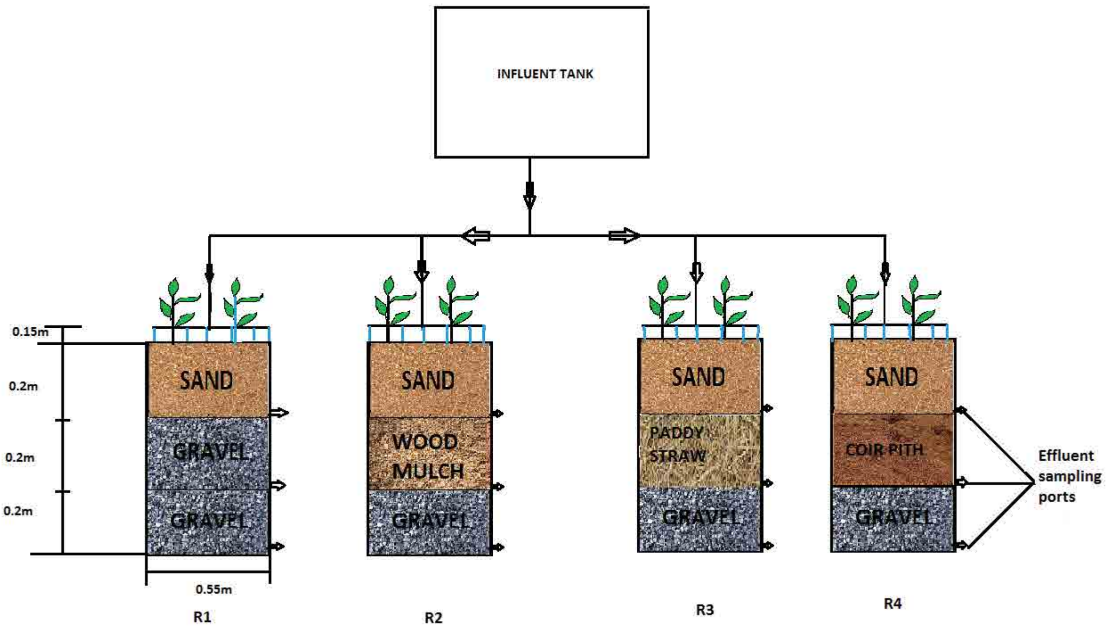

Fig. 1. Schematic diagram of vertical flow constructed wetland system arrangement.

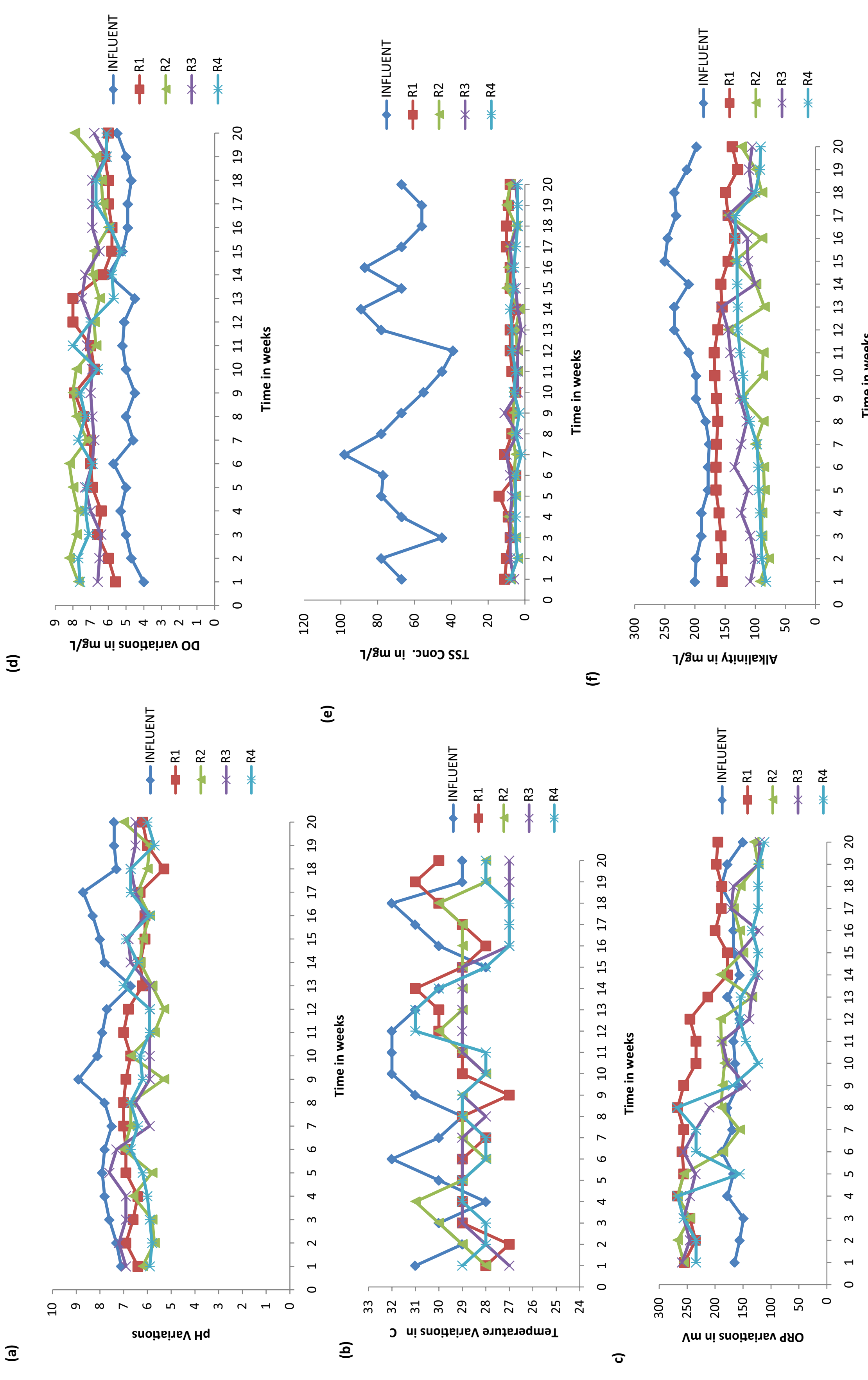

Fig. 2. Variation of (a) pH, (b) temperature, (c) ORP, (d) DO, (e) TSS, and (f) alkalinity in the influent and effluent during the experimental study.

After the flooding period, the systems were fed with real domestic wastewater continuously for 5 d and a resting period of 2 d was given in a week. After 3 months, as the systems stabilized, the reactors were washed with tap water. This was done to remove the deposited nutrients on the media. Then experimental work was commenced by feeding synthetic wastewater at a hydraulic retention time (HRT) of 72 h. This HRT of 72 h is based on the previous literature [19]. Each VFCW held 80 L of wastewater in each cycle and effluent samples were discharged from the sampling ports at the bottom of the VFCWs. A resting period of 10 h was given and then the next loading was batched into the system. This methodology was followed for 20 weeks. Intermittent feeding was done to increase the oxygen diffusion and to avoid bioclogging in the wetland [20,21].

2.4. Meteorological conditions

Meteorological data during the experimental period were obtained from the Indian Meteorological Department, Chennai. An average temperature of 30°C, average humidity of 85% and average rainfall of 1,196.5 mm was observed during the experimental period. Variations due to evapotranspiration were not considered in this study.

2.5. Sampling and analysis

Wastewater samples of influent were analyzed before each feed. Effluent from the systems was sampled from the bottom sampling port after the retention time of 72 h. The samples were refrigerated at 4°C for temporary storage until analysis.

The influent and effluent samples were taken to determine the following parameters: pH, temperature, oxidation and reduction potential (ORP), dissolved oxygen (DO), total suspended solids (TSS), chemical oxygen demand (COD), ammonia nitrogen (NH_4–N), nitrate nitrogen (NO_3–N), total nitrogen (TN), total phosphorous, alkalinity and fecal coliform (FC).

The values of pH were measured by pH meter (Elico L1 120, Hyderabad, India). Temperature was measured by digital water temperature thermometers (Hanna Instruments, Limena, Italy). ORP was measured by using Hach ORP testing probe. DO was analyzed by dissolved oxygen probe (Vernier, Beaverton, OR, USA). TSS was analyzed by gravimetric method (2540 D). COD by open reflux titration method (5220 B), NH_4–N by distillation followed by titration (4500 NH_3–B, C), NO_3–N by ultraviolet spectrophotometric screening method (4500 NO_3–B), TN were analyzed by using total organic carbon analyser. Analyses of TP were done by spectrophotometry- stannous chloride method (4500 P D) and alkalinity by titration method (2320 B). All the tests were carried as per the APHA manual, standard methods for wastewater treatment process. Fecal coliform analysis was done by Indian Standard methods of sampling and microbiological examination of water - IS (1622: 1981).

2.6. Statistical analysis

The statistical analysis was carried out using SPSS version 21.0 software. Effluent pollutant concentration (mg/L) across VF wetlands was analyzed through one-way ANOVA test to clarify statistical significance ($p < 0.05$) of the differences in terms of mean effluent concentration. If significant difference was observed among four wetland system, then post hoc test; Tukey test was performed ($p < 0.05$) as a multiple post hoc comparison.

2.7. Mass balance analysis of nitrogen

The mass balance of the nitrogen in the system was analyzed. The factors considered were amount of nitrogen added to and exported from the constructed wetland system, amount of nitrogen assimilations by plants, amount of nitrogen stored in the substrates (e.g., adsorbed, precipitated) and gasification of nitrogen (e.g., losses due to denitrification and periphyton growth).

2.7.1. Plant biomass analysis

Representative plant sample was harvested after the start up period, that is before the starting of experimental period and it was analyzed for biomass content and nitrogen content. Similarly it was harvested after the completion of experimental period and it was analyzed for biomass and nitrogen content. During sampling, samples consisting of the root, stem and leaves of the plants were taken from all the wetlands. These samples were dried in a hot air oven at 70°C for a period of 2 d (until it reached a constant weight). The dried biomass was weighed, powdered and sieved using 2 mm mesh [22]. Powdered materials were analyzed for the nitrogen. The nitrogen content of the samples was measured using standard Kjeldahl method (acid digestion method) as per AOAC (1995) [23].

The TN storage in plants was estimated by the equation:

$$\text{Storage in plants } \left(\text{g/m}^2\right) = \frac{\text{Biomass} \times \text{Nitrogen concentration in plants}}{\text{unit area of wetland}} \quad (1)$$

where biomass is the average dry biomass per unit, nitrogen concentration in plants is the average nitrogen concentration as percentage of dry weight.

2.7.2. Media analysis

The substrate materials (media) of 50 g each were collected from the upper sand layer, the middle layer (gravel, wood mulch, paddy straw and coir pith) and the bottom gravel layer using hand-operated auger bore. The collected samples were stored in an air tight container. Like plant biomass, the collected samples were dried, powered, sieved and analyzed for nitrogen using standard Kjeldahl method (acid digestion method) as per AOAC [23]. The nitrogen content of media was analyzed separately for sand, organic media and gravel and it is represented totally as N_{media}.

2.7.3. Mass balance calculations

By the principle of conservation of mass, the mass flow remains constant. The amount of nitrogen entering the system through the influent (N_{in}) is equal to the sum of mass of nitrogen leaving the system via the effluent (N_{out}), mass assimilated by the plants (N_{plant}), mass stored in the media by adsorption, precipitation and microbial action (N_{media}) and mass of nitrogen lost through gasification (N_g).

$$N_{in} = N_{out} + N_{plant} + N_{media} + N_g \left(g/m^2\right) \tag{2}$$

$$N_{in} = C_{in} \times V_{in} \text{ per wetland area and days of operation} \tag{3}$$

where C_{in} – influent nitrogen concentration in mg/L; V_{in} – volume of influent in L.

$$N_{out} = C_{out} \times V_{out} \text{ per wetland area and days of operation} \tag{4}$$

where C_{out} – effluent nitrogen concentration in mg/L; V_{out} – volume of effluent in L.

$$N_{plant} = \left(BM_{final} \times NP_{final} - BM_{ini} \times NP_{ini}\right) \text{ per unit area and days of operation} \tag{5}$$

where BM_{ini}, BM_{final} – dry biomass per wetland initially and finally NP_{ini}, NP_{final} – nitrogen concentration in plants as a percentage of dry weight initially and finally

$$N_{media} = W_{media} \times NM_{media} \tag{6}$$

where W_{media} – dry weight of media per wetland; NM_{media} – nitrogen concentration in the media as a percentage of dry weight.

$$N_g = N_{in} - \left(N_{out} + N_{plant} + N_{media}\right) \tag{7}$$

2.8. Scanning electron microscope and energy dispersive X-ray analysis

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

The morphological study of the organic media was done using Carl Zeiss EVO (Thornwood, NY, USA) – before the media were filled in the wetlands and after the experimental period. Similarly, the composition of organic media was analyzed by energy dispersive X-ray analysis (EDAX) before the media were filled in the wetlands and after the experimental period.

3. Results and discussion

3.1. Overall performance of the four wetland systems

The average removal performance of COD, NH_4–N, NO_3–N, TN, TP, alkalinity and FC in the four VFCWs during the experiment is shown in Table 1. Values of COD,

Table 1
Mean pollutant concentration in the influent and effluent across the wetland systems (fixed HLR and fixed influent)

Parameters	Unit	Influent	Effluent concentration R1	Effluent concentration R2	Effluent concentration R3	Effluent concentration R4	Standard limits for reuse
pH	–	7.7 ± 0.5	6.5 ± 0.5	6.2 ± 0.5	6.5 ± 0.5	6.2 ± 0.6	5.5–9.0
Temperature	°C	30 ± 1.3	29 ± 1	29 ± 1	28 ± 1	29 ± 1	NA
ORP	mV	167 ± 11.1	227 ± 30.8	189 ± 45.2	187 ± 51.7	179 ± 58.1	NA
DO	mg/L	4.9 ± 0.6	6.5 ± 0.9	7.3 ± 0.7	6.8 ± 0.4	6.9 ± 0.8	>2
TSS	mg/L	67 ± 15.3	8 ± 2.2	6 ± 2.1	6 ± 2.3	5 ± 1.6	10
COD	mg/L	210 ± 11.3	19.4 ± 9.3	35.2 ± 7.2	44.5 ± 13.5	29.61 ± 11.8	10
NH_4–N	mg/L	42.3 ± 3.9	10.48 ± 2.1	7.4 ± 3.29	8.44 ± 3.15	6.02 ± 2.7	50
NO_3–N	mg/L	6.2 ± 0.7	2.69 ± 0.8	1.07 ± 0.6	1.15 ± 0.5	0.87 ± 0.5	10
Total Nitrogen	mg/L	45.47 ± 4.2	21.8 ± 4.6	10.6 ± 4.5	9.18 ± 2.2	9.36 ± 2.5	NA
Total phosphate	mg/L	6.7 ± 0.7	2.6 ± 0.7	1.1 ± 0.9	1.71 ± 1.1	1.37 ± 1.1	5
Alkalinity	mg/L	207 ± 22.8	155 ± 11.2	100 ± 20.6	116 ± 25.4	107 ± 18.8	NA
Fecal coliform	MPN/100 mL	830 ± 102	47.5 ± 11.3	39.9 ± 15.3	33.4 ± 20.3	28.2 ± 23.6	Not detectable /100 mL

NH_4–N, NO_3–N, TN, TP, alkalinity and FC differed significantly between control and organic wetlands. The variation of pH, temperature, ORP, DO, TSS and alkalinity in the influent and effluent during the experimental study is shown in Fig. 2.

3.1.1. COD removal

Table 1 shows the influent and effluent water quality of all four wetlands. Fig. 3 shows the variation of COD in the influent and effluents of all four wetlands. Concerning the COD removal, the effluent COD concentration was 35.2 ± 7.2 mg/L, 44.5 ± 13.5 mg/L and 29.61 ± 11.8 mg/L in organic media wetlands R2, R3 and R4, respectively, with removal rates of 83%, 79% and 86%, respectively. In control wetland R1 (inorganic media), it was 19.4 ± 9.3 mg/L with a removal rates of 91% which was higher than that of other systems. It should be noted that in organic matter degradation, conventional wetlands without organic materials were more efficient. A possible explanation could be that these organic media wetlands might leach out some organic carbon from the organic media which might increase the COD concentration in the effluent. Similarly it may have some components such as lignin which is difficult for microorganisms to degrade, making the COD concentration to increase in the effluent [24,25]. The higher effluent COD concentration of R3, could be theoretically explained as, the paddy straw release more carbon available to promote denitrification followed by wood mulch, and coir pith releasing the least. The COD concentration in the effluent of all four reactors were within the effluent discharge standards (not more than 50 mg/L of COD) of Central Pollution Control Board (CBCP). In addition, the COD removal efficiency of organic media wetlands in this study was higher than that in other studies such as rice husk in baffled sub surface flow –59% ± 2% [9], sugarcane bagasse in a hybrid flow system for the treatment of textile wastewater –62.5% to 70.6% [8] and using coco peat media in vertical flow wetland –57% [12]. But other systems such as intermittent aerated VFCW –96% [26], intermittent feeding strategies SSFCW –96% [27] and SSFCW –96% [28] had better COD removal efficiency.

3.2. Nitrogen removal

3.2.1. Nitrification process in wetland systems

Microbial processes such as nitrification and denitrification are the main mechanisms for removing nitrogen from wastewater in constructed wetlands. Nitrification is a two-step process in which NH_4–N is converted to nitrite nitrogen (NO_2–N) in the presence of oxygen by strictly chemolithotrophic *Nitrosomonas, Nitrosococcus* and *Nitrosospira* bacteria, and then by facultative chemolithotrophic bacteria – *Nitrospira* and *Nitrobacter* to nitrate nitrogen (NO_3–N) [29]. It is believed that the process of nitrification is mainly dependent on the presence of dissolved oxygen [30]. If oxygen is present in a high enough concentration to support the growth of aerobic nitrifying bacteria (*Nitrosomonas* and *Nitrobacter)*, an effective nitrification process occurs. The source of oxygen in VF wetlands is through diffusion of atmospheric oxygen, wind effect and macrophyte root transfer in the plant rhizosphere. The transfer of oxygen from plants in constructed wetlands ranges from 0.02 to 0.8 g O_2/m^2. The porous nature of the substrates promotes higher diffusion of atmospheric oxygen [7]. DO is also enhanced as supply of influent is intermittent and allows the wetlands to breathe.

Fig. 4 shows the NH_4–N effluent concentration in four wetlands during the experimental period. The NH_4–N removal efficiency of R1, R2, R3, R4, were 75%, 82%, 80% and 86%, respectively. There was no significant difference among the organic media wetlands. Porosity of the media, intermittent feed of influent and oxygen transfer by the plants enhance the oxygen diffusion in the vertical flow constructed wetland, which plays a vital role in NH_4–N removal efficiency. True to the above statement, NH_4–N removal of wetland system was R4 > R2 > R3 > R1 as per their porosities. The output concentrations of NH_4–N in the wetlands were 10.48 ± 4.02, 7.40 ± 3.29, 8.44 ± 3.15 and 6.03 ± 2.7 mg/L. The mass NH_4–N input of these wetland systems was 4.7 $g/m^2/d$ and mass NH_4–N outputs of R1, R2, R3 and R4 were 1.18, 0.85, 0.95 and 0.67 $g/m^2/d$, respectively. The mass NH_4–N removal rates of R1, R2, R3 and R4 were 3.52, 3.85, 3.75 and 4.03 $g/m^2/d$, respectively. These results indicate slightly higher nitrification process in organic media VF wetlands when compared with inorganic media (control) wetland.

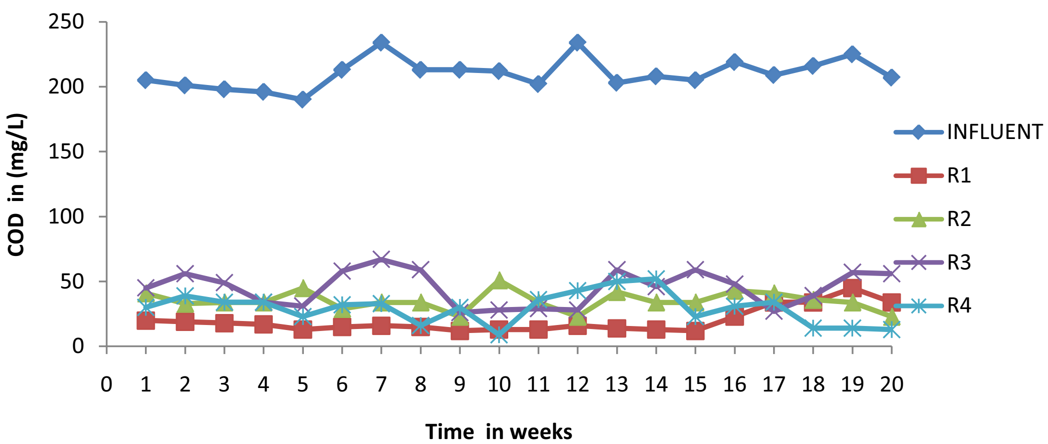

Fig. 3. Variation of COD concentration in the influent and effluent during the experimental study.

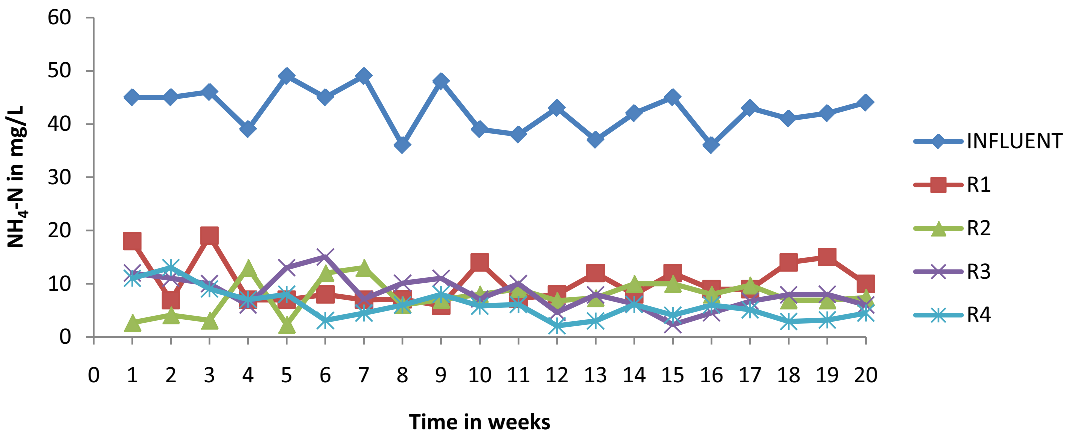

Fig. 4. Variation of NH_4–N concentration in the influent and effluent during the experimental study.

The porous nature of the organic media enabled higher penetration of oxygen into the media resulting in higher NH_4–N removal compared with gravel wetland R1. The correlation plot of DO against NH_4–N removal rates for R1, R2, R3, R4 VF wetland system is shown in Fig. 5. The correlation graph shows a positive correlation between DO and NH_4–N. The R^2 value for R1, R2, R3 and R4 are 0.514, 0.541, 0.691 and 0.625, respectively, as shown in Fig. 5. Higher removal rates of NH_4–N with higher DO values imply that the removal of NH_4–N depends on the availability of oxygen and is in accordance with the nitrification process principle. Increase of ORP value from 167 ± 11.1 mV in the influent to 227 ± 30.8, 189 ± 45.2, 187 ± 51.7 and 179 ± 58.1 mV for R1, R2, R3 and R4 respectively, alkalinity reduction and pH drop across VF wetlands (Table 1) indicate that NH_4–N removal was achieved via nitrification in these wetlands.

The NH_4–N removal efficiency achieved in this study in the organic media wetland systems was higher when compared with the removal rates of other research studies such as baffled and non-baffled wetland system using rice husk as a media –84% and 70%, respectively [9], coco peat as a media in vertical flow wetland system –52% [12], sugarcane bagasse in a vertical flow wetland system –66.4% [8] and organic straw in a vertical flow wetland system –52.8% [31]. But was lower than other systems such as wood mulch in vertical flow wetland system – 99.4% [7].

3.2.2. Denitrification process in wetland systems

Denitrification is a microbial process in which nitrate is reduced and a series of intermediate gaseous nitrogen oxide products ultimately produce molecular nitrogen (N_2). Denitrifying microbes require less than 10% of oxygen and organic carbon for energy. Fig. 6 represents the influent and effluent concentration of NO_3–N in the wetland system during the experimental period. Table 1 shows the NO_3–N and TN effluent concentrations were 2.69 ± 0.8, 1.07 ± 0.6, 1.15 ± 0.5, 0.87 ± 0.5 mg/L and 21.78 ± 4.7, 10.6 ± 4.5, 9.18 ± 2.2, 9.3 ± 2.5 mg/L for R1, R2, R3, R4, respectively. The NO_3–N and TN removal efficiencies were 57%, 83%, 82%, 86% and 52%, 76%, 80%, 79% for R1, R2, R3, R4, respectively. In this study, higher nitrate removal rates were observed in organic media wetlands when compared with control wetland (R1) filled with gravel. These results suggest that there were favorable anoxic conditions prevailing in organic media wetland for effective denitrification. Organic media enhances the denitrification of nitrates produced via nitrification in the anoxic portions of the VF columns by supply of carbon from the media [32,33]. Organic carbon leaching from the organic media causes an increase of COD concentration (Table 1) across R2, R3, R4 wetlands thereby increasing COD concentration. This increase of COD concentration assists the denitrification process.

Fig. 7 represents the negative correlation between effluent COD concentration and effluent NO_3–N concentration in the wetland systems. As observed in Fig. 7, higher effluent COD concentration was associated with lower effluent NO_3–N concentration (higher NO_3–N removal efficiency) across the wetland columns indicating the organic carbon is necessary for denitrification. Contrastingly, the reverse trend was observed for the control wetland R1. As the COD concentration decreased the NO_3–N concentration increased in the effluent indicating there was not effective denitrification due to lack of organic carbon resulting in NO_3–N accumulation. Fig. 8 shows the TN variations in the influent and effluents of the wetlands during the experimental study.

3.3. Mass balance study of nitrogen

Further to confirm the hypothesis that organic media enhances the denitrification process by supplying carbon, mass balance study of nitrogen was carried out during the study.

Table 2 shows the Nitrogen mass balance and proportion of plant uptake in all the four wetland systems during the experimental period. Mass balance study of nitrogen shows that 20%–23% of the nitrogen goes in the effluent in the organic media wetland whereas in control wetland it was nearly 48% of the nitrogen goes in the effluent. This result indicates that there is an effective nitrogen removal in organic media wetland. Irrespective of the media used in VF wetland system, the nitrogen uptake by plants was 43%–53%.

Roots of the plant absorb nitrate and ammonia nitrogen. Photosynthesis, leaf growth and biomass assimilation rate

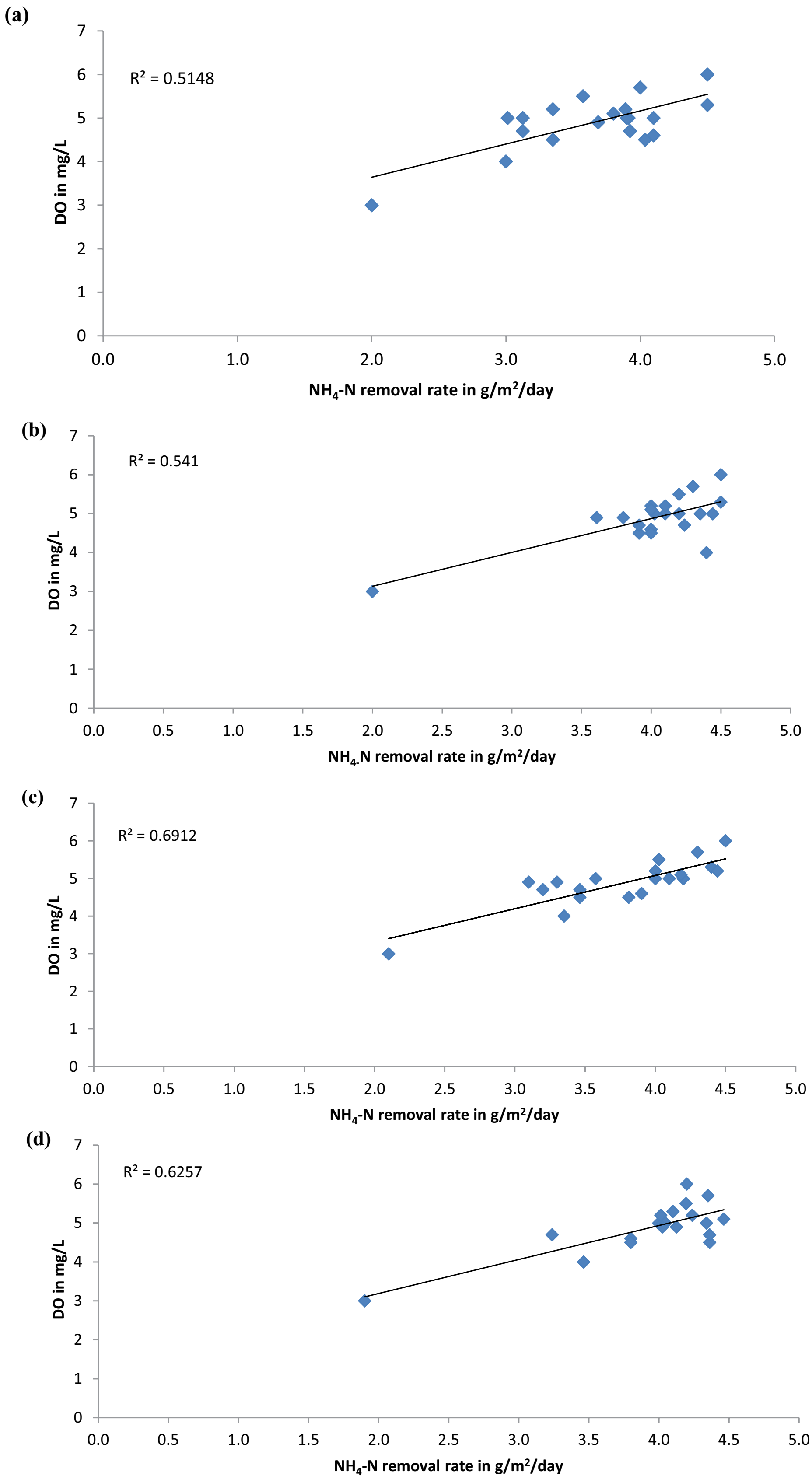

Fig. 5. Correlation graph between DO and NH_4–N mass removal rate for (a) R1, (b) R2, (c) R3, and (d) R4 VF wetland system.

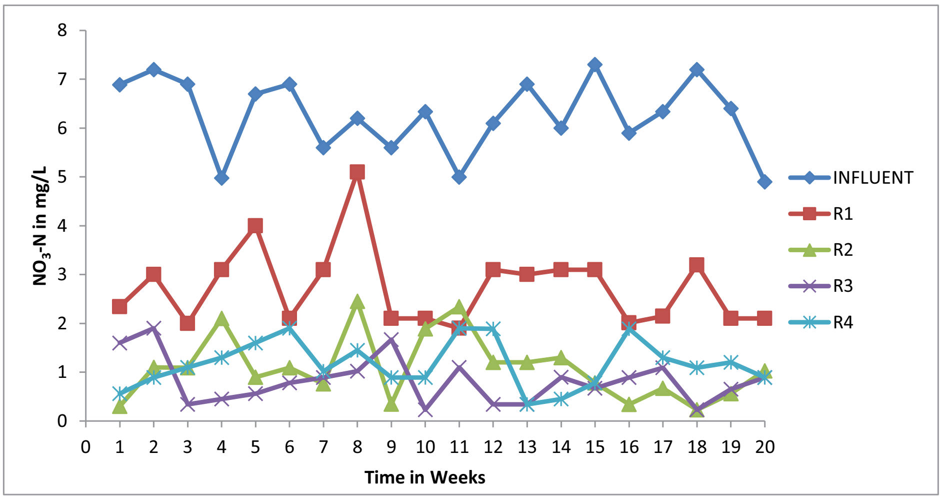

Fig. 6. Variation of NO_3–N concentration in the influent and effluent during the experimental study.

of the plants are enhanced by nitrogen [34,35]. The nitrogen intake of the substrate materials (media) is by adsorption, precipitation and microbial action. In this study, the nitrogen storage by the media of control wetland was 6% and by organic media wetlands were 10%–14%, which is very less when compared with plant uptake. Fig. 9 shows the schematic mass flow diagram of nitrogen in the wetlands.

Nearly 3% of nitrogen is decreased by gasification in control wetland (inorganic media). This unaccountable loss of nitrogen by gasification is very less in control wetland system when compared with organic media wetland system which was 17%–23%. This nitrogen loss was mostly through nitrification and denitrification process [36]. This result implies that there is effective nitrification and denitrification process in organic media wetland. Oxygen is transported to the wetland system by intermittent loading, porosity of the media and by the plants to the rhizosphere. Thus, creating an aerobic zone next to the roots and rhizomes where ammonia is oxidised to nitrite and then to nitrate by nitrifying bacteria. Usually nitrification is followed by denitrification. In the VF wetland system, at larger depths, in the saturated zone there always exists an anaerobic condition which is conducive for denitrification process. The organic carbon needed for denitrification is supplied by the organic media which enhances the denitrification. In denitrification process, nitrate is converted into nitrogen gas and released into the atmosphere.

3.4. TP removal

Wetland media plays the greatest role in TP removal and could be most amenable. The average TP removal efficiencies in four CW systems are shown in Fig. 10. The percentage removal of phosphorous was 61%, 83%, 75% and 80% in R1, R2, R3 and R4, respectively. The CWs with organic media shows a better TP removal performance than the CW with no addition.

The phosphorus removal in organic media wetlands occurs by adsorption on the humus materials. The humus material in the organic media (wood mulch, paddy straw and coir pith) could have played an important role in terms of higher phosphorous removal through TP adsorption in humus materials [7].

3.5. Fecal coliform (FC) removal

Fig. 11 represents FC count in the effluent. The removal efficiencies were 95%, 95%, 96% and 97%, for R1, R2, R3 and R4, respectively. This high removal efficiency may be due to predominantly aerobic conditions in these wetland columns and intermittent loading of influent. Media porosity is also thought to have played an important role in removing FCs.

In these wetlands, higher media porosity leads to aerobic conditions that increase the removal of FCs. Within a 3-d HRT, nearly 95% of FC is removed irrespective of the wetland media used. There is no need for longer residence time. From this study, it is also inferred that the media has no significant effect on the FC removal. The FC removal is above 95% in this study which is similar to the previous study of Soundaranayaki and Ganthimathi [37], and Saeed and Sun [38].

3.6. SEM analysis

SEM analysis shows the external morphological structure of the media. The SEM analysis of the organic media indicated that there was rupture of outer layer of the organic media after 9 months of experimental study, which indicates the carbon contribution of media for the denitrification process. Fig. 12a represents the wood mulch in the initial stage (before filling the wetland system) without any rupture, but significant rupture can be noted in the wood mulch after the experiment period in Fig. 12b.

Similarly in Fig. 13a, paddy straw before filling the wetland was noted without any rupture but significant rupture can be noticed in Fig. 13b. In Fig. 14a the initial coir is seen without any rupture but a noticeable rupture can be seen in Fig. 14b. SEM analysis confirms there is some rupture on the external surface of the media after the experimental period.

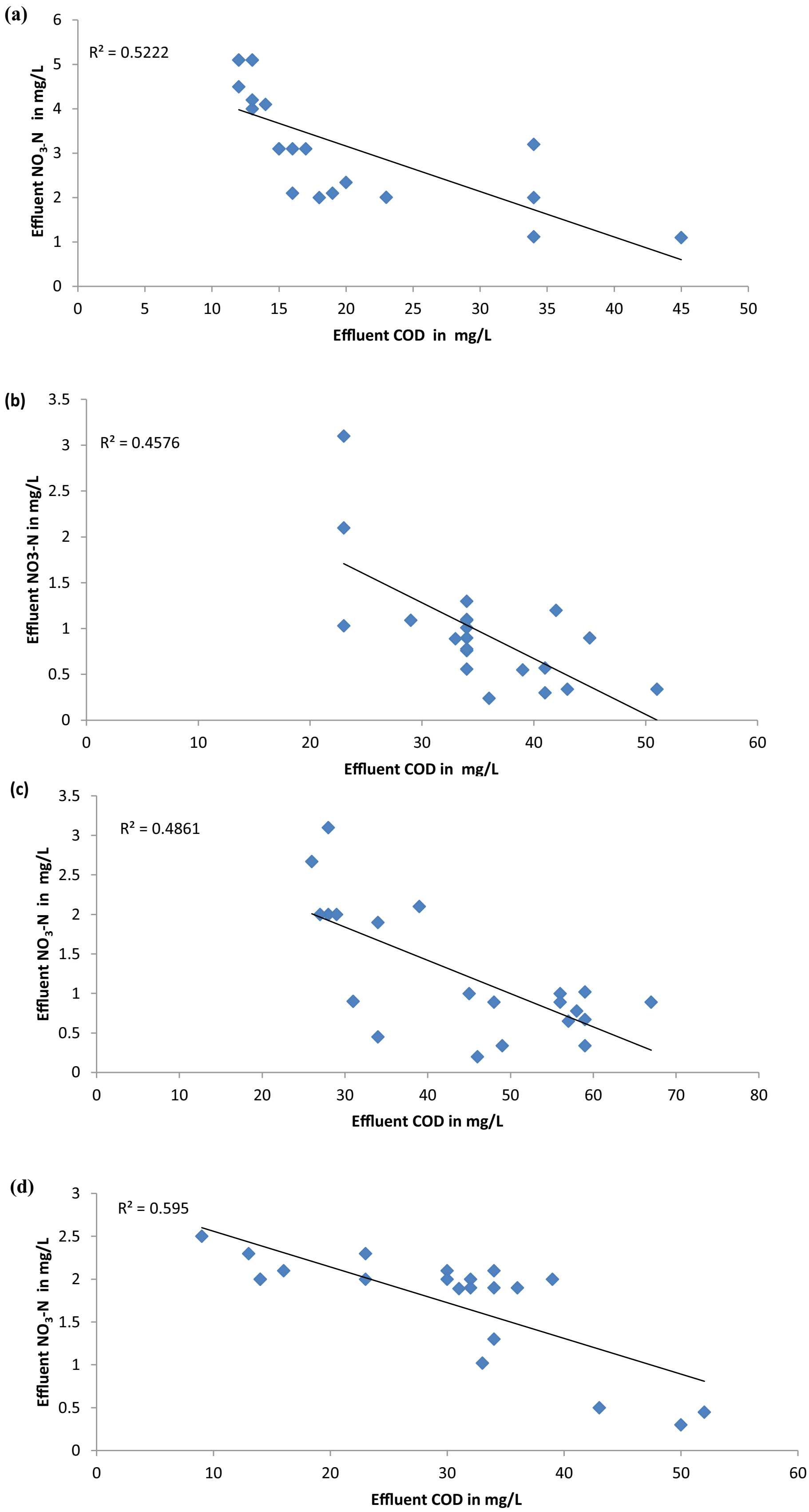

Fig. 7. Correlation plot of effluent COD concentration vs. effluent NO_3–N concentration of (a) R1, (b) R2, (c) R3, and (d) R4 VF wetland system.

3.7. EDAX results

EDAX highlights the chemical or elemental composition of the material. In the result, many chemical compounds are seen in the media – carbon, oxygen, sodium, magnesium, aluminium, silica, potassium, etc. But the main focus of this study was on the carbon and oxygen content of the organic media. In Fig. 15a for wood mulch, initial carbon content was 56.82% and it was reduced to 35.43% in Fig. 15b. From the result, it is understood that there is carbon leaching in the wood mulch media. The percentage of carbon leaching was 37.6%, while oxygen increased from 43.15% to 46.3%. This indicates there is an increase in oxygen level of media after the experiment. In Fig. 16a for paddy straw, initially the carbon content was 41.25% and it was reduced to 26.28% in Fig. 16b. The percentage of carbon leaching was 36.2% and oxygen content increased from 42.99% to 52.64%. Nearly 22.4% of oxygen increase can be noted. In Fig. 17a the carbon content of coir pith before the experimental period was 51.46% and it was reduced to 47.08% as shown in Fig. 17b. The percentage of carbon leaching was 8.5%. The oxygen content of the coir pith before the experimental period was 35.90% and after the experimental period was 34.70%. There was a reduction in oxygen content of coir of about 3.3%. From the EDAX, carbon leaching was in the order of wood mulch > paddy straw > coir pith.

Table 2
Nitrogen mass balance and proportion of plant uptake in the wetland systems through the experimental period

Nitrogen	R1	R2	R3	R4
Influent (N_{in}) (g/m^2)	306.9			
Effluent (N_{out}) (g/m^2)	147.7	71.7	61.4	62.1
Plant uptake (N_{plant}) (g/m^2)	131.7	147.6	141.7	164
Media uptake (sand, organic media and gravel) N_{media} (g/m^2)	18.4	35.3	32.4	31.2
Gasification N_g (g/m^2)	9.1	52.3	71.4	49.6

4. Conclusion

The pilot-scale constructed wetland systems with different media were operated for 9 months. The wetland systems filled with organic media performed satisfactorily in pollutant removal (especially in nitrogen, phosphorus and FC removal) when compared with the control (inorganic media)

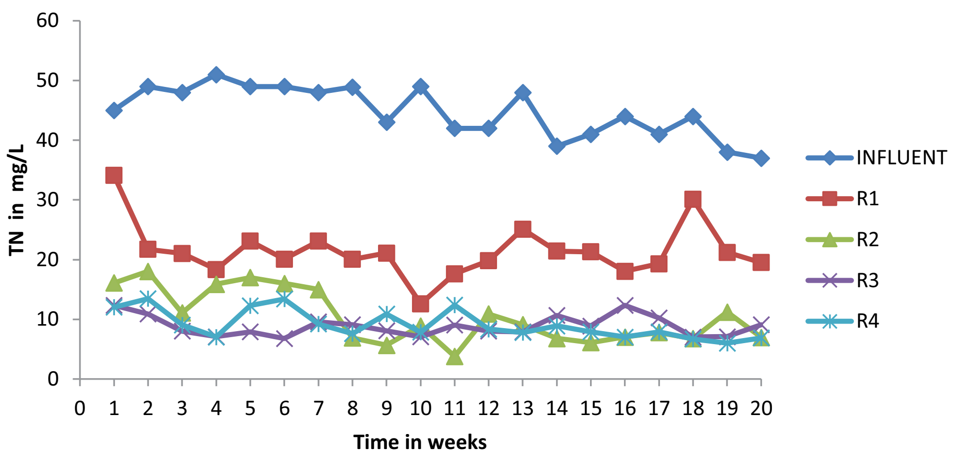

Fig. 8. Variation of TN concentration in the influent and effluent during the experimental study.

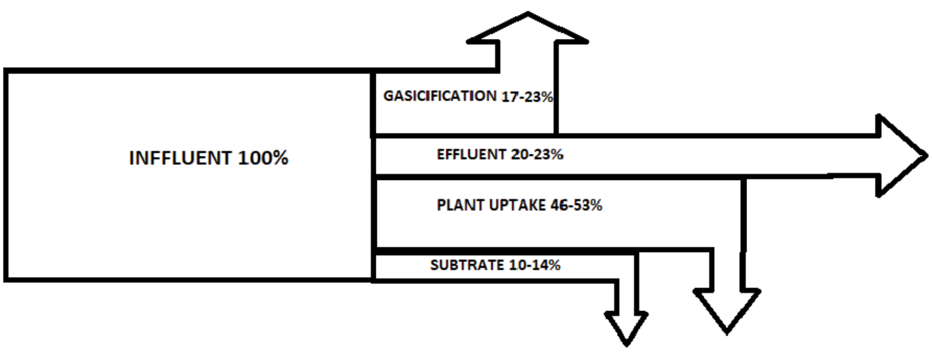

Fig. 9. Mass flow diagram of nitrogen in organic media wetlands.

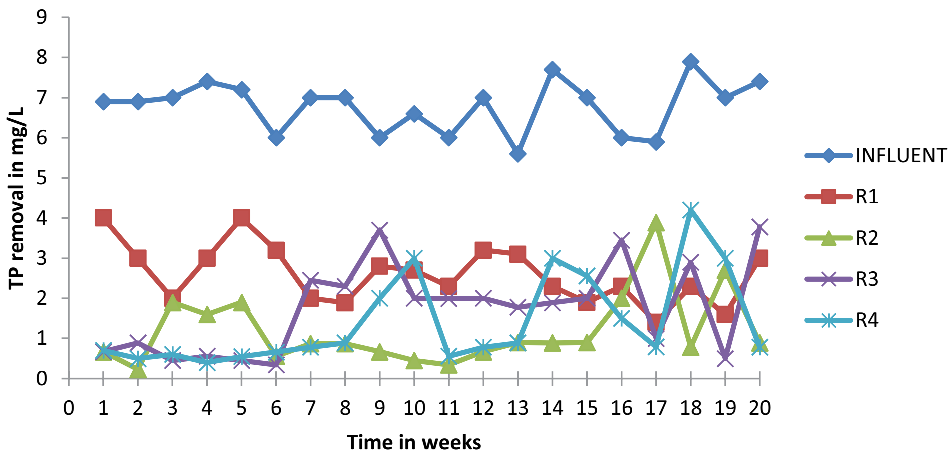

Fig. 10. Variation of TP concentration in the influent and effluent during the experimental study.

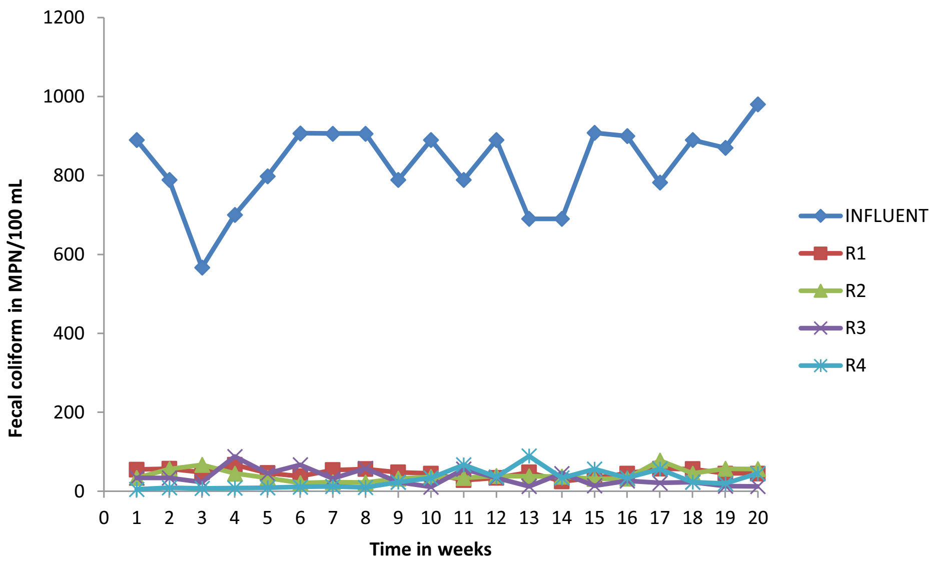

Fig. 11. Variation of FC concentration in the influent and effluent during the experimental study.

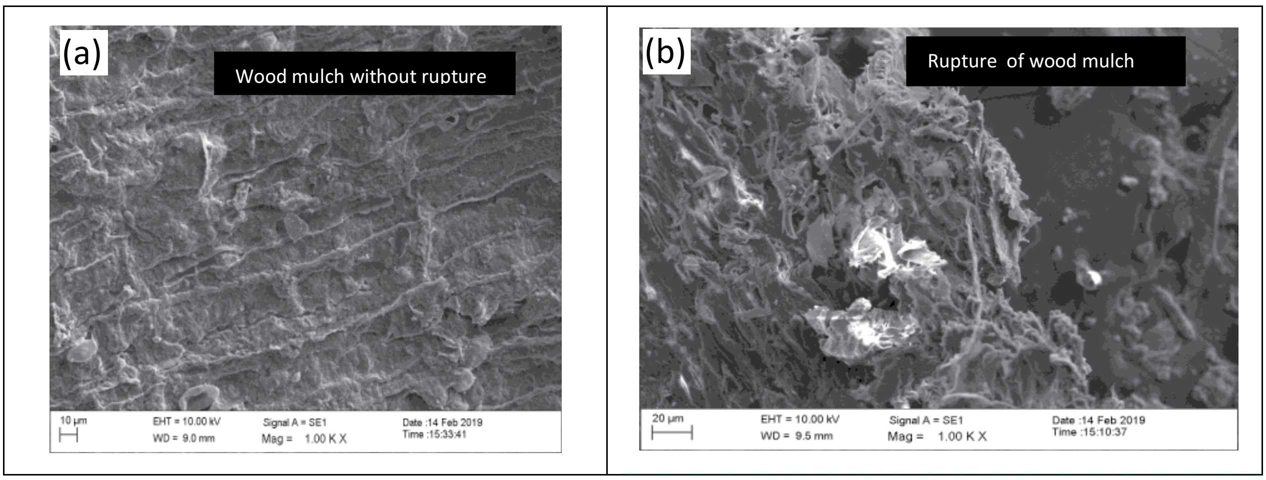

Fig. 12. SEM analysis of wood mulch (a) before the experimental period and (b) after the experimental period.

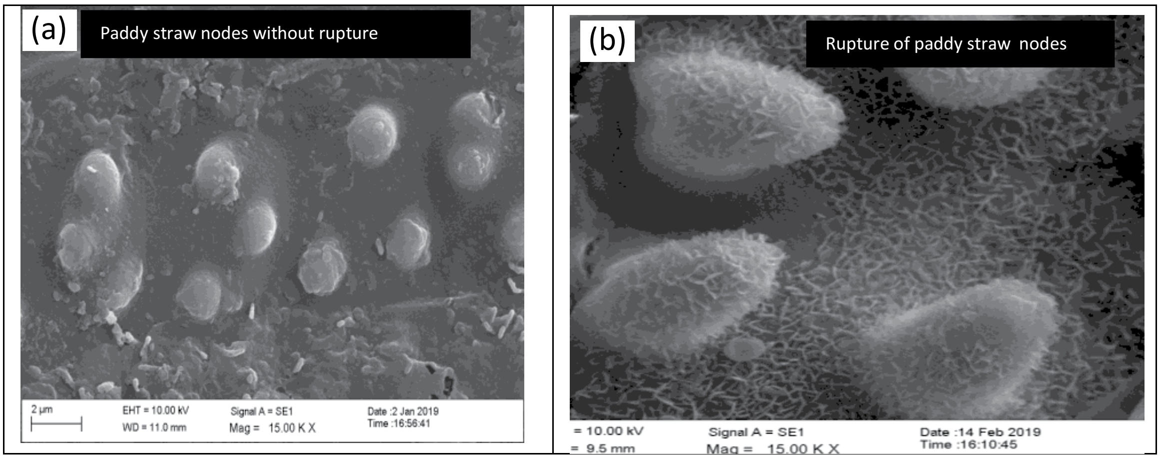

Fig. 13. SEM analysis of paddy straw (a) before the experimental period and (b) after the experimental period.

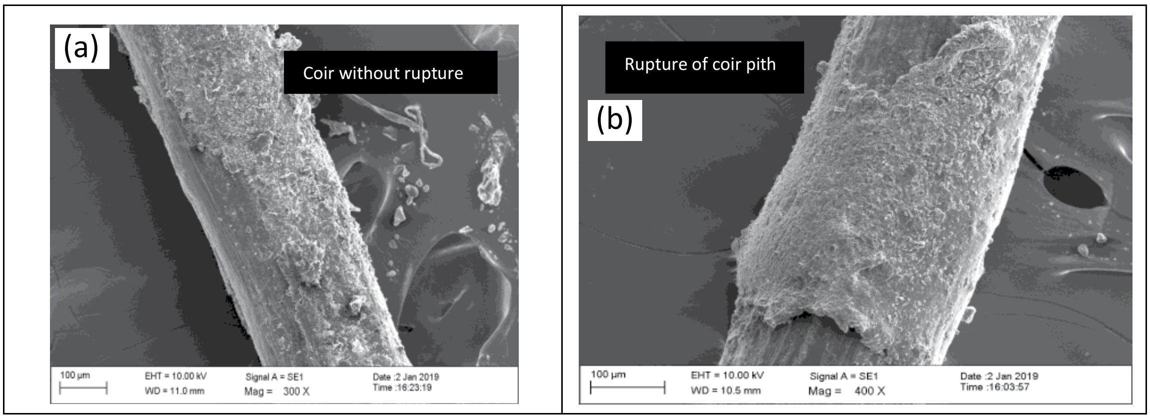

Fig. 14. SEM analysis of coir pith (a) before the experimental period and (b) after the experimental period.

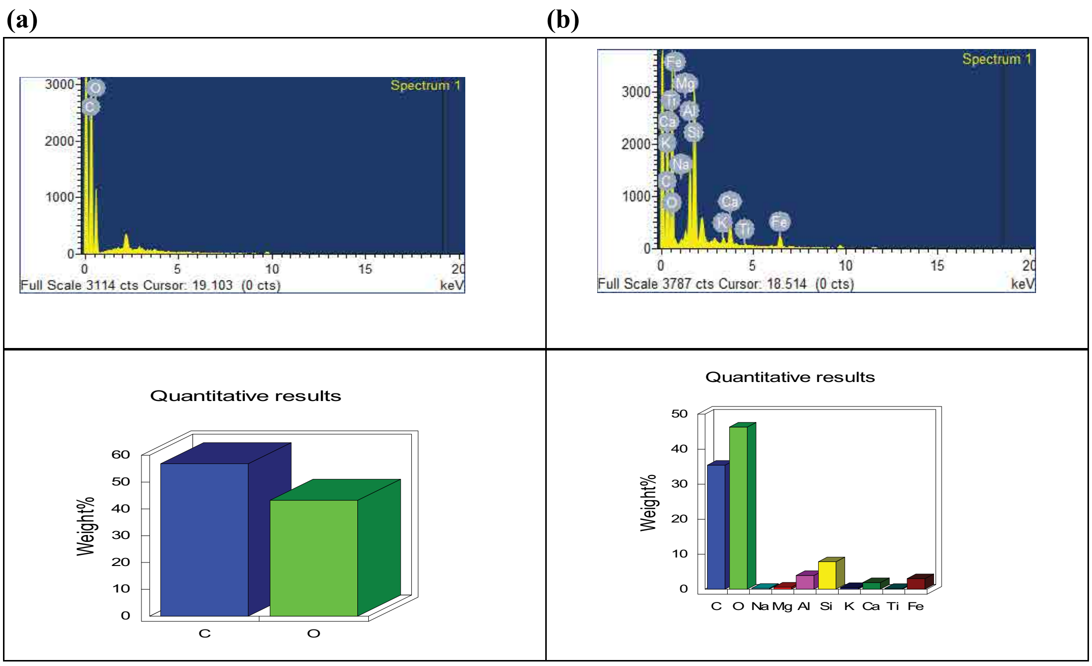

Fig. 15. EDAX of wood mulch (a) before the experimental period and (b) after the experimental period.

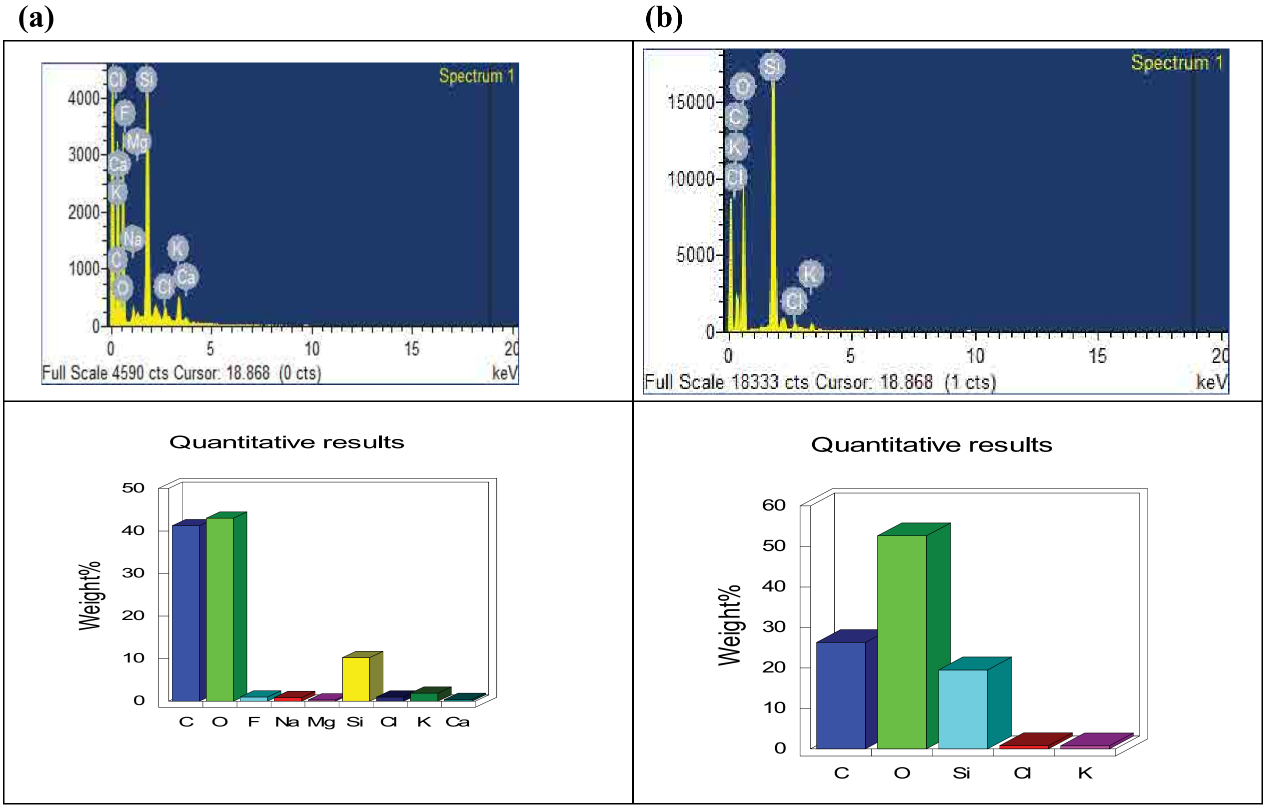

Fig. 16. EDAX of paddy straw (a) before the experimental period and (b) after the experimental period.

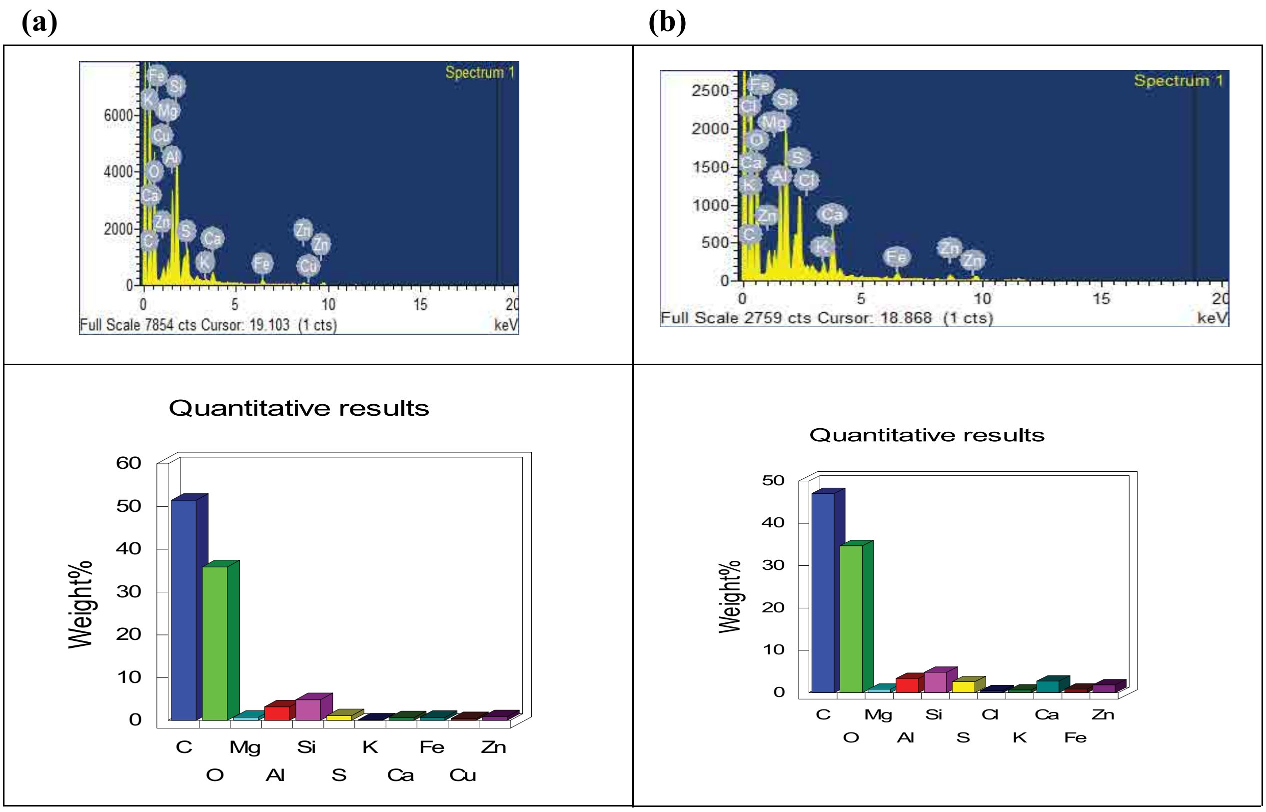

Fig. 17. EDAX analysis of coir pith (a) before the experimental period and (b) after the experimental period.

wetland system. But the control wetland system outperformed the organic media wetland system in COD removal.

The results showed that the media porosity and intermittent supply of influent loading can enhance the nitrification process by increasing the atmospheric oxygen diffusion. The methodology of intermittent loading can avoid the usage of an artificial aerator used to increase the oxygen diffusion.

The NO_3–N results indicate that the organic media supplied sufficient carbon for denitrification process. The right selection of organic media avoids the addition of external carbon source such as glucose, sodium acetate, methanol and starch for enhancing the denitrification process in wetlands.

Mass balance study of nitrogen indicates that the major nitrogen removal was by plant uptake and through gasification (nitrification and denitrification process).

The SEM and EDAX proved that the organic carbon leaching from the organic media might enhance the denitrification process. The EDAX result indicated there was an increase in oxygen content of the media, which is essential for nitrification process.

Overall, the result implies the provision of organic media in the wetland will surely enhance the nitrogen removal. The pilot-scale experiment results suggested that the usage of organic material as carbon source in constructed wetland will be a cost effective and sustainable technology since the organic media used in this study is an agricultural waste which is easily biodegradable and cheaply available in India. Further study on amount of organic media to be used and mechanism of carbon source released from the media is necessary. Other locally available organic media can also be studied.

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