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Removal of Congo red dye from simulated wastewater using vertical subsurface flow constructed wetland packed with sewage sludge bed

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ABSTRACT

Recycling of textile wastewater for non-potable purposes by sustainable constructed wetlands (CWs) has gained a great attention. In this work, unplanted and planted vertical subsurface flow CWs have been applied to remediate simulated wastewater contaminated with Congo red dye. This treatment implemented in four containers packed with sewage sludge bed under the variation of hydraulic retention time (HRT, 1–5 d) and inlet dye concentration (10–40 mg/L). Measurements stated that the heights and densities of *Phragmites australis* as well as *Typha domingensis* were increased from 0.15 m and 5 plant/unit at the beginning of plantation to values ≤1.65 m and 59 plant/unit, respectively, after 136 d. Results proved that the pH of the treated water ranged from 6.5 to 8.5, which is considered acceptable from an environmental view point. Also, an increase in the retention time with decrease of inlet dye concentration can accompany with a significant increment in the removal efficiencies of dye concentration and, consequently, the chemical oxygen demand (COD). Approximately 96.5% and 46% of dye concentration and COD, respectively, have been removed at the end of treatment period (=5 d) when the inlet concentration is 10 mg/L. The measurements of the effluent dye concentrations as a function of the retention times were well simulated by Grau second-order kinetic model. Based on the FT-IR analysis for sewage sludge beyond the treatment process, the removal of the Congo red dye from aqueous solution was enhanced by different functional groups such as phenols, carboxyl, aldehydes, lactones, ketones, quinones and anhydrides.

Keywords: Wetland; Textile wastewater; Congo red dye; Sewage sludge; Sustainable

1. Introduction

Coloured textile effluents are considered severe environmental problems as they contain mixture of organic and inorganic compounds such as dyes, solvents, detergents and salts [1]. Among all industries, textile industry consumes huge quantities of water ranging from 800 to 1,000 m^3/ton; thus, it represents the largest producer of wastewater [2]. This wastewater can be emitted from different processing units such as bleaching, scouring, dyeing, printing, finishing and packing [3]. The ratio of biochemical oxygen demand (BOD) to chemical oxygen demand (COD) is less than 0.1 for wastewater of this industry indicating its non-biodegradable nature [4]. Unfortunately, the direct disposal of textile effluents to the water bodies without any treatment can lead to severe deterioration in the quality of receiving water. The existence of dyes makes the water not only aesthetically objectionable but also may cause many diseases including nausea, ulceration of the skin and mucous membrane, hemorrhage, dermatitis and irritation of the skin [5]. Artificial dyes cause serious side effects, such as hyperactivity in children as well as cancer and allergies [6]. Congo red is an acidic and anionic dye that can be used as an antifungal therapeutic agent in the

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field of aquaculture, commercial fish hatchery, and animal husbandry. It has several negative effects on human beings such as amyloidosis [7–9]. Most of the dyes are stable hence their degradation by the traditional treatment methods may be difficult [2].

Several technologies were tested in the earlier studies to decolourize from wastewater such as coagulation – flocculation, advanced oxidation, membrane separation, electrochemical treatment, hydrogen peroxide, reverse osmosis and ozonation [3,10]. In addition, adsorption method was recorded as the popular technique that was applied to eliminate the different types of contaminants from aqueous solutions using various kinds of sorbents [11–14]. The sorbents should be easily available, cost effective, non-hazardous materials to ensure that the water is not secondarily contaminated. They should maintain their reactivity for a long period of time with uniform particle size distribution to prevent clogging [15–19]. High costs for investment and maintenance, reliable power demand, complexity of components and uncertainty of effectiveness on the long period are familiar limitations for mentioned technologies in the treatment of dyes-rich wastewater [20]. So, the efforts of researchers and authorities are directed in the past few years towards the benefit from systems that simulated natural wetland ecosystems. This was done by benefit from the ability of these systems in self-purification through establishing the best conditions for physical, chemical and biological processes required for treatment [21]. Constructed wetland (CW) is an example of such systems, which have several properties such as appropriateness, low energy requirements, simplicity, low operating cost and environmental friendliness. The CW can significantly decrease the usage of mechanical devices, energy-intensive and technical sophistication. Based on the water level, free water surface flow (FWSF) and subsurface flow (SSF) are popular classifications of CW. The second type can be either the horizontal flow (HF) or vertical flow (VF) according to the direction of water movement [22]. Aquatic vegetation used in the CW units for improving the reclamation of wastewater can include *Typha*, *Phragmites australis*, *Typhonium flagelliforme*, *Eichhornia crassipes*, lemna, etc. [23].

Previous publications revealed that the CWs have high efficacy in treating urban runoff, animal husbandry wastewater and mine disposal [24,25], petroleum wastewater [26,27], textile wastewater [28,29] and domestic sewage [30–34]. The VF CWs glass basins were situated in Turkey to reduce dye concentration (BB41; 11 mg/L influent) using river sand vegetated with *P. australis* and Manchurian wild rice for retention time of 3, 6, 9 and 18 d. The results elucidated that the percentage of dye removal was increased with the retention time [35]. The VF CW was utilized to treat wastewater contaminated with Acid Yellow 2G E107. Three vertical wetland units have been packed with sand, fine gravel and zeolite. One of these units was unplanted and the remaining units have been planted with *Canna indica* and *Typha Angustifolia*. The results signified that the removal percentages of colour were 87% for unplanted unit and 98% for others [36]. The VF CW for treating the wastewater containing fertilizer mixed with tap water and textile dyes specifically direct orange 46, AB113, reactive blue 198 (RB198), and basic red 46 (BR46) at low (7 mg/L) and high (215 mg/L) concentrations was operated. Measurements revealed that this wetland could remove the BR46 and AB113 dyes with efficiencies ranging from 68% to 96% [37].

The sewage sludge is a by-product resulted from wastewater treatment plant and, according to a survey of European Union in 2010, approximately 11.5 million tons of dry sludge can be produced. It is expected that this value will be 13.0 million tons in 2020; so, the reuse of this sludge in the treatment of wastewater can be considered a good application for sustainable concepts [38]. Therefore, the uniqueness of the present study is the experimental investigation with kinetic modelling for the VF CWs packed with sewage sludge as an alternative to the sand in the treatment of simulated wastewater contaminated with Congo red dye under the influence of *Phragmites australis* and *Typha domingensis* in comparison with unplanted units.

2. Kinetic modelling

The operation of CW is very complicated because the treatment of influent wastewater depends on the physical, chemical and biological processes that occurred simultaneously; hence, the representation of these processes mathematically considered unique task. Although there is development of sophisticated models, most CW design still uses "rules of thumb" that is based on the knowledge of engineers or simple first-order decay models [39]. However, the first-order models are insufficient for the design of constructed wetlands [40]. A variety of regression equations are developed to design CWs [41]. Some equations depend on the first-order degradation kinetics while others suppose the approaching of contaminants concentrations to zero when the retention time tends to infinity, which is not consistently found in CW.

Kinetic model is a useful tool for understanding the biological and basic transport mechanisms within the reactor [42]. Constants of the kinetic equation are called bio-kinetic coefficients or growth constants, which can describe and estimate the performance of the system. Bio-kinetic constants are influenced by (1) the type of microbial species, (2) environmental conditions such as pH, dissolved oxygen, temperature, inhibitory substances, nutrients, and (3) decomposition of organic substrates in wastewater. There are many mathematical models in the literature to describe the processes occurred within systems identical to CW such as the first-order model, Grau second-order model, Sundstrom model, Stover–Kincannon model, Chen model, Contois model, and Michaelis–Menten type kinetic model [43,44]. The Grau second-order model was applied in this study to simulate the removal of Congo red dye under the effects of different dye concentrations versus the HRT variation. This model can be expressed as follows [45,46]:

$$\frac{S_i \times \mathrm{HRT}}{S_i - S_e} = a + b \times \mathrm{HRT} \quad (1)$$

where S_i is the influent contaminant concentration (mg/L), S_e is the effluent contaminant concentration (mg/L), $a = S_i/k_2X$ (X is the biomass concentration in the reactor;

and k_2 is the second-order rate constant (per day), and b is the constant >1. Eq. (1) can be simplified to be:

$$S_e = S_i \left(1 - \frac{1}{b + \frac{a}{\mathrm{HRT}}} \right) \tag{2}$$

The constants (a) and (b) can be determined from the fitting of Eq. (2) with experimental measurements for removal of Congo red dye using nonlinear regression in the Excel-Microsoft office 2016.

3. Experimental work

3.1. Contaminant and material

Contaminant chosen in this investigation is represented by acidic Congo red dye, which has molecular weight equal to 696.66 g/mol. At acidic condition, this dye gives blue colour for aqueous solution and it changes to red colour for pH greater than 5. Wavelength opposite to maximum absorbance of 498 nm is adopted to measure the dye concentration [47] using UV-VIS spectrophotometer (Model: T80+, Cary100 conc., Varian, USA) after the filtration of samples by 0.45 μm filter. Based on the previous study conducted on the textile wastewater [48], four concentrations specifically 10, 20, 30 and 40 mg/L have been tested in this work.

Sewage sludge is selected to be the substrate for CW units as alternative to sand bed and it mostly consists of heterogeneous cultures. This bio-sorbent can be collected as a slurry from drying beds of Al-Rustumiya third extension municipal wastewater treatment plant, Baghdad/Iraq, at depth of 50 cm. This slurry must dry in the air for 5 d to obtain the particles with geometric mean diameter of 0.775 mm. The physical properties of this sludge are hydraulic conductivity coefficient of 35.2×10^{-5} m/s, bulk density of 1.109 g/cm^3 and porosity of 0.243. Preliminary tests prove that the sewage sludge has the ability to release the organic material in the wastewater under treatment and a remarkable increase in the COD concentration can be observed. To avoid this problem, sewage sludge must be modified by the application of H_2SO_4 before usage. Many tests are conducted to specify the suitable quantity of this acid that must be added to the sewage sludge for preventing the release of organic matter; however, 40 mL of H_2SO_4 mixed with 500 g will be sufficient for this purpose.

3.2. Wetland set-up

Constructed wetland units were manufactured using four plastic containers (Fig. 1) to represent the vertical subsurface flow (VSSF) system that was used to treat the simulated wastewater containing Congo red dye. These units have been situated at position of 33′ 18′ 18″ N 44′ 30′ 19″ E in Baghdad, Iraq, under natural conditions with mean temperature of 23°C. The work had been extended from 1 September 2019 to 1 April 2020 and the movement of wastewater within each unit was in the vertical direction to enhance the aerobic biodegradation of organic materials. The performance of CW units in the treatment of contaminated water was investigated under the effects of retention time, type of plant and inlet dye concentration. Each container (Fig. 1) has total depth of 60 cm with upper and lower diameters of 50 and 40 cm, respectively, to obtain the total volume of 90 L. The container was packed with three layers arranged from the bottom as follows: 1) coarser gravel (>10 mm), 2) finer gravel (<10 mm) and 3) sewage sludge (SS). The depth of each layer was 15 cm and the sludge represents the main layer for plants while the gravel was utilized to prevent the clogging of outlet. There is an outlet valve at the bottom of each unit to withdraw samples. This valve is connected with 12.5 cm diameter PVC pipe to maintain the level of wastewater below the sludge surface to satisfy the subsurface flow requirement. The packed bed was aerated by embedded perforated PVC pipe with diameter and length of 5 and 75 cm, respectively [49].

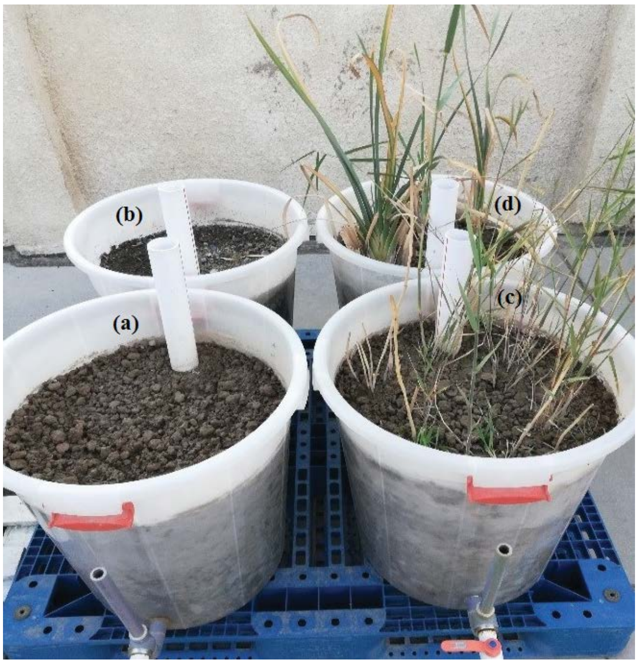


Fig. 1. Constructed wetland units manufactured in the present study (a & b) unplanted, (c) planted with *Phragmites australis* and (d) planted with *Typha domingensis*.

Phragmites australis and *Typha domingensis* have been utilized because they are common plants in the environment of Iraq. Healthy species with height of 0.3 m were submerged with tap water for 2 d. Then, they were planted in the prepared units with density of 5 plant per unit after trimming their height to 0.15 m to ensure the rapid growth [50]. The plantation process with acclimation required the period from September to December 2019 and experiments for treating the textile wastewater have begun in January 2020. The four manufactured containers were arranged as below:

- The first container was unplanted and fed with tap water only to be the reference or control (C); so, it is labelled as "control constructed wetland packed with sewage sludge, CWSSC".
- The second container was also unplanted but fed with water containing Congo red dye. The designation of

"constructed wetland packed with sewage sludge, CWSS" was used for this unit.

- The remaining two containers were planted (P) with *Phragmites australis* (P) and *Typha domingensis* (T) where they must be irrigated with dye water; hence, can be designated as CWSSPP and CWSSPT, respectively.

3.3. Operation of the system

Batch flow mode for operation of CW units was adopted to avoid expenditures such as pumping and automatic control costs. Wastewater was stayed within each unit for duration not exceeding 5 d and, then, it must be drained by "outlet valve". The CW unit must be rested for duration not less than 10 d between two successive cycles of operation to obtain partially saturated condition and this can prepare the suitable aeration for the microbes in the biofilm. Samples of 30 mL were taken periodically after 1, 2, 3, 4 and 5 d to measure the values of pH, temperature, dissolved oxygen (DO), COD, dye concentration and nutrient. The DO (mg/L) and temperature (°C) of water were measured using a hand-held mi 605 portable dissolved oxygen, MARTINI (Italy). The pH was measured by hand-held E-1 portable pH electrode Digital Meter (China). COD was measured by "closed reflux 5220 C method" described in Standard Methods for the Examination of Water and Wastewater and Environmental Chemistry, Selected Analytical Methods, UNESCO-IHE.

4. Results and discussion

4.1. Variation of acidity and oxygen demand

Fig. 2 signifies that the pH of influent wastewater is either 7.5 or 7.6; however, this parameter for effluents from all VSS CW ranged from 6.5 to 7.4, which is

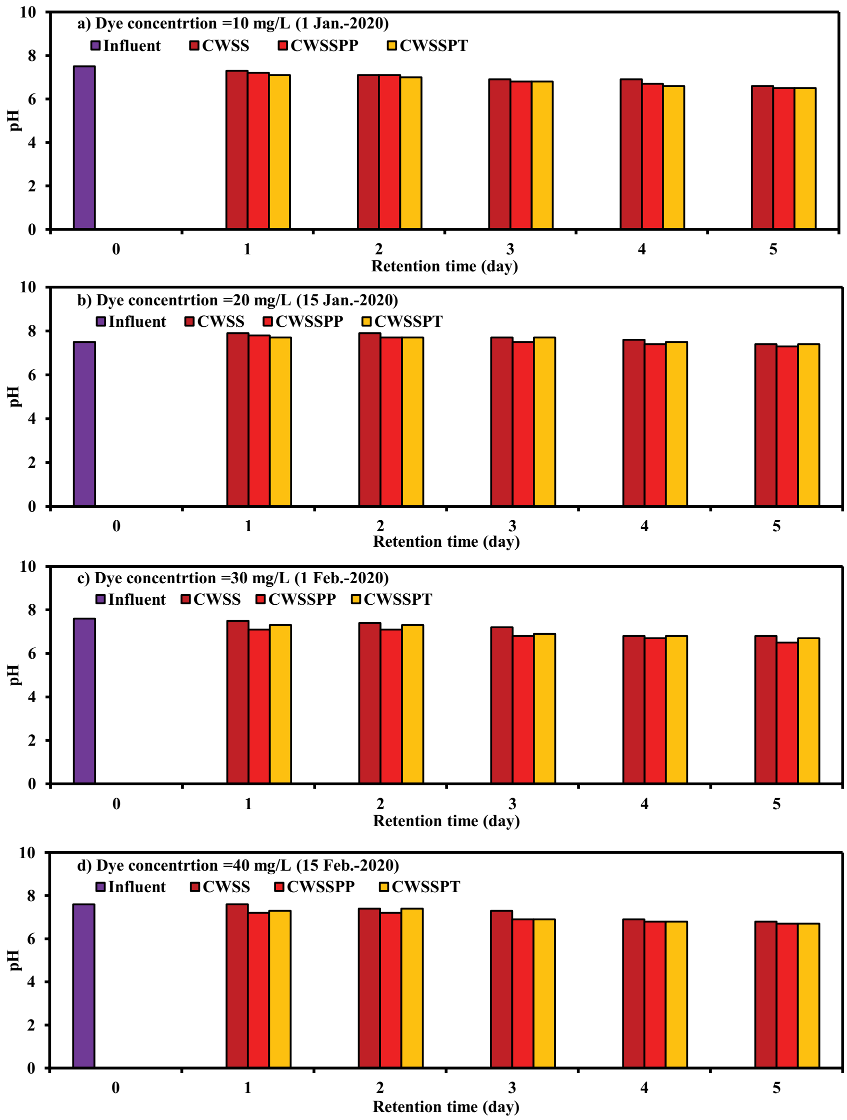


Fig. 2. Influent and effluent values of pH vs. the detention time in the unplanted and planted CW units packed with sewage sludge for different Congo red dye concentrations.

compatible with acceptable limits of WHO specified by the range (6.5–8.5) [51]. For different dye concentrations, the decrease of pH with an increase of contact time may result from the metabolism of nitrogenous and phosphate compounds that are present in high concentration within the sewage sludge. Nitrification consumes alkalinity and produces H^+ ions, which results in reduced pH values [52].

Organic contaminants are represented by COD and correlated with DO in water. The COD in simulated wastewater contaminated with Congo red dye prior to VSSF CW treatment was in the range 30.51–126.6 mg/L and the preliminary tests signified that there is no removal in these concentrations. This may be attributed to release of organic material from sewage sludge; hence an attempt was conducted to stabilize the organic matter through the modification of this sludge by addition of H_2SO_4. The modified sludge was utilized and results elucidated that there is a significant decrease in the COD of effluents from vegetative and non-vegetative units with removal efficiencies not exceeding 46% as shown in Fig. 3. The plants play a significant role in removingorganic matter by providing habitat for several decomposing microbes [53] and by transferring oxygen to their roots and rhizomes [54]. Maximum removal in COD was equal to 46% at 5 d HRT for planted units when dye concentration of 10 mg/L. Decrease of HRT and increase of dye concentration can cause a clear decrease in the removal percentage specially for unplanted CW unit and, in this case, the minimum removal reached to 12% for HRT of 1 d and dye concentration of 40 mg/L. Results signified that the height and density of plants increased dramatically with the age of vegetation. They are increased from 0.15 m and 5 plant/unit to 1.65 m and 35 plant/unit, respectively, for *P. australis* after 136 d; however, these parameters have values of 1.20 m and 59 plants/unit beyond the same period for *Typha domingensis*.

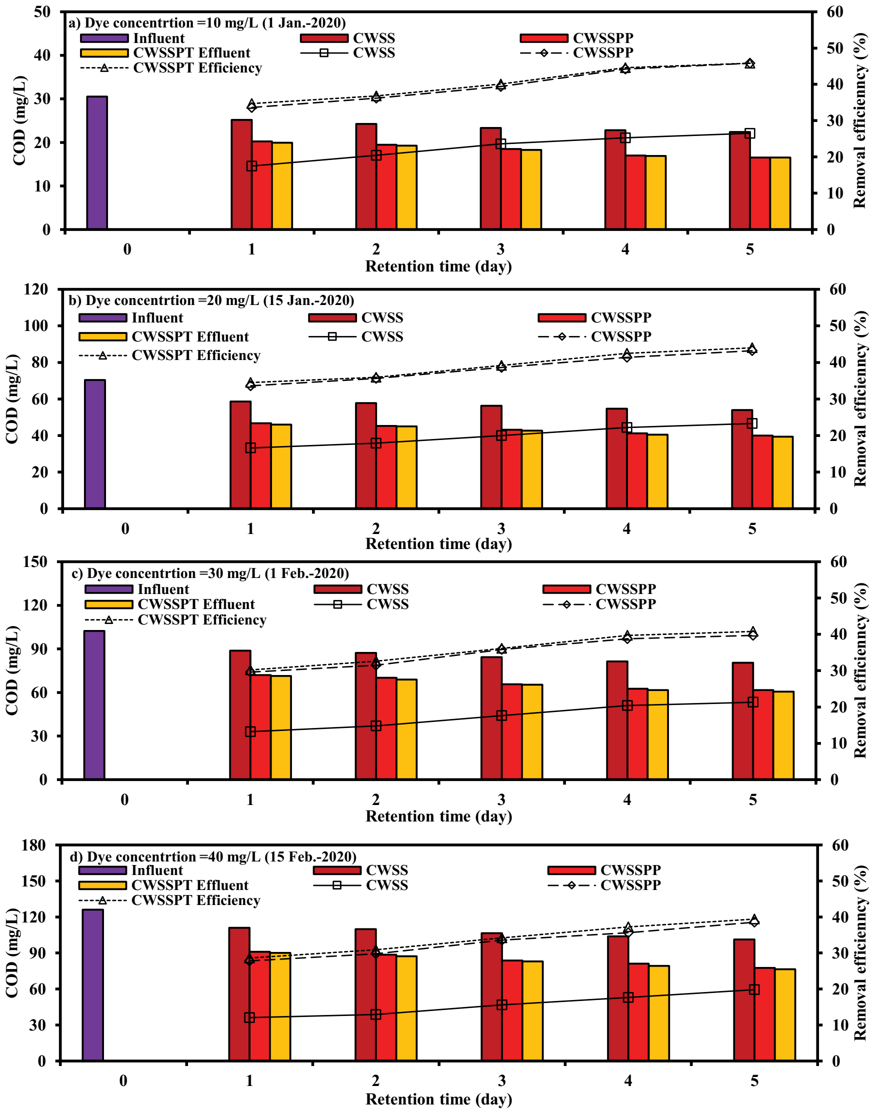


Fig. 3. Influent and effluent values of COD with removal efficiencies vs. the detention time in the unplanted and planted CW units packed with sewage sludge for different Congo red dye concentration.

The degradation of organic matters must be accompanied with an increase in the consumption of DO over time (Fig. 3) and anaerobic conditions can be recognized for unplanted units [55] while these conditions were less anaerobic for planted units. This can be caused by the dead macrophytes and phytoplankton settle at the bottom of the water body and an increase in the community of living organisms in SS, which stimulates microbial breakdown processes that require oxygen. Ultimately, the dissolved oxygen will be low in the treated effluent of wetland units. Water temperature (Fig. 4) is also a very important factor for all operations associated with microbial vitality including water treatment and soil. Changes in temperature can influence on microbial activity, which in turn leads to an improvement in the water quality [56].

4.2. Effluent concentrations of Congo red dye and nutrient

Measurements of effluent dye concentrations with removal percentages for unplanted and planted CWs for influent dye concentrations of 10, 20, 30 and 40 mg/L with different HRT are plotted in Fig. 5. It seems that there is a high reduction in the effluent dye concentrations with removal efficiencies not less than 86.6% and identical effluent concentrations not greater than 5.36 mg/L. The removals of Congo red dye in the CWSS, CWSSPP and CWSSPT are consistent with behaviour of COD removal. Microbial communities acquire fundamental role in the degradation of dye that contaminated water because the microorganisms change the dye chemistry and its transport through reduction, accumulation, packaging

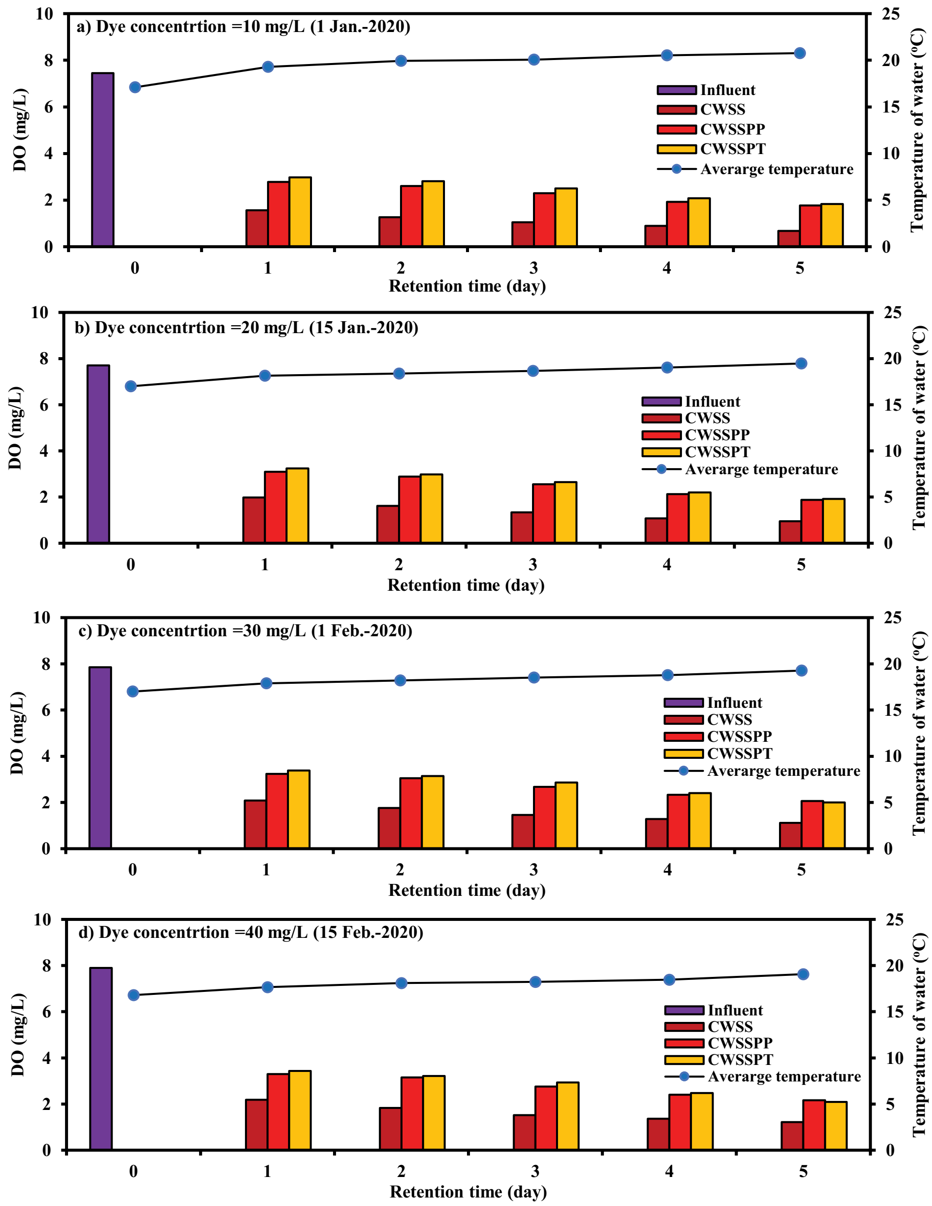


Fig. 4. Influent and effluent concentrations of DO with water temperature vs. the detention time in the unplanted and planted CW units packed with sewage sludge for different Congo red dye concentrations.

and paralysis [57]. The appearance of influent and effluent wastewater treated by CW units after retention time of 5 d for influent dye concentration of 40 mg/L can be observed in Fig. 6a. The colour of the influent wastewater is red, which can be removed with different percentages based on the type of CWs unit. It seems that these units have a good ability in the elimination of red colour from effluent but unfortunately the yellow colour can be recognized, which may be produced from the low reduction efficiency of COD (Fig. 3). In addition, the existence of vegetative has a significant role in producing clear water in comparison with effluent from unplanted units.

The concentrations of NH_4–N and NO_3–N in simulated wastewater entered into CWs are equal to 0.45 and 12.8 mg/L for 40 mg/L dye concentration and these values are decreased with decrease of dye concentration. The CWSS, CWSSPP and CWSSPT units have acceptable ability for eliminating of NH_4–N and NO_3–N. For example, the maximum average efficiencies of NH_4–N in the CWSS, CWSSPP and CWSSPT units havenot exceeded 25.03%, 39.48% and 41.85%, respectively, for dye concentration of 10 mg/L, while these efficiencies for NO_3–N have values not greater than 27.23%, 42.37% and 42.65%, respectively, for same units and dye concentration. Taking into account the nitrification and denitrification processes, the reduction of inflowing ammonia and nitrates can be attributed to nitrogen from ammonia mixed with nitrates attached to the media surface followed by the release of nitrates produced in wastewater by aerobic conditions [58].

4.3. Control wetland unit

Additional CW unit packed with sewage sludge material and fed by tap water only designated as CWSSC was achieved to be a reference for the performance of CWSS, CWSSPP and CWSSPT units. The CWSSC unit is

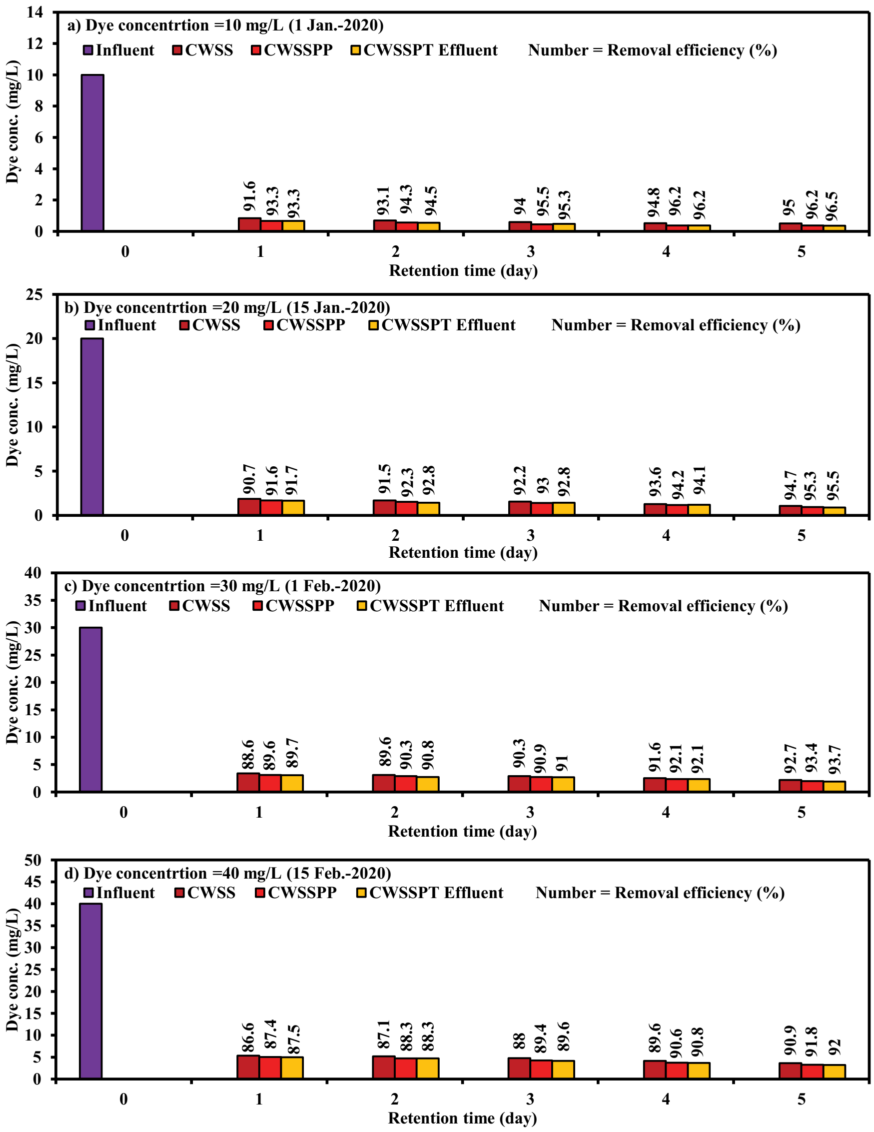


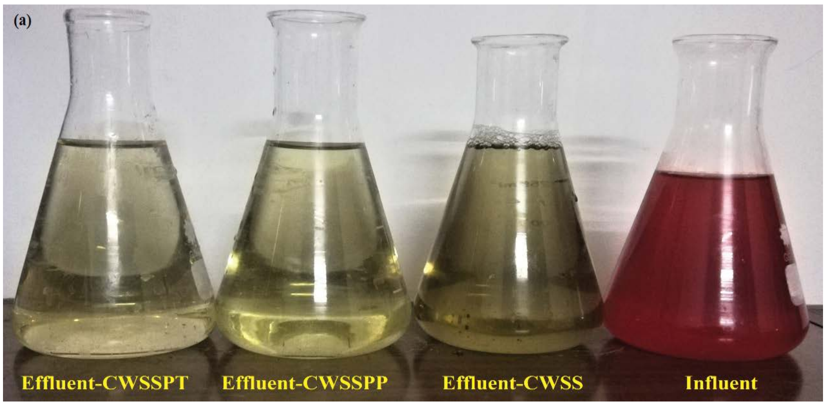
Fig. 5. Influent and effluent concentrations of Congo red dye with removal efficiencies vs. the detention time in the unplanted and planted CW units packed with sewage sludge.

very important for specifying the effect of Congo red dye addition on the properties of the tap water used to simulate the wastewater contaminated with this dye identical to the effluents of the textile industry. Results signified that the pH of influent tap water to CWSSC was equal to 7.3 and it decreased with time until stabilized on 6.8 after 5 d because of the dissolution of carbon dioxide. The pH values of influent tap water and wastewater containing Congo red dye are closer to each other. The monitoring process elucidated that the DO in tap water entering CWSSC unit through March is equal to 7.26 mg/L, which slightly differs from DO of simulated wastewater. This difference may result from the changing in the quality of tap water with January, February and March months that adopted to implement the mentioned tests on the units packed with sewage sludge. However, a high difference in the influent values of organic material (i.e., COD) can be recognized between units feeding with wastewater polluted by the Congo red dye, (the values equal to 30.51, 70.34, 102.33 and 126.2 mg/L for dye concentrations of 10, 20, 30 and 40 mg/L, respectively), and unit irrigated by tap water only with COD of 7.21 mg/L. This high difference in the values of COD is attributed to the addition of organic compound (i.e., Congo red dye) in the tap water and, consequently, the tap water cannot be the source for organic matter. Measurements proved that the DO was decreased with the retention time because it exhausted in the oxidation of organic matter. The values of DO and COD in the effluents from CWSSC unit beyond 5 d were equal to 1.51 and 4.96 mg/L, respectively. Finally, the temperatures of water entering and leaving the CWSSC unit were almost identical to those values of CWSS, CWSSPP and CWSSPT units.

4.4. FT-IR analysis

The surface chemistry of the virgin sewage sludge in comparison with sewage sludge samples taken from CWSS, CWSSPP and CWSSPT units beyond the sorption of Congo red dye can be explained by FT-IR analysis as explained in Fig. 6b. Phenols, carboxyl, aldehydes, lactones, ketones, quinones and anhydrides are familiar functional groups in the sewage sludge. This sludge has several functional groups in the hosts specifically from volatile components. Broader band of 4,000–3,700 cm^{-1} resulting from the -OH groups and the water molecules that adsorbed physically. Both moisture and hydroxyl (OH) groups can lead to splayed peak at 2,517.1 cm^{-1} [59].

Alcohols, carboxyl and phenols have represented the structures containing hydroxyl. The absorption band at 3,800–2,500 cm^{-1} was designated as OH within a group of carboxyl [60]. The peaks at 430.13, 460.99, 501.49, 601.79,



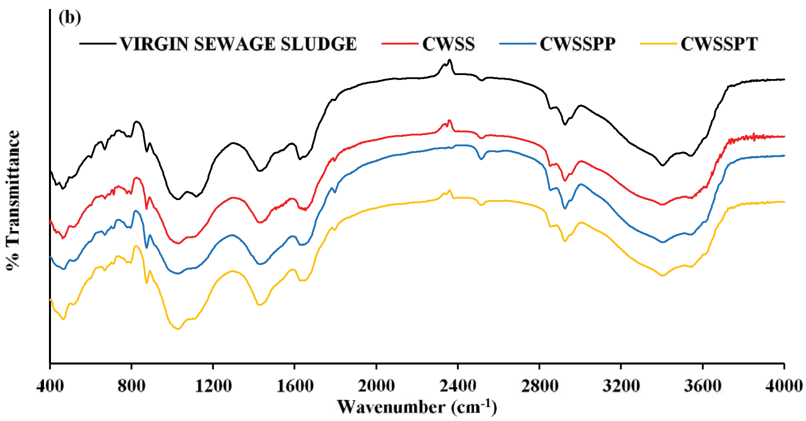


Fig. 6. (a) Appearance of influent and effluent wastewater treated by different CW units packed with sewage sludge after 5 d and influent dye concentration of 40 mg/L, (b) Infrared absorption spectrums for sewage sludge of unplanted and planted CWs units before and after sorption of Congo red dye.

669.3, 707.88, 779.2, 794.6 and 875.68 cm^{-1} are aliphatic C–H, while C–C bond occurred at 1,429.3 cm^{-1} [61]. Due to the vibration movements, the NH groups existed at 1,795.7 cm^{-1}. Hence, the composition of this sludge is rich with functional groups and organic groups such as C–C, C=C and NH can be excited to cause a change in intensity due to the presence of root residuals. The FT-IR analysis before and after dye sorption illustrates the existence of additional peaks at 1,429.3 and 2,856.6 cm^{-1}, which represents C=C in the aromatic ring of Congo red dye. Also, the shift in other peaks indicates the adsorption of Congo red dye on the sewage sludge.

4.5. Grau second-order kinetic model

All experimental measurements for effluent concentrations of Congo red dye in the wastewater remediated by unplanted and planted units of CW filled with sewage sludge are simulated mathematically by Grau second-order kinetic model. The simulation process is depended on the application of "solver" option in Excel 2016 to achieve nonlinear fitting between Eq. (2) and experimental measurements. The major outcomes of the fitting are the values of constants (*a*) and (*b*) with statistical measures such as coefficient of determination (R^2) and sum of squared error (SSE) to evaluate the concurrence between the measured and predicted effluent concentration.

Grau second-order kinetic model was utilized for simulating the measurements of Congo red dye concentrations in the treated effluents as a function of HRT for all CW units for inlet concentration under consideration. The concurrence between this model and concentration measurements can be observed in Fig. 7. All constants resulted from fitting with values of R^2 and SSE have been listed in Table 1. It seems that there is a satisfactory matching between experimental results and model predictions as clear from values of SSE in combination with R^2.

5. Conclusions

Measurements of pH with concentrations of COD, DO and Congo red dye in the effluents from planted and unplanted VSSF CW units packed with sewage sludge signified the importance of these units in the reclamation of simulated coloured wastewater. The values of pH for

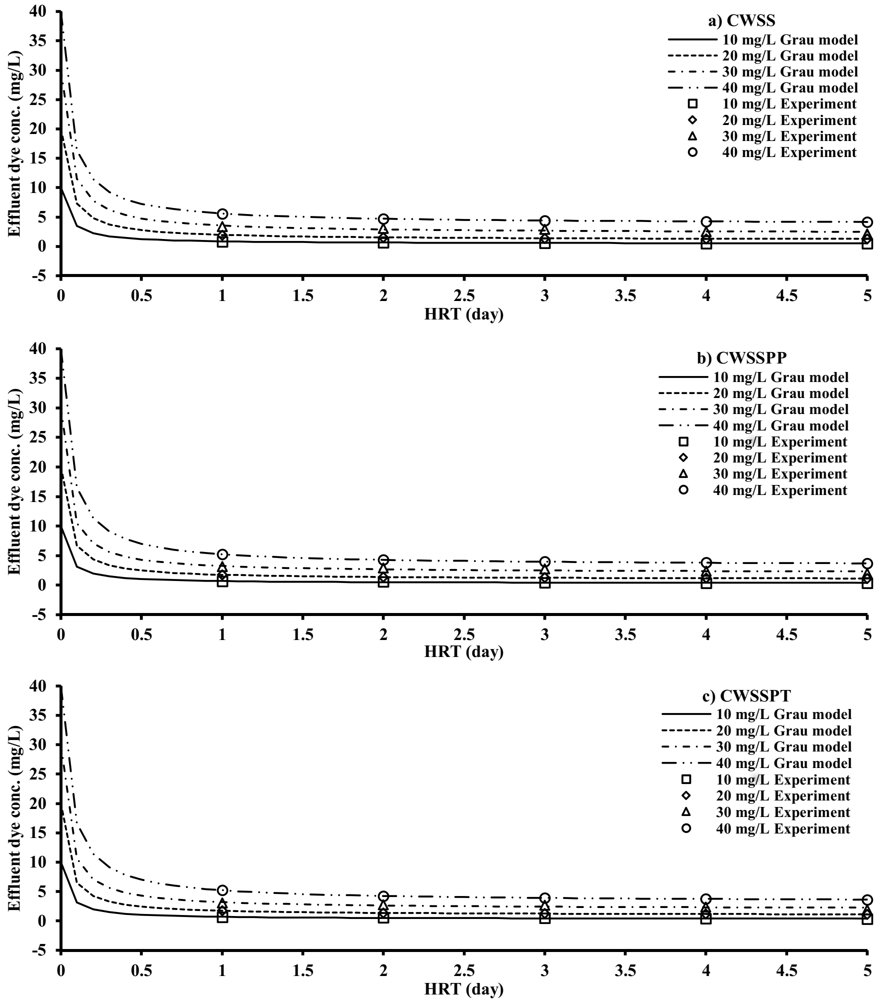


Fig. 7. Grau second-order kinetic model for effluent concentrations of Congo red dye in comparison with experimental measurements vs. the detention time in the unplanted and planted CW units packed with sewage sludge.

Table 1
Kinetic parameters of Congo red dye removal with Grau second-order model in the unplanted and planted CW units packed with sewage sludge

Influent dye conc. (mg/L)	CWSS				CWSSPP				CWSSPT			
	a	*b*	R^2	SSE	*a*	*b*	R^2	SSE	*a*	*b*	R^2	SSE
10	0.0483	1.0454	0.9567	0.0033	0.0419	1.0325	0.9067	0.0061	0.0425	1.0317	0.9158	0.0056
20	0.0513	1.0575	0.7420	0.1084	0.0450	1.0517	0.7186	0.0976	0.0430	1.0512	0.6759	0.1099
30	0.0543	1.0796	0.7685	0.2175	0.0464	1.0748	0.6779	0.2592	0.0473	1.0718	0.6938	0.2523
40	0.0588	1.1042	0.6632	0.6899	0.0615	1.0895	0.7686	0.4698	0.0624	1.0875	0.7610	0.5067

treated water from all units are within the range (6.5–8.5), which satisfy the environmental prescribed limits. The lowest values of removal efficiencies for COD (≈12%) and Congo red dye (86.6%) were observed in the unplanted unit at inlet dye concentration of 40 mg/L beyond 1 d. Significant increments in the removals of COD and Congo red dye were observed with decrease of inlet dye concentration (10 mg/L) to be more than 45% and 96%, respectively, for planted units beyond 5 d. These increments were accompanied with a remarkable decrease in DO due to the degradation process to obtain the lowest values in the planted units after 5 d regardless the dye concentration. Also, the heights and densities of plants increased dramatically to reach the values not greater than 1.65 m and 59 plant/unit, respectively, after 136 d from plantation process. In addition, the units planted with *Phragmites australis* and *Typha domingensis* are more efficient in the treatment process from the unplanted ones; however, the used plants have approximately the same effect on the effluent characteristics. Results proved that the Grau second-order kinetic model has a high ability in the description of the dye concentration in the treated water with time. Finally, FT-IR test demonstrated that there are a number of functional groups responsible for the enhancement of the removal of Congo red dye onto sewage sludge.

Acknowledgments

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References

[1] T.G. Bulc, A. Ojstršek, The use of constructed wetland for dye-rich textile wastewater treatment, J. Hazard. Mater., 155 (2008) 76–82.
[2] A. Shenoy, N. Ahsan, M. Shakeel, Wastewater pollution from textile industry and its control, J. Basic Appl. Eng. Res., 2 (2015) 678–684.
[3] D. Sivakumar, D. Shankar, A.J.V. Prathima, M. Valarmathi, Constructed wetland treatment of textile industry wastewater using aquatic macrophytes, Int. J. Environ. Sci., 3 (2013) 1223–1232.
[4] N. Azbar, T. Yonar, K. Kestioglu, Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent, Chemosphere, 55 (2004) 35–43.
[5] G.S. Gupta, G. Prasad, V.N. Singh, Removal of chrome dye from aqueous solutions by mixed adsorbents: fly ash and coal, Water Res., 24 (1990) 45–50.
[6] J. Mittal, Permissible synthetic food dyes in India, Resonance J. Sci. Educ., 25 (2020) 567–577.
[7] A.A. Ahmad, B.H. Hameed, N. Aziz, Adsorption of direct dye on palm ash: kinetic and equilibrium modeling, J. Hazard. Mater., 141 (2007) 70–76.
[8] P. Frid, S.V. Anisimov, N. Popovic, Congo Red and protein aggregation in neurodegenerative diseases, Brain Res. Rev., 53 (2007) 135–160.
[9] A. Mittal, J. Mittal, A. Malviya, V.K. Gupta, Adsorptive removal of hazardous anionic dye "Congo red" from wastewater using waste materials and recovery by desorption, J. Colloid Interface Sci., 340 (2020) 16–26.
[10] T. Kurbus, A.M. Le Marechal, D.B. Voncina, Comparison of H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+} processes for the decolorisation of vinylsulphone reactive dyes, Dyes Pigm., 58 (2003) 245–252.
[11] I. Anastopoulos, A. Mittal, M. Usman, J. Mittal, G.H. Yu, A. Núñez-Delgado, M. Kornaros, A review on halloysite-based adsorbents to remove pollutants in water and wastewater, J. Mol. Liq., 269 (2018) 855–868.
[12] C. Arora, S. Soni, S. Sahu, J. Mittal, P. Kumar, P.K. Bajpai, Iron based metal organic framework for efficient removal of methylene blue dye from industrial waste, J. Mol. Liq., 284 (2019) 343–352.
[13] V.K. Gupta, S. Agarwal, R. Ahmad, A. Mirza, J. Mittal, Sequestration of toxic congo red dye from aqueous solution using ecofriendly guar gum/activated carbon nanocomposite, Int. J. Biol. Macromol., 158 (2020) 1310–1318.
[14] I. Anastopoulos, I. Pashalidis, A.G. Orfanos, I.D. Manariotis, T. Tatarchuk, L. Sellaoui, A. Bonilla-Petriciolet, A. Mittal, A. Núñez-Delgado, Removal of caffeine, nicotine and amoxicillin from (waste)waters by various adsorbents. A review, J. Environ. Manage., 261 (2020) 110236, doi: 10.1016/j.jenvman.2020.110236.
[15] A.H. Sulayman, A.A.H. Faisal, Z.T. Abd Ali, Performance of granular dead anaerobic sludge as permeable reactive barrier for containment of lead from contaminated groundwater, Desal. Water Treat., 56 (2015) 327–337.
[16] A.H. Sulaymon, A.A.H. Faisal, Q.M. Khaliefa, Cement kiln dust (CKD)-filter sand permeable reactive barrier for the removal of Cu(II) and Zn(II) from simulated acidic groundwater, J. Hazard. Mater., 297 (2015) 160–172.
[17] M. Alshammari, M.F. Al Juboury, L.A. Naji, A.A.H. Faisal, H. Zhu, N. Al-Ansari, M. Naushad, Synthesis of a novel composite sorbent coated with siderite nanoparticles and its application for remediation of water contaminated with Congo red dye, Int. J. Environ. Res., 14 (2020) 177–191.
[18] M.F. Al Juboury, M.H. Alshammari, M.R. Al-Juhaisi, L.A. Naji, A.A.H. Faisal, Mu. Naushad, E.C. Lima, Synthesis of composite sorbent for the treatment of aqueous solutions contaminated with methylene blue dye, Water Sci. Technol., 81 (2020) 1494–1506.
[19] N.A.-A. Ayad A.H. Faisal, Israa M. Ali, Laith A. Naji, Huda M. Madhloom, Using different materials as a permeable reactive barrier for remediation of groundwater contaminated with landfill's leachate, Desal. Water Treat., 175 (2020) 152–163.
[20] S.E. Mbuligwe, Comparative treatment of dye-rich wastewater in engineered wetland systems (EWSs) vegetated with different plants, Water Res., 39 (2005) 271–280.

[21] M. Scholz, J. Xu, Performance comparison of experimental constructed wetlands with different filter media and macrophytes treating industrial wastewater contaminated with leadand copper, Bioresour. Technol., 83 (2002) 71–79.
[22] J. Vymazal, The use of hybrid constructed wetlands for wastewater treatment with special attention to nitrogen removal: a review of a recent development, Water Res., 47 (2013) 4795–4811.
[23] N.M. Azeez, A.A. Sabbar, Efficiency of duckweed (*Lemna Minor* L) in phytotreatment of wastewater pollutants from Basrah oil refinery, J. Appl. Phytotechnol. Environ. Sanit., 1 (2012) 163–172.
[24] P. Mays, G. Edwards, Comparison of heavy metal accumulation in a natural wetland and constructed wetlands receiving acid mine drainage, Ecol. Eng., 16 (2001) 487–500.
[25] E.R. Rozema, A.C. Vanderzaag, J.D. Wood, A. Drizo, Y. Zheng, A. Madani, R.J. Gordon, Constructed wetlands for agricultural wastewater treatment in Northeastern North America: a review, Water, 8 (2016) 1–14.
[26] R. Al-Isawi, A. Sani, S. Almuktar, M. Scholz, Vertical-flow constructed wetlands treating domestic wastewater contaminated by hydrocarbons, Water Sci. Technol., 71 (2015) 938–946.
[27] R. Al-Isawi, M. Scholz, Y. Wang, A. Sani, Clogging of vertical-flow constructed wetlands treating urban wastewater contaminated with a diesel spill, Environ. Sci. Pollut. Res., 22 (2015) 12779–12803.
[28] L.C. Davies, G. Cabrita, R. Ferreira, C. Carias, J. Novais, S. Martins-Dias, Integrated study of the role of Phragmites australis in azo-dye treatment in a constructed wetland: from pilot to molecular scale, Ecol. Eng., 35 (2009) 961–970.
[29] B.J. Bedah, A.A.H. Faisal, Use of vertical subsurface flow constructed wetland for reclamation of wastewater contaminated with Congo red dye, Plant Arch., 20 (2020) 8784–8792.
[30] A. Sani, M. Scholz, L. Bouillon, Seasonal assessment of experimental vertical-flow constructed wetlands treating domestic wastewater, Bioresour. Technol., 147 (2013) 585–596.
[31] J. Paing, A. Guilbert, V. Gagnon, F. Chazarenc, Effect of climate, wastewater composition, loading rates, system age and design on performances of French vertical flow constructed wetlands: a survey based on 169 full scale systems, Ecol. Eng., 80 (2015) 46–52.
[32] M.A. Rahi, A.A.H. Faisal, Performance of subsurface flow constructed wetland systems in the treatment of Al-Rustumia municipal wastewater using continuous loading feed, Iraqi J. Chem. Pet. Eng., 20 (2019) 33 – 40.
[33] M.A. Rahi, A.A.H. Faisal, Using horizontal subsurface flow constructed wetland system in the treatment of municipal wastewater for agriculture purposes, Iraqi J. Agric. Sci., 50 (2019) 1208–1217.
[34] M.A. Rahi, A.A.H. Faisal, L.A. Naji, S.A. Almuktar, S.N. Abed, M. Scholz, Biochemical performance modelling of non-vegetated and vegetated vertical subsurface-flow constructed wetlands treating municipal wastewater in hot and dry climate, J. Water Process Eng., 33 (2020) 101003.
[35] O. Keskinkan, M.L. Göksu, Assessment of the dye removal capability of submersed aquatic plants in a laboratory-scale wetland system using anova, Brazilian J. Chem. Eng., 24 (2007) 193–202.
[36] A. Yalcuk, G. Dogdu, Treatment of azo dye Acid Yellow 2G by using labscale vertical-flow intermittent feeding constructed wetlands, J. Selcuk Univ. Nat. Appl. Sci., (2014) 355–368.
[37] A. Hussein, M. Scholz, Dye wastewater treatment by vertical-flow constructed wetlands, Ecol. Eng., 101 (2017) 28–38.
[38] M. Samolada, A. Zabaniotou, Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy management in Greece, Waste Manage., 34 (2014) 411–420.
[39] D.P. Rousseau, P.A. Vanrolleghem, N. De Pauw, Model based design of horizontal subsurface flow constructed treatment wetlands: a review, Water Res., 38 (2004) 1484–1493.
[40] R.H. Kadlec, The inadequacy of first-order treatment kinetic models, Ecol. Eng., 15 (2000) 105–119.
[41] M.T. Wynn, S.K. Liehr, Development of a constructed subsurfaceflow wetland simulation model, Ecol. Eng., 16 (2001) 519–536.
[42] B.K. Acharyaa, H. Pathak, S. Mohana, Y. Shouche, V. Singh, D. Madamwar, Kinetic modelling and microbial community assessment of anaerobic biphasicfixed film bioreactor treating distillery spent wash, Water Res., 45 (2011) 4248–4259.
[43] S. Sandhya, K. Swaminathan, Kinetic analysis of treatment of textile wastewater in hybridcolumn upflow anaerobic fixed bed reactor, Chem. Eng. J., 122 (2006) 87–92.
[44] M.T. Jafarzadeh, N. Mehrdad, S.J. Hashemian, Kinetic constants of anaerobic hybrid reactor treating petrochemical waste, Asian J. Chem., 21 (2009) 1672–1684.
[45] S.Q. Ni, S. Sung, Q.Y. Yue, B.Y. Gao, Substrate removal evaluation of granular Anammox process in a pilotscale upflow anaerobic sludge blanket reactor, Ecol. Eng., 38 (2012) 30–36.
[46] I.N. Faekah, S. Fatihah, Z.S. Mohamed, Kinetic evaluation of a partially packed upflow anaerobic fixed film reactor treating lowstrength synthetic rubber wastewater, Heliyon, 6 (2020) e03594.
[47] V.K. Gupta, S. Khamparia, I. Tyagi, D. Jaspal, A. Malviya, Decolorization of a mixture of dyes: a critical review, Glob. J. Environ. Sci. Manage., 1 (2015) 71–94.
[48] C. Lavanya, R. Dhankar, S. Chikara, S. Sheoran, Degradation of toxic dyes: a review, Int. J. Curr. Microbiol. Appl. Sci., 3 (2014) 189–199.
[49] A.I. Stefanakis, V.A. Tsihrintzis, Effects of loading, resting period, temperature, porous media, vegetation and aeration on performance of pilot-scale vertical flow constructed wetlands, Chem. Eng. J., 181–182 (2012) 416–430.
[50] A. Stefanakis, C.S. Akratos, V.A. Tsihrintzis, Vertical flow constructed wetlands: Eco-engineering systems for wastewater and sludge treatment, Elsevier Science, Amsterdam, 2014, 392 pages, ISBN: 978-0124046122.
[51] World Health Organization, Guidelines for Drinking-Water Quality Volume 1 Recommendations, WHO, Vol. 1, 2004, 515 pages.
[52] R.H. Kadlec, S.D. Wallace, Treatment Wetlands, Taylor and Francis group, 2009, 366 pages.
[53] C.R. Taylor, P.B. Hook, O.R. Stein, C.A. Zabinski, Seasonal effects of 19 plant species on COD removal in subsurface treatment wetland microcosms, Ecol. Eng., 37 (2011) 703–710.
[54] S. Kouki, F. M'hiri, N. Saidi, S. Belaid, A. Hassen, Performances of a constructed wetland treating domestic wastewaters during a macrophytes life cycle, Desalination, 246 (2009) 452–467.
[55] C. Carliell, S. Barclay, N. Naidoo, C. Buckley, D. Mulholland, E. Senior, The anaerobic decolourization of reactive dyes in conventional sewage treatment processes, Water South Africa, 20 (1994) 341–344.
[56] R.H. Kadlec, K.R. Reddy, Temperature effects in treatment wetlands, Water Environ. Res., 73 (2001) 543–557.
[57] A. Kumar, D.K. Jaiswal, R.R. Yadav, Analytical solutions of one-dimensional temporally dependent advection-diffusion equation along longitudinal semi-infinite homogeneous porous domain for uniform flow, J. Math., 2 (2012) 01–11.
[58] Y. Feng, Y. Yu, L. Qiu, Y. Yang, Z. Li, M. Li, L. Fan, Y. Guo, Impact of sorption functional media (SFM) from zeolite tailings on the removal of ammonia nitrogen in a biological aerated filter, J. Ind. Eng. Chem., 21 (2015) 704–710.
[59] A.A.H. Faisal, S.F.A. Al-Wakel, H.A. Assi, L.A. Naji, M. Naushad, Waterworks sludge-filter sand permeable reactive barrier for removal of toxic lead ions from contaminated groundwater, J. Water Process Eng., 33 (2020) 101112.
[60] F.A.A. Tirkistani, Thermal analysis of chitosan modified by cyclic oxygenated compounds, Polym. Degrad. Stab., 61 (1998) 161–164.
[61] M.S. Shafeeyan, W.M.A.W. Daud, A. Houshmand, A. Shamiri, A review on surface modification of activated carbon for carbon dioxide adsorption, J. Anal. Appl. Pyrol, 89 (2010) 143–151.