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Rate constants for the removal of pollutants in wetlands: A mini review

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ABSTRACT

The constructed wetlands (CWs) possess tremendous significant potential for the treatment, reuse and recycle of wastewater. As compared with conventional wastewater treatment methods, CW has great significance in terms of resource enhancement at lower cost. The enhanced applications of CWs for the treatment purposes have led to the development of better design of CW systems. To describe the treatment processes in CWs, the various numerical models have been proposed in the literature. Considering the large applicability of CWs all over the world, the researchers have derived values of the rate constants. Based on kinetic data from the pilot-scale or laboratory observations, few studies have been reported for the estimation of rate constants. Most of the researchers have used the first-order kinetics for estimation of rate constants for removal of several pollutants including biochemical oxygen demand (BOD), chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP) in various types of wetlands comprising CWs as well as free water surface wetlands. The present study delivers a comprehensive review on the rate constants for the removal of numerous pollutants such as BOD, COD, TN and TP in different wetlands around the world.

Keywords: Constructed wetland; Kinetics; Rate constants; Wastewater treatment; Wetland design

1. Introduction

In India, direct discharge of huge volume of wastewater into natural watercourses has generated problem of pollution of the coastal zones and drinking water reservoirs [1]. The contamination caused by various discharges into natural watercourses has very high concentrations in comparison with regulatory standards for their discharge. Considering the pollution due to different discharges, current regulations and also the approach of regulatory agencies seem to be inadequate to address this pollution issue.

In the recent years, even though a number of wastewater treatment plants have been increased in urban India, this growth is not satisfactory to keep pace with growing generation of wastewater. Furthermore, the existing wastewater treatment plants are not functioning properly in rural areas due to poor maintenance, high cost and requirement of highly skilled manpower [2]. In India, nearly 73% of population is residing in small villages where collection of wastewater at large-scale is impossible [3]. Therefore, the main aspect should be design of sewage treatment plants for Indian villages. Hence, the natural treatment systems, in particular, constructed wetlands (CWs) seem to be attractive candidatures for the treatment of wastewater [4–7]. The CWs possess tremendous significant potential for treatment and recycling of wastewater to attain improved water quality [5,8–12]. Furthermore, in terms of resource enhancement at lesser cost, CW has great significance in comparison with conventional wastewater treatment methods [13–19].

Several researchers in the past have investigated engineered CWs or natural wetlands receiving urban runoff or partially treated domestic sewages (some recent review papers are by Vymazal [20,21]; Hoffmann et al., [22] and Wu et al., [23]). Moreover, for the treatment of effluent from industries

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or mixtures of industrial effluents with domestic sewages; engineered CWs or natural wetlands have been employed by several researchers in the past (some recent review papers are by Vymazal [20,21] and Sultana et al., [24,25]). However, relatively limited studies have been reported in the literature which has estimated rate constants based on their laboratory observations or the kinetic data from the wetlands investigated in their studies.

Several numerical models have been reported in the literature for the description of treatment processes in CWs. Most of the researchers have used the first-order kinetics for the estimation of rate constants for removal of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP) in various types of wetlands including natural as well as CWs. Hence, the present work focuses on the review of rate constants for removal of various pollutants in different types of wetlands around the globe. For the development of better design of wetland systems across the world, these rate constants are likely to play significant role.

2. Estimation of rate constants in wetlands

The rate constant is dependent on several factors such as pollutant loading, presence of vegetation, oxygen transfer, etc. Different wetlands have different rates of removal. In the literature, area-based rate coefficients are reported as most processes in wetlands are dependent on wetland area (K_A). Furthermore, volume-based rate coefficients (K_V) are also reported for most of the wetlands as the treatment is dependent on volume of the reactor.

In the kinetic study of CWs, the majority of the models of are concentrated on the input-output data and the production of either linear regression equations or first-order decay laws. The most common form of the simple first-order kinetic model is represented by the following equation [26]:

$$C\left(t\right) = C_0 .\, e^{-K_{v}.t} \tag{1}$$

where $C(t)$ is the instantaneous concentration of pollutant (BOD or COD or TP or TN) at time t (mg/L), C_0 is the initial concentration at time $t = 0$ and K_v is the volumetric rate constant (d^{-1}).

Typically, in the literature, the rate constants are reported for a temperature of 20°C – which are further calculated for the water temperature using the following equation. The temperature effect on rate constant is determined using an Arrhenius equation. The expression for rate constant $K_{v,T}$ is as follows [26]:

$$K_{v,T} = K_{v,20} . \theta^{(T-20)} \tag{2}$$

where $K_{v,T}$ is removal rate constant at water temperature, T°C, $K_{v,20}$ removal rate constant at 20°C, θ is dimensionless temperature coefficient.

The rate constants reported in the present paper are volume-based rate constants, at water temperature. If $\theta > 1$, reaction rates are slower due colder water temperatures and vice-versa. Most of the researchers have used above simple first-order kinetic model to estimate the rate constants [26].

3. Rate constants in subsurface flow constructed wetlands

In horizontal subsurface flow (HSSF) CWs, the wastewater is continuously fed from a side of the CW bed. The wastewater flows slowly in a more or less horizontal path through the porous medium under the surface of the bed until it reaches the outlet zone where the treated water is collected at the opposite side of wetland [27]. For wide range of diverse applications including treatment of sewages; storm-water run-off; agricultural effluent; remediation of acid mine drainage and polishing the effluent from sewage treatment plants, HSSF CWs are employed as they deliver a relatively simple, robust and inexpensive solution for the treatment [20,21,24].

Several studies have explored the possibility of employing a CW to treat certain bio-degradable components present in industrial wastewaters as well as domestic sewages [20–25]. For example, in south-west Victoria of Australia, the experimental gravel-based subsurface flow CWs were employed for the treatment of stormwater collected from the hard-pan and other surfaces of a dairy processing factory using the two emergent macrophytes such as *Arundo donax* and *Phragmites australis* [28]. In order to increase the insight on the functioning and dynamics of CW systems, the modelling of CWs has gained interest in recent years which enable the design of these systems. Proper design of CW is important which attributes to minimizing the size and the construction cost on one hand and maximizing the removal efficiency on the other hand [29].

For the optimization of design and operation of CWs as well as for the improvement of CW treatment efficiency, the various numerical models have been proposed in the literature for the interpretation of data. For the removal of organic matter in wetlands, first-order kinetics is considered to be the basic model which is being extensively used in the United States, Australia and European countries [30]. Also, many researchers adopted the plug-flow model for steady-state conditions as several controversies have been reported in the literature regarding the real hydrodynamics of HSSF CWs. Moreover, complete mix tanks in series model have been also adopted by the designers as the model behaviour can approach complete mix conditions (when number of tanks are close to 1) or plug-flow conditions (when number of tanks are large) depending on the number of tanks in series.

For the prediction of effluent concentrations in the design of HSSF CWs, simple first-order kinetic model is most commonly employed which predicts an exponential decay of the concentration until reaching asymptotically to the value of zero.

To determine the reaction rate constants of specific pollutants in greywater from a staff canteen of the University of Moratuwa (Sri Lanka), a pilot-scale CW was studied by Karunaratne et al. [31]. *Typha latifolia* was used for vegetation in the wetland bed having effective volume approximately 4,000 L with porosity of 0.5. The design parameters were estimated using first-order model for optimization of design considerations and sizing requirements of CW concerning to the local conditions. In tropical climatic conditions, the estimated parameters can effectively be applied in sizing the CWs. The estimated reaction rate constants for the removal of COD, BOD, TP and TN are depicted in Table 1. This study shows that by utilizing the newly estimated parameters, the surface area of subsurface flow CW can be reduced by a considerable percentage.

To investigate the feasibility of CWs for the treatment of sanitary landfill leachate, the study was conducted by Sawaittayothin and Polprasert [32]. A synthetic wastewater and landfill leachate collected from a nearby sanitary landfill was fed to the two pilot-scale subsurface flow CW units situated at the Asian Institute of Technology, Thailand campus. The first-order reaction rate constants are shown in Table 1.

To illustrate the removal of pollutants, the first-order kinetic model associated with plug flow is more extensively used. However, Kadlec and Knight [42] proposed

Table 1
Rate constants for horizontal subsurface flow CWs

S. No.	Parameter	Type of wastewater	Influent concentration (mg/L)	Effluent concentration (mg/L)	Wetland area (m^2)	Type of plants	Rate constant (d^{-1})	Reference
1	BOD	Greywater	NA	NA	8.6	*Typha latifolia*	0.7564	[31]
		Landfill leachate	110–130	10–45	4	*Typha angustifolia* L.	0.201	[32]
		Stormwater	NA	NA	574	Grass swale	1.17	[33]
		Dairy farm	57 ± 7.5	11–27	152	*Schoenoplectus validus*	0.17–0.22	[34]
		Domestic	40–80	16–21	19.2	*Phragmites vallatoria*	0.1–0.24	[35]
		Domestic	NA	NA	3,125	*Phragmites australis* and *Typha latifolia*	0.079	[36]
		Mixture of domestic and pig farm	28–83	10–45	5	*Sesbania sesban*	0.08–0.21	[37]
2	COD	Municipal	88	26	72.3	*Typha latifolia*	0.81–0.86	[30]
		Greywater	NA	NA	8.6	*Typha latifolia*	0.5609	[31]
		Landfill leachate	250–460	70–376	4	*Typha angustifolia* L.	0.121	[32]
		Domestic	197	10–25	1.6	*Phragmites australis, Lythrum salicaria, Cladium mariscus, Iris pseudacorus*	0.22–0.55	[44]
		Stormwater	NA	NA	574	Grass swale	0.85	[33]
		Domestic	124–169	23–63	19.2	*Phragmites vallatoria*	0.06–0.08	[35]
		Mixture of domestic and pig farm	126–264	60–150	5	*Sesbania sesban*	0.07–0.17	[37]
		Domestic	240	NA	0.35	*Typha latifolia*	0.49	[38]
3	TP	Greywater	NA	NA	8.6	*Typha latifolia*	0.3993	[31]
		Stormwater	NA	NA	574	Grass swale	1.44	[33]
		Domestic	NA	NA	19.2	*Phragmites vallatoria*	0.11–0.18	[35]
		Mixture of domestic and pig farm	135–143	50–70	5	*Sesbania sesban*	0.07–0.25	[37]
		Dairy farm	11.2 ± 1.9	NA	19	*Schoenoplectus validus*	0.14	[39]
		Domestic	7.9	5.2	3,125	*Phragmites australis* and *Typha latifolia*	0.032	[40]
4	TN	Greywater	NA	NA	8.6	*Typha latifolia*	0.2459	[31]
		Landfill leachate	1.3–25.7	1.1–3.0	4	*Typha angustifolia* L.	0.247	[32]
		Stormwater	NA	NA	574	Grass swale	1.34	[33]
		Domestic	NA	NA	19.2	*Phragmites vallatoria*	0.03–0.07	[35]
		Mixture of domestic and pig farm	478–703	300–350	5	*Sesbania sesban*	0.06–0.25	[37]
		Dairy farm	38.2 ± 15.7	NA	19	*Schoenoplectus validus*	0.16	[39]
		Domestic	60.23	25.08	3,125	*Phragmites australis* and *Typha latifolia*	0.302	[40]
		Municipal	9.14	NA	7.2	*Phragmites australis*	0.371–0.552	[41]

NA, not available.

a modified first-order model known as K–C* model which predicts that the effluent concentration will reach a residual or background concentration (C*), instead of reaching to a zero value. This model depicts the decomposition of plant material and organic compounds in the wetland as well as the existence of a recalcitrant organic matter fraction which attributes to constant generation of organic matter within the system. According to the plug-flow regime model, different first-order rate constant values has been reported by several researchers for numerous constituents in HSSF CWs [43].

Sperling and Paoli [30] used three models (plug flow, dispersed flow and complete mix tanks in series) for prediction of the mean COD concentration profile along the HSSF CWs. Also, the same researcher reported good prediction of first-order reaction coefficient value (0.81 d^{-1}) based on the plug-flow assumptions which were within his expected range. For the dispersed-flow and tanks-in-series models, the first-order reaction coefficients were 0.85 and 0.86 d^{-1} – which indicated that these models are equivalent [30].

Villaseñor et al. [44] studied the kinetics of COD removal from synthetic wastewater using HSSF CWs with different plant species. The rate constants for removal of COD in CWs using various plants, namely, *Phragmites australis, Lithrum salicaria, Cladium mariscus* and *Iris pseudacorus* were 0.22, 0.37, 0.35 and 0.55 d^{-1}, respectively. Using the simple first-order decay model, Noor et al. [33] estimated the reaction rate constants from the kinetic data acquired from the CWs at Humid Tropics Center as well as USM Engineering Campus in Malaysia (Table 1).

According to different authors, the first-order rate constants for removal of various pollutants in HSSF CWs have been overviewed and represented in Table 1. From Table 1, it is evident that the rate constants for the removal of BOD are higher as compared with COD in most of the cases. In general, it can be concluded that the temperature at the location of the wetland, wastewater concentrations, size of CW and the macrophytes significantly affects the removal rate constants – which leads to variable range of the rate constants in the wetland.

4. Rate constants in vertical flow constructed wetlands

In case of vertical flow (VF) CWs, the wastewater is fed throughout the whole surface area of the wetland. VF CWs are most commonly fed intermittently with wastewater. The wastewater flows vertically downward through the media to the bottom of the wetland. The wetland is completely drained after the treatment which allows refilling of the bed with the air leading to excellent transfer of oxygen and hence attributes higher nitrification. The filtration bed oxygenation is enhanced due to the diffusion of oxygen from the air than the transfer of oxygen through plants aerenchyma system [27,45]. On one hand, due to the mostly aerobic conditions, the nitrification is higher in VF CWs as oxygen requiring nitrifying bacteria are favoured. On the other hand, denitrification may not occur to a large magnitude [27,46,47]. As reviewed by Wang et al., [48], VF CWs have shown higher removal efficiencies for total suspended solids (TSS) than HSSF CWs. However, relatively lower removal efficiencies for BOD_5 and COD have been observed for the VF CWs. In contrast, HSSF CWs exhibited high removal efficiencies for TSS, BOD_5 and COD [48].

Dan et al. [37] studied the potential of *Sesbania sesban* plants in vertical CW systems for the treatment of high-strength wastewater – which was a mixture of domestic and pig farm wastewater. The tropical conditions, high-strength wastewater as well as the high loading rates had attributed to higher removal rate constants than other studies reported in the literature (Table 2). For the first time, this study documented the use of *S. sesban* in CW systems for the treatment of wastewater – which also can be used for mulch for home-gardens or animal fodder [37].

In a pilot vertical subsurface flow wetland with red ferralitic soil and *Cyperus alternifolius* plants, the kinetics of organic matter and nutrient removal from domestic wastewater was studied by Pérez et al. [51]. The removal rate constants for BOD and TN were 3.64 and 3.27 d^{-1}, respectively.

The first-order rate constants for removal of pollutants in VF CWs have been overviewed and depicted in Table 2. In case of VF CWs also, it has been observed that the rate constants for the removal of BOD are higher as compared with COD.

5. Rate constants in free water surface wetlands

In free water surface (FWS) wetlands, the water surface is exposed to the atmosphere. The water flows over a vegetated soil surface from an inlet zone to an outlet zone. Most natural wetlands are FWS systems [50]. FWS CW has been reported by several researchers for the treatment of runoff waters such as urban, road and highway, airport, golf course, agriculture, dairy, drainage waters from coal mines, municipal sewage, landfill leachate, wood waste leachate, refinery process waters, pulp and paper effluents, fish hatcheries, etc. [52].

Recently, Noor et al. [33] reported reaction rate constants estimated from interpretation of the kinetic data obtained from natural wetland in Malaysia using the simple first-order decay model. A pseudo-first-order rate expression was used for estimating the reaction rate constants for Putrajaya Wetlands Park in Malaysia (Table 3). The capability of wetland for significant removal of BOD, TN, TP and TSS under tropical climate has been demonstrated by this study which enhances the knowledge in designing the wetlands under tropical climate. Teng et al. [53] also investigated the rate constants for seven different wetland sites in Taiwan.

According to different authors, the rate constants reported for free water surface wetlands are depicted in Table 3.

6. Conclusions

Inaccurate design, poor removal efficiencies of pollutants and operation problems are some of the failures due to lack of understanding on pollutant dynamics. The kinetics of removal of pollutants plays a significant role in designing the appropriate wetland system. Therefore, present study reviews the rate constants reported by several researchers for the removal of various pollutants such as BOD, COD, TN and TP in different types of wetlands. The first-order kinetic model is most commonly employed for the investigation of rate constants in wetlands. It has been observed that, for the estimation of rate constants, limited number of studies exist in the literature. Owing to warm temperatures and the associated higher rates of microbial activity, the treatment capacity

Table 2
Rate constants for vertical flow CWs

S. No.	Parameter	Type of wastewater	Influent concentration (mg/L)	Effluent concentration (mg/L)	Wetland area (m^2)	Type of plants	Rate constant (d^{-1})	Reference
1	BOD	Domestic	102	30	0.05	*Phragmites australis*	0.603	[49]
		Mixture of domestic and pig farm	28–83	10–30	1	*Sesbania sesban*	0.13–0.34	[37]
		Domestic	NA	NA	20	*Cyperus alternifolius*	3.64	[51]
2	COD	Domestic	1,516	684	0.05	*Phragmites australis*	0.301	[49]
		Mixture of domestic and pig farm	126–264	40–110	1	*Sesbania sesban*	0.11–0.35	[37]
		Domestic	27–87	21–45	9	*Phragmites australis*	0.111	[50]
3	TN	Domestic	84	54	0.05	*Phragmites australis*	0.995	[49]
		Mixture of domestic and pig farm	478–703	50–150	1	*Sesbania sesban*	0.19–0.62	[37]
		Domestic	NA	NA	20	*Cyperus alternifolius*	3.27	[51]
		Domestic	10–37	2–22	9	*Phragmites australis*	2.0	[50]
4	TP	Mixture of domestic and pig farm	135–143	5–25	1	*Sesbania sesban*	0.41–0.76	[37]

NA, not available.

Table 3
Rate constants for free water surface wetlands

S. No.	Parameter	Type of wastewater	Influent concentration (mg/L)	Effluent concentration (mg/L)	Wetland site	Total area (ha)	Rate constant (d^{-1})	Reference
1	BOD	Municipal	39.9 ± 24.9	14.3 ± 7.1	Hua-Jiang	13	0.179	[53]
		Municipal	38.7 ± 26.7	15.6 ± 13.0	Hsin-Hai Bridge (I)	10.9	0.343	[53]
		Municipal	38.5 ± 25.5	8.1 ± 5.9	Hsin-Hai Bridge (II)	4.9	0.901	[53]
		Municipal	40.1 ± 19.4	16.1 ± 8.2	Hsin-Hai Bridge (III)	6.5	0.200	[53]
		Municipal	41.0 ± 36.5	6.6 ± 1.6	Fu-Zhou	80	0.089	[53]
		Municipal	24.6 ± 19.4	10.0 ± 8.1	Daniaopi	13.1	0.800	[53]
		Municipal	30.9 ± 17.0	11.5 ± 8.4	Chen-Lin	26.5	0.026	[53]
		Stormwater	NA	NA	Putrajaya	38.24	1.16	[33]
2	COD	Stormwater	NA	NA	Putrajaya	38.24	0.98	[33]
3	TP	Stormwater	NA	NA	Putrajaya	38.24	1.34	[33]
4	TN	Stormwater	NA	NA	Putrajaya	38.24	3.44	[33]

NA, not available.

of CWs is likely to be high in tropical areas such as India. Considering the large applicability of CWs in developing countries as well as to achieve the better design of wetland systems across the globe, the research can be intended to derive values of the removal rate constants in CWs as limited kinetic studies are present in the literature.

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