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NUTRIENT REMOVAL FROM SYNTHETIC WASTEWATER CONTAINING CIPROFLOXACIN AND AMOXICILLIN USING HORIZONTAL FLOW CONSTRUCTED WETLAND

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Abstract:

The removal efficiency of ciprofloxacin and amoxicillin in wastewater treatment can be significantly influenced by monthly variations (January-February & March-April) and the presence of vegetation. CWs are one such alternative that can efficiently remove variety of pollutants from wastewater. Constructed Wetland (CWs) is viewed as a low-cost treatment technology with proven treatment efficiency. CWs can treat a variety of contaminants using low energy and natural systems by altering various design parameters. In this study two horizontal flow constructed wetlands (HFCW) are used and the concentration of antibiotics namely ciprofloxacin and amoxicillin, in each synthetic wastewater is 50ppm. The parameters were studied for influent and effluent wastewater. This study reports comparative pollutants removal from synthetic wastewater using HFCW. The water samples were collected as grab samples after 24 hours of duration. Results showed that CWs with reeds shows higher removal efficiency than without reed CWs considering nitrate and phosphate. From the results, it was also concluded that the removal efficiency of nitrate (49-89%) and removal efficiency (%RE) of phosphate ranges between (39-96%) in planted and non-planted CW.

Keywords: Constructed wetland, synthetic wastewater, Nitrate and Phosphate.

Nomenclature

CW = constructed wetland

CIP = ciprofloxacin

AMX = amoxicillin

%RE= removal efficiency

Introduction:

Environmental contamination has taken many forms in the last few decades due to the industrial revolution, urbanization, and high population development. When untreated wastewater is released into receiving water bodies (such as rivers, streams, or lakes), the quality of the water will deteriorate, creating an issue with clean water for human use (Emparan, Q., et al., 2019; Alsubih, Majed, et al., 2022a; Alsubih, Majed, et al., 2022b; Khan et al., 2023). In addition, the release of wastewater into a receiving body of water that has an excessive amount of nutrients (such as nitrogen or phosphorus) can cause eutrophication, which lowers the water's oxygen content (Lau et al., 1997). In the freshwater system, phosphorus in the form of orthophosphates is typically recognized as the limiting nutrient. Nevertheless, eutrophication may result from runoff wastewater with an excessive phosphorus concentration (Cai et al., 2013). Although nitrate is a naturally occurring substance in water, its high concentration in public water is undesirable because it can lead to serious health issues like methemoglobinemia (blue baby syndrome) or become a source of nitrosamines when it reduces to nitrite (Schoeman and Steyn, 2003; Abdel-Raouf et al., 2012). The aim of eliminating phosphate from wastewater is to prevent eutrophication of the water, as mentioned by Abdel-Raouf et al. (2012). Human activity has led to an increase in nutrient concentrations in water systems, posing serious environmental issues (Dalu et al., 2019). Harmful algal blooms caused by eutrophication can change the bio-physicochemical characteristics of nearby water systems

(Harding et al., 2019), produce off-flavors in drinking water (Kehoe et al., 2015), and cause cyanobacteria to produce toxins. Thus, mitigating eutrophication requires limiting nutrient releases, particularly those of nitrogen (N) and phosphorus (P), from agricultural sources and wastewater treatment facilities (WWTPs) (Fallahi, Alireza, et al. 2021; Mumtaj, Zeba Ali, et al., 2024). However, primary (settling tank) and secondary (e.g., activated sludge) treatment are used in the majority of wastewater treatment facilities worldwide (Asgharnejad and Sarrafzadeh, 2020), which has a limited capacity to remove N and P (Wang and Higgins, 2020). Furthermore, according to Su et al. (2012), conventional activated sludge reactors often have low phosphorus removal effectiveness. Phosphorus can be found in an aquatic environment as a particulate or dissolved phase. Both inorganic and organic phosphorus are found in the dissolved phase, while phosphorus adsorbed to particulates, phosphorus precipitates, and amorphous phosphorus are found in the particulate phase (Mumtaj, Zeba Ali, et al., 2024). Actually, there are usually no unique requirements necessitating phosphorous removal for smaller wastewater treatment plants (less than 100 m³ per day). Constructed wetlands need to be planned for high phosphorous removal rates if more decentralised systems—especially in rural areas—are to be given priority because to their cheaper costs (Lüderitz et al., 2001). In addition to being found naturally in our ecosystem, constructed wetlands can be designed to mimic the characteristics and activities of real wetlands. According to Sundaravadivel (2001), constructed wetlands serve as transitional districts between the terrestrial and aquatic systems. Wetlands have the ability to absorb pollutants, nutrients, and sediments; the wetland system can employ this ability to treat wastewater. Any of the aforementioned purposes for wetlands, such as constructed habitat, constructed flood control, constructed aquaculture, and constructed wastewater treatment, can be achieved by the construction of wetlands (Sundaravadivel 2001). Because constructed wetlands are made to execute a certain job as well as possible, they are more efficient than natural wetlands. Constructed treatment wetlands are made to allow wastewater from a source to enter the wetland and eventually depart it (Khanijo, I. 2002; Mumtaj, Zeba Ali, et al., 2024a). Wetlands that are constructed are lined so that groundwater is not impacted. The hydraulic residence time (HRT) is the amount of time that water stays in the wetland. The effectiveness of a designed treatment wetland is determined by how well it removes nutrients and contaminants from wastewater. Sakadevan's 1999 study states that constructed wetlands have the ability to remediate wastewater by eliminating N and P. Acid mine drainage, storm water runoff, industrial wastewater, municipal wastewater, and agricultural effluent from animal operations have all been treated using constructed wetlands (Lin, Ying-Feng, et al. 2002; Khan et al., 2022). Studies have shown that treatment wetland systems are capable of eliminating large volumes of organic matter, nitrogen, phosphorus, trace elements, suspended particles, and microorganisms from wastewater (Knight, R.L., Kadlec, R.H. and Ohlendorf, H.M., 1999; Khan et al., 2022; Mumtaj, Zeba Ali, et al., 2024b). The benefits of constructed wetland systems include reduced energy consumption and maintenance needs, reasonable capital expenditures, and enhanced wildlife habitat (International Water Association, 2000). The nitrogen and phosphorus standing stocks of the majority of tall macrophytes, like *Phragmites australis* and *Phalaris arundinacea*, typically range from 30 to 80 g N m⁻² and 2 to 6 g P m⁻², respectively. Nonetheless, standing stocks in stands with extremely high biomass might surpass 150 g N m⁻² and 15 g P m⁻² (Vymazal et al., 2005). According to reports from artificial and natural wetlands used for wastewater treatment, there is little to no variation in the N and P standing stocks (Vymazal et al., 1999). Nutrient-limited settings may have significantly reduced standing stocks; wastewaters do not exhibit this behavior (Vymazal, 2011; Mumtaj, Zeba Ali, et al., 2024a).

The aim of this study was to investigate the removal efficiency of HFCW for nitrate and phosphate removal in synthetic wastewater of Ciprofloxacin (CIP) and Amoxicillin (AMX).

Method and Materials:

Preparation of Synthetic wastewater: Synthetic wastewater should be supplemented by carbon-containing material, nutrients (nitrogen, phosphate) and other condiments (Lima et al. , 2018). In the current study, the synthetic wastewater composition used consists of glucose 40 mg/L, acetic acid 50 mg/, K₂HPO₄ 10 mg/L, urea 60 mg/L (Tang et al. , 2019), MnCl₂. 4H₂O 0.5 mg/L,

$\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ 0.5 mg/L, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 7.5 mg/L, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 100 mg/L were the trace elements observed (Biplob et al., 2011). Towards avoid variations in pH level use 0.5 mol/L NaHCO_3 (Nasseri et al., 2014). In the synthetic wastewater, the level of antibiotic concentration is at 50mg/l. The antibiotics employed in synthetic wastewater are Amoxicillin and Ciprofloxacin.

Study site and Design of horizontal flow constructed wetlands: Horizontal flow Constructed Wetlands were set up in Integral University (IUL), Kursi Road, Lucknow, and Uttar Pradesh in India, Latitude 26.95862 ° or 26° 57' 31" north. The experiment consisted of two horizontal flow constructed wetlands of 1m width and 2m length; one planted (CW1) with *Arundo donax* and the other without plant (CW2). They range from 1.5 inches in length to 0.5 inches in width.

The sampling was conducted on the outlets at 24 HRT (hydraulic retention time). Clean and pre-rinsed polypropylene (PVC) bottles of 500 ml each were used for sampling. The bottles used to collect the samples were 500 ml capacity polypropylene bottles which had been previously cleaned and rinsed.

Removal efficiency (%RE) was calculated as the percent removal for each parameter and was calculated by-

$$\%RE = (C_{in} - C_{out} / C_{in}) \times 100 \dots \dots \dots (1)$$

Where,

C_{in} = Antibiotics concentration in influent

C_{out} = Antibiotics concentration in effluent

Research laboratory examination (influent and effluent): Removal of nutrient- Nitrate concentration was identified with the help of UV-visible spectrophotometric technique and the concentration of sulphate anion was determined using a spectrophotometer or turbidity meter. The Figure 1%2 shows the %RE of CFD in CW1 and CW2 during January, February, March and April. According to studies, constructed wetlands can eliminate anywhere from 30% and 94% of phosphorus inputs (Vymazal, 2007). However, most constructed wetlands only removed around 50% of the phosphorus.

Results: The removal efficiency of ciprofloxacin and amoxicillin in wastewater treatment can be significantly influenced by monthly variations (January-February & March-April) and the presence of vegetation. This study evaluates the removal efficiencies of two antibiotics— Ciprofloxacin and Amoxicillin. The results are compared between non-planted and planted constructed wetlands during January- February and March- April. Table 1 and 2 shows the nitrate and phosphate %RE of Ciprofloxacin and Amoxicillin in non-planted and planted constructed wetlands during January- February and March- April.

Table 1 shows the Removal rates (%RE) of Nitrate (nitrogen)

Antibiotics	Nutrients	CW1 (January)	CW2 (January)	CW1 (February)	CW2 (February)	CW1 (March)	CW2 (March)	CW1 (April)	CW2 (April)
Ciprofloxacin	Nitrate	50%	53%	49%	57%	69%	78%	85%	93%
Amoxicillin	Nitrate	46%	51%	61%	68%	64%	72%	82%	88%

Table 2 shows the Removal rates (%RE) of Phosphate (phosphorous)

Antibiotics	Nutrients	CW1 (January)	CW2 (January)	CW1 (February)	CW2 (February)	CW1 (March)	CW2 (March)	CW1 (April)	CW2 (April)
Ciprofloxacin	Phosphate	62%	69%	70%	72%	71%	80%	89%	96%
Amoxicillin	Phosphate	39%	49%	66%	75%	75%	83%	80%	86%

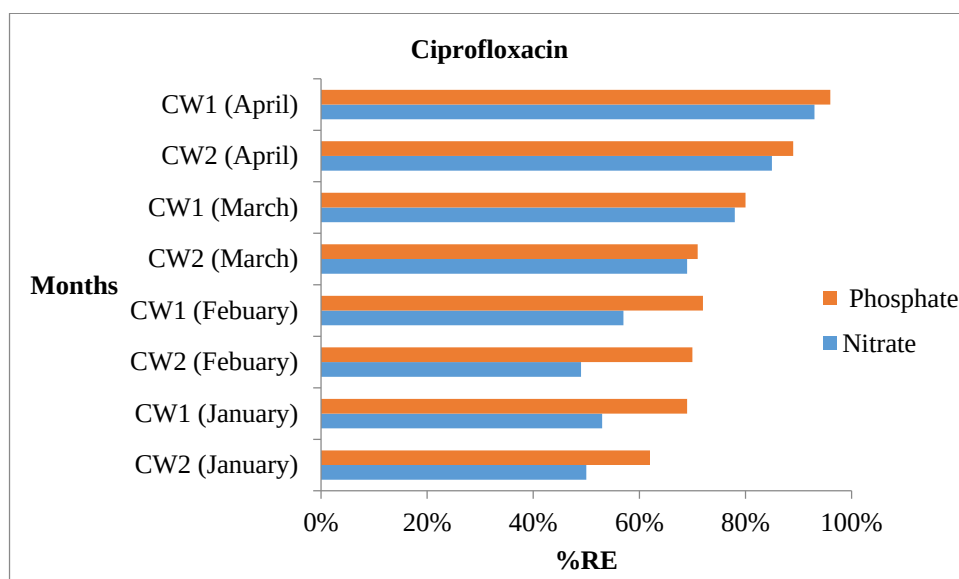


Figure 1 shows the %RE of CIP in CW1 and CW2 during January, February, March and April.

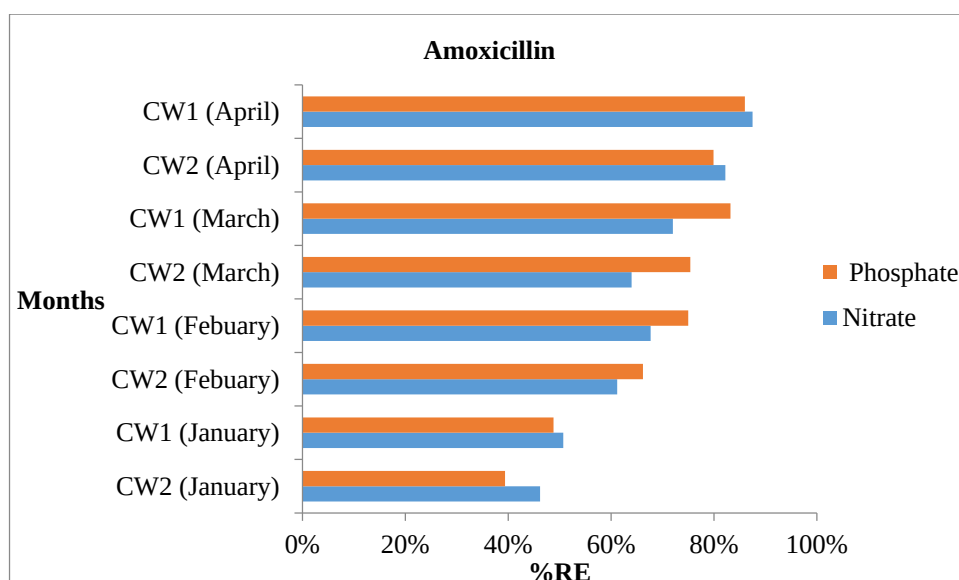


Figure 2 shows the %RE of AMX in CW1 and CW2 during January, February, March and April.

Conclusion: During our survey, we examined the removal of plant nutrients in constructed wetland, which was built for the treatment of synthetic wastewater. Considering the removal of plant nutrients, unfortunately, the nitrogen removal is not always satisfactory in the system. Percent removal rate of phosphorous is in accordance with the results of scientific literature and indicates effective phosphorous removal in the CW. Results showed that CWs with reeds shows higher removal efficiency than without reed CWs considering nitrate and phosphate. From the results, it was also concluded that the removal efficiency (%RE) of nitrate (49-89%) and removal efficiency of phosphate ranges between (39-96%) in planted and non-planted CW.

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