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Wastewater Stabilisation Ponds: Removal of Emerging Contaminants

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ABSTRACT

Wastewater stabilisation ponds are the simplest, and most economical and maintainable way of municipal wastewater treatment. The fate of selected emerging contaminants using algal monocultures has been studied. However, in an actual wastewater treatment plant, it is likely to be different. Accordingly, a need was felt to take up this study. A waste stabilisation pond based wastewater treatment plant having five ponds in an area of approximately 14 hectares and working for 30 years was selected. High removal (> 75%) was observed in the case of paracetamol and carbaryl. Moderate removal efficiencies (50-75%) were found for malathion, erythromycin, clofibric acid and 17beta-estradiol while low (< 50%) removal efficiencies were witnessed in the case of aldrin, endosulfan, dichlorodiphenyltrichloroethane, hexachlorocyclohexane and diclofenac. Results show that most of the removal takes place in initial ponds, with higher efficiencies in summer and lower in winter. Results suggest that waste stabilisation pond based wastewater treatment plant is capable of removing emerging contaminants to some extent.

KEYWORDS

Waste stabilisation pond, Emerging contaminants, Natural wastewater treatment, Pharmaceuticals, Endocrine disruptors, Pesticides.

INTRODUCTION

Wastewater Stabilisation Ponds (WSPs) are simple and easy to build and operate. WSPs can tolerate high organic and hydraulic loadings and are less susceptible to shock loadings. WSPs have large surface area and shallow depth. Mechanisms operative in WSPs are complex and depend on temperature, pH, Dissolved Oxygen (DO), daylight hours, light intensity, etc. Accumulation of sludge is higher in winter months due to lower microbial activity. In WSPs, processes responsible for the removal of organic matter, nutrients, pathogens, etc. are both physicochemical and biological. In developing countries, wherever sufficient land is available, use of WSPs is the simplest and most sustainable way of wastewater treatment. WSPs are also in use in Europe and the USA in communities with inhabitants ranging from as low as 2,000 to 5,000 [1]. Furthermore, in

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North Africa, the Middle East, Asia and South America, due to the higher temperatures, communities with the population as high as one million are successfully utilising WSPs for the wastewater treatment [1].

With the change in lifestyle and rapid progress in technology, many new products/materials are being released to the aquatic environment, particularly to the wastewaters. This has led to the rise of a completely new class of pollutants over the last decade called Emerging Contaminants (ECs) which are mostly pharmaceuticals, pesticides, personal care products, endocrine disruptors, etc. These compounds occur in wastewaters in highly varying range, i.e. from nanograms per litre [ng/L] to hundreds of micrograms per litre [µg/L] [2]. Most of these pollutants are suspected of being carcinogenic and highly toxic. The adverse effects of these pollutants include chronic eco-toxicity and buildup of antibiotic resistance in humans and livestock. In general, current conventional wastewater treatment processes are not capable of attenuating ECs. Therefore, ECs can still be present in unacceptable quantity in the effluents from Wastewater Treatment Plants (WTPs). Discharge of such effluents to the environment can cause contamination of water sources used for drinking and agricultural.

WSPs, originally designed for the removal of organic matter and pathogens have been in use for decades. Even though WSPs are not designed to remove ECs, however, certain mechanisms of removal peculiar to WSPs result in higher removal of ECs in WSPs as compared to other processes, e.g. activated sludge process [3]. Abinandan and Shanthakumar [4] suggested that conditions like high Hydraulic Residence Time (HRT) favour the removal of ECs, which otherwise have slow kinetics. They further proposed that exposure to sunlight favour the removal of some of the ECs by photo-degradation. An additional consequence of the extremely high HRT is that the pollutants are exposed to ever-changing temperature and photo intensity. Another unique feature which makes WSPs effective in the removal of both pathogens and ECs is the community dynamics between autotrophic and heterotrophic organisms, i.e. algae and bacteria. A symbiotic relationship between the bacteria and microalgae exist. Bacteria under aerobic conditions convert organic matter to carbon dioxide (CO_2), ammonium cations (NH_4^+), and phosphate anions (PO_4^-) which are taken by algae for their growth. In turn, algae enrich aqueous media with oxygen to support the biodegradation of organics under aerobic conditions. This unique feature helps in increasing biomass productivity, which in turn increases the removal of ECs by sorption [4]. The photosynthesis carried out by the algae cause a daily change in the pH and DO levels which change the redox conditions inside the pond. The varying redox conditions assist in the breakdown of ECs [4].

Recently, some researchers have used certain strains of microalgae for the removal of certain ECs. Lopez-Serna *et al*. [5] studied the removal of five pharmaceuticals and personal care products (ibuprofen, naproxen, salicylic acid, triclosan and propylparaben) using two novel algae-bacteria reactors. It was found that naproxen and salicylic acid were mainly removed due to biodegradation while sorption contributed for the removal of ibuprofen, triclosan and propylparaben. Parlade *et al*. [6] reported that algae-bacteria consortium under favourable seasonal conditions could remove 93.7% of 17beta-estradiol. Wang *et al*. [7] studied the removal of triclosan using three freshwater algae, *scenedesmus obliquus*, *desmodesmus sp*. and *chlorella pyrenoidosa*. It was reported that *chlorella pyrenoidosa* removed triclosan by cellular uptake and scenedesmus obliquus and *desmodesmus sp*. by biotransformation. Norvill *et al*. [8] found that in high rate algal ponds the removal of tetracyclin changes from 99% to 93% when changing the HRT from 7 to 4 days. Main removal mechanisms were photo-degradation and sorption. Gentili and Fick [9] reported the removal of different contaminants using green algae *dictyosphaerium*. They found that ciprofloxacin and trimethoprim removal is lower than 11%. Bai and Acharya [10] found that *namnochloris sp*. are capable of removing 100% ciprofloxacin, but show lower removal of less than 10% for carbamazepine and trimethoprium. Ali *et al*. [11] studied the removal of tramadol using *scenedesmus obliquus* cultured in BG-11 media and reported removal of 91%. De Godos *et al*. [12] carried out pioneer work using High Rate Algal Ponds (HRAP) for the removal of antibiotic tetracycline from synthetic wastewater. Matamoros *et al*. [13] reported that solar radiation and HRT affects the removal efficiency of certain ECs in an HRAP pilot plant processing real wastewater. Only selected ECs have been tried. Xiong *et al*. [14] reported that *chlamydomonas mexicana* and *scenedesmus obliquus* removed 35 and 28% carbamazepine by biodegradation, respectively. Escapa *et al*. [15] studied the removal of paracetamol and salicyclic acid using *chlorella sorokinia* from synthetic wastewater. Peng *et al*. [16] used *scenedesmus obliquus* and *chlorella pyrenoidosa* for studying the biotransformation of norgestrel and progesterone. Hom-Diaz *et al*. [17] reported that *selenastrum capricornutum* and *chlamydomonas reinhardtii* removed 42 and 54% of beta-estradiol and 17alfa-ethylestradiol, respectively, from centrate of the anaerobic digester. Escapa *et al*. [18] proved that *chlorella vulgaris*, *scenedesmus obliquus* and *chlorella sorokiniana* are capable of removing diclofenace from the water. de Wilt *et al*. [19] found that *chlorella sorokiniana* removed six pharmaceuticals (diclofenac, ibuprofen, paracetamol, metoprolol, carbamazepine and trimethoprim) during the batch study using urine and diluted anaerobically treated blackwater. Liu *et al*. [20] tested antibiotic sorption on *microcystis aeruginosa*, which was cultivated in BG-11 media. Shi *et al*. [21] used a mixture of six algae species (*anabaena cylindrica*, *chlorococcus*, *spirulina platensis*, *chlorella*, *scenedesmus qu*., and *anaebena var*.) cultivated in synthetic wastewater and found 52-56% biodegradation of endocrine distributors.

So far, most of the studies have been carried out on laboratory/pilot scale using monocultures of algae or a mixture of few known species only. It is believed that fate of a particular EC in a controlled environment having a particular algal monoculture is likely to be different compared to in an actual WSP having a wide variety of algal and bacterial species treating a blend of ECs under changing environmental conditions. WSPs consists of different types of ponds which have their unique properties, i.e. anaerobic, aerobic-anaerobic (facultative) and aerobic (maturation). This unique feature makes WSPs effective in removing ECs and pathogens. Accordingly, a need was felt to take up the study regarding the attenuation/fate of ECs at a full-scale WSP based WTP. Thus, this study aimed to quantify the destiny of ECs in WSP along with the assessment of possible mechanisms responsible for their attenuation. Also, attempts have been made to correlate physicochemical properties of a particular EC with the predominant mechanism responsible for its removal. WSP based WTP located at Lakkarghat, Rishikesh (latitude 30° 6’ N, longitude 78° 18’ E) was selected for the study. It is situated in the foothills of Shivalik ranges of the Himalayas on the bank of river Ganga and is in operation since last 30 years. Although it was initially designed for a wastewater flow of 6 million litres per day [MLD] from Rishikesh, at present it receives around 15 MLD of wastewater serving a population of more than 1 lakh.

MATERIALS AND METHODS

A schematic flow diagram of the WSP based WTP is shown in Figure 1. It consists of five ponds, i. e. one anaerobic, two facultative and two maturation ponds in series covering an area of approximately 14 hectares. Dimensions and HRT of each pond are given in Table 1. The WTP also has a pretreatment unit, i. e. screens for the removal of floating materials. The treated effluent of the WTP is discharged into Song River, which ultimately discharges into River Ganga.

Sampling

Sampling was done once or sometime twice a month from six locations in WTP, as shown in Figure 1, from September 2016 to December 2017. Sampling points have been marked from ‘a’ to ‘f’. ‘a’ indicates influent, ‘b’ indicates outlet of the anaerobic pond, ‘c’ and ‘d’ indicate the outlets of facultative ponds 1 and 2, respectively, and ‘e’ and ‘f’ indicate outlets of maturation ponds 1 and 2, respectively. Twenty one samples were collected from each sampling point. The samples were collected in 1-litre amber glass bottles to inhibit photo-degradation. Before sampling, the sampling bottles were washed with distilled water and later rinsed with acetone to remove any traces of organic contaminants.

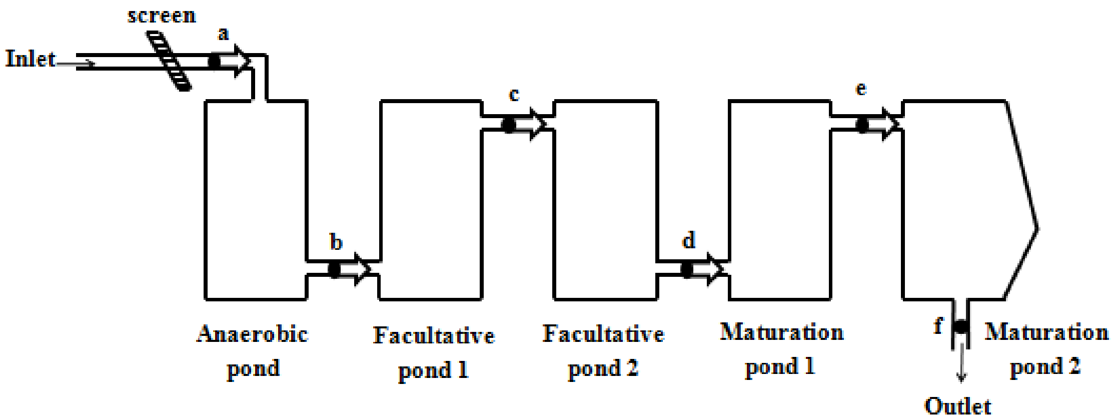

Figure 1. Schematic flow diagram of WSP based WTP depicting sampling locations

Table 1. Waste stabilisation ponds: dimensions and hydraulic retention times

Ponds	Area [m^2]	Depth [m]	Volume [m^3]	HRT (days)
Anaerobic pond	14,028	1.5	21,042	1.40
Facultative pond 1	14,028	1.2	16,833.6	1.12
Facultative pond 2	14,028	1.2	16,833.6	1.12
Maturation pond 1	14,534	0.59	8,575.1	0.57
Maturation pond 2	10,470	0.65	6,805.5	0.45

Chemicals/Cartridges used

Standard solutions of selected pharmaceuticals, pesticides and endocrine disruptor were purchased from Sigma Aldrich (Bangalore, India). Solid Phase Extraction (SPE) was carried out using 200 mg Bond Elut Plexa cartridge (Agilent Technologies, India). HPLC-grade methanol, n-hexane, ethyl acetate, acetone, water and acetonitrile (Merck, India) were used as solvents for the preparation of calibration standards and extraction of samples. Distilled water used for rinsing the glassware was produced using Elix Essential 3 water purification system (Merck Millipore, USA). The stock standards were stored in amber glass bottles at a temperature of 4 °C.

Extraction of Emerging Contaminants

The SPE cartridges were rinsed with 3 mL methanol, 3 mL 50:50 v/v ethyl acetate: acetone and 3 mL HPLC grade water. The wastewater samples were then transferred to the cartridges maintaining a flow rate of 6-8 mL min^{-1} under vacuum. After this, cartridges were washed with 5% methanol-water and vacuum dried for 10 minutes. Hereafter, successive dilution of ECs was carried out with 3 mL n-hexane, 3 mL ethyl acetate and 3 mL ethyl acetate: acetone (50:50 v/v). Elutes from the cartridges were then evaporated to make a final volume of around 100-150 µL. A mild stream of nitrogen was maintained during the evaporation. Derivatisation of the samples was carried by adding 70 µL of N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) in each of the condensed elute and keeping the mixture at 70 °C for 35 min.

Gas Chromatograph-Mass Spectrometry analysis

Quantification of ECs was carried using the calibration curve for every sample. Gas chromatographic seperation was carried out using Agilent 7890B Gas Chromatograph-Mass Spectrometry (GC-MS) using split/splitless injector. DB-5MS capillary column (Agilent) of length 30 m, internal diameter 0.25 mm, coated with a 0.25 μm film of 5% phenyl, 95% dimethylarylene siloxane was used. The 99.999% ultrapure helium was used as a mobile gas. The flow rate of 1 mL min^{-1} and a temperature of 250 °C was maintained in the transfer-line. The splitless mode was used to inject the 3 μL samples. For GC separation, temperature program was arranged at five different steps: started at 80 °C (held for 2 min), then set at 5 °C min^{-1} to 180 °C (held for 5 min), set at 5 °C min^{-1} to 250 °C (held for 5 min), set at 5 °C min^{-1} to 280 °C and then was held isothermally at 280 °C for 5 min. The GC was connected to an ion trap mass spectrometer operated under electronic impact mode at 70 eV using scan mode (scan range from 50-1,000 amu).

RESULTS AND DISCUSSION

During the sampling, eleven ECs were regularly detected in the influent (sampling location, a) and outlets of the different ponds (sampling locations, b, c, d, e, and f). Table 2 shows some of the relevant physio-chemical properties of these ECs, mainly pharmaceuticals and pesticides. All pharmaceuticals, selected in this study were polar, having higher water solubility compared to Endocrine Disruptors (EDs) and pesticide, as shown in Table 2. Only paracetamol among pharmaceuticals has a lower solubility in water. Lower values of log K_{ow} (K_{ow} – octanol-water partition coefficient) suggest hydrophilicity and higher values suggest hydrophobicity. Paracetamol has the lowest value of log K_{ow} among emerging contaminants studied (Table 2), which suggest that it is hydrophilic. Granberg and Rasmuson [24] reported that paracetamol contains alcohol and amide group which make paracetamol polar, able to form a hydrogen bond. However, the methyl group and aromatic rings in paracetamol impact the nearby molecules of water to the extent that net result has low water solubility. Diclofenac and erythromycin are hydrophobic. Their removal can occur due to adsorption or photo-degradation as compared to biodegradation. 17beta-estradiol is hydrophilic and has slightly lower water solubility but can biodegrade too. The structure of 17beta-estradiol has a hydroxyl group which can easily be biodegraded by aerobic and anaerobic bacteria [25]. Pesticides have the recalcitrant structure of organochlorines and are persistence in nature. They have high half-life and are highly hydrophobic. Both of these factors suggest that their removal can occur due to sorption or photo-degradation. Carbaryl shows higher water solubility among the selected pesticides. It does not contain organochlorine and has ammine as a functional group which can be biodegraded.

The primary sources of pharmaceuticals in the plant influent appear to be domestic and hospital wastewaters and leachate from the landfill. Larsson *et al*. [26] found that waste from the pharmaceutical industries located at Hyderabad, India contained 61 drugs, out of which 11 drugs exceeded > 100 μg/L. The maximum concentration of 31 mg/L was found for ciprofloxacin. In a country like India, where agriculture is the mainstay of the economy, pesticides are used in large quantities. India started the production of pesticides in 1952 and currently ranks second in the production in Asia and 12th overall in the world [20]. The indigenous production of pesticides in the country has been on the rise from 5,000 T being produced in 1958 to 102,240 T in 1998 [27]. Globally, consumption of pesticide is estimated to be 2×10^6 T/year [28], 2% of which is consumed in India [27]. The main source of pesticides in wastewater seems to be agricultural runoff.

Removal in this study refers to the conversion of a particular emerging contaminant to a compound other than the parent compound. Physical removal was due to sorption of particular organic contaminants on the surface of biomass or settling of organic matter.

Biochemical removal may be due to the biodegradation by algae or bacteria, and photo-degradation due to the breaking of the biochemical bond of particular contaminants by sunlight which induces singlet oxygen or hydroxyl radicals.

Table 2. Physico-chemical properties of selected ECs [22, 23]

S. No.	Name of the compound	Molecular weight [g/mol]	log K_{ow}	Water solubility [mg/L]	P-polar, NP-non polar
		Pharmaceuticals			
1	Clofibric acid	214.64	2.57	582.5	P
2	Diclofenac	296.15	4.51	4.518	P
3	Paracetamaol	151.163	0.46	0.0227	P
4	Enthromycin	733.97	3.06	4.2	P
		Endocrine disruptors			
5	17beta-estradiol	272.38	4.01	3.6	P
		Pesticides			
6	Endosulfan	406.92	3.83	1.48	NP
7	Aldrin	364.9	6.5	0.014	NP
8	Dichlorodiphenyltrichloroethane	354.47	6.91	5.50×10^{-3}	P
9	Hexachlorocyclohexane	296.851	5.28	-	P
10	Carbaryl	245.31	3.18	48.71	P
11	Malathion	313.65	-	-	P

Occurrence and removal of pharmaceuticals in Wastewater Stabilisation Ponds

Out of the 4 pharmaceuticals detected, paracetamol, diclofenac and clofibric acid are Analgesic/Non-steroid Anti-Inflammatory Drugs (NSAIDs) while erythromycin is an antibiotic. The analgesics were detected in higher quantities in raw influent as they are unregulated over the counter drugs and are consumed in relatively higher doses.

The fate of paracetamol at different stages of WTP is shown in Figure 2. It is quite clear that the bulk of paracetamol is removed in the anaerobic and facultative ponds due to the action of anaerobic and aerobic bacteria while the balance gets removed in the maturation ponds due to photolysis process. As per standards laid down by WHO, the permissible daily dose of paracetamol is as high as 3 g per adult [29]. Due to this fact, paracetamol has been detected in higher concentrations in the influent (143-215 µg/L, average around 200 µg/L) to the Lakkarghat WTP. Paracetamol being a biodegradable compound with high biodegradation constant (K_{biol}) > 10^2 $g_{ss}{}^{-1}d^{-1}$ [19], (K_{biol} – biodegradability constant, g_{ss} – gram suspended solids) displayed high removal efficiency (~79%) in the present case. In the case of surface waters, De Laurentiis *et al.* [30] showed that photolysis is an important mechanism for the removal of paracetamol. Mohapatra *et al.* [31] studied the removal efficiency of paracetamol in a WTP having 4 facultative ponds in series with HRT of two days each and found removal to be 45-90% which is in line with the 59-89% removal efficiency found in the present study.

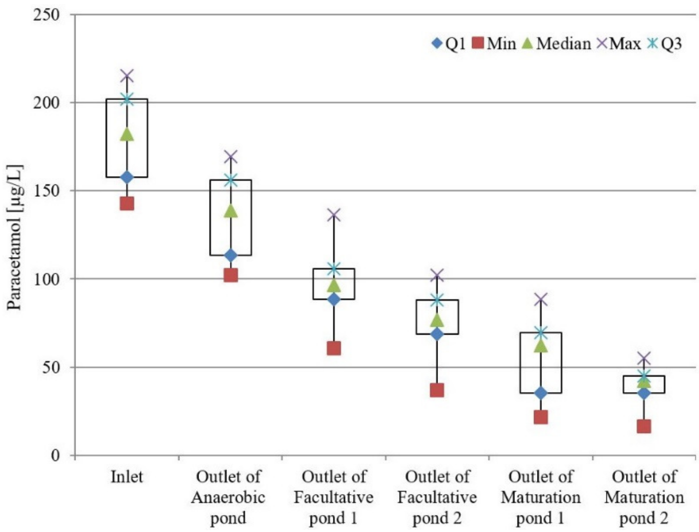

Figure 2. The fate of paracetamol at different stages of WSP based WTP

The fate of diclofenac at different stages is shown in Figure 3. It appears that almost the same order of removal takes place at different stages. The removal efficiency was in the range of 24-40%. The reason for lower removal of diclofenac appears to be its high log K_{ow} (> 4) indicating that it is a hydrophobic compound not easily dissolved in water. Kimura *et al.* [32] reported that diclofenac was a difficult compound to biodegrade, and sorption was the main removal process. Radjenovic *et al*. [33] found that diclofenac has slow biodegradability. Studies were conducted for the removal of diclofenac by monocultures of algal species sorokinion by de Wilt *et al*. [19] and *chlorella sorokiniana* and *chlorella vulgaris* by Escapa *et al*. [11]. They observed the removal efficiencies to be between 40-60% and 22-30%, respectively. Tixier *et al*. [34] studied the removal of diclofenac in surface water and found direct photo-transformation as the main removal process. It was also concluded by de Wilt *et al*. [19] that for the removal of diclofenac, the predominant mechanism was photo-transformation. Comparing the results of the present study and the study carried out by Radjenovic *et al*. [33] it appears that in WSPs slightly better removal (31% compared to 25%) of diclofenac takes place compared to ASP.

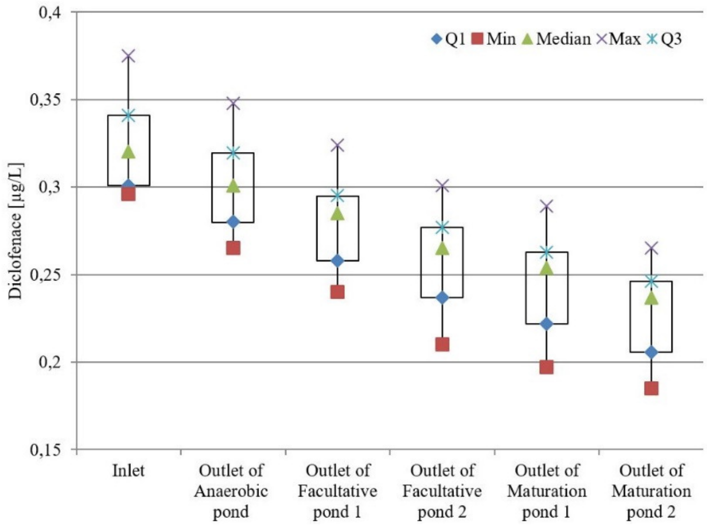

Figure 3. The fate of diclofenac at different stages of WSP based WTP

The fate of erythromycin at different stages of WTP is shown in Figure 4. Erythromycin has moderate log K_{ow} (3.06) and is slightly hydrophobic. The removal efficiency observed was in the range of 51-75%. Erythromycin is an antibiotic while other pharmaceuticals studied were analgesic/NSAID. It appears from Figure 4 that most of the removal in case of erythromycin take place in facultative and maturation ponds and not in the anaerobic pond as it was observed in case of other pharmaceuticals studied. Zhou *et al*. [35] also noticed the good removal of erythromycin (55-70%) when using four microalgae species, *chlamydomonas reinhardtii*, *scenedesmus obliquus*, *chlorella pyrenoidosa* and *chlorella vulgaris*. Ruhmland *et al*. [36] carried a study near Berlin using 1,550 m^2 WSP with four days HRT and showed that the removal efficiency varied from 37-79%. Results of the present study and studies by Zhou *et al*. [35] and Ruhmland *et al*. [36] indicate that processes occurring in algal ponds (biodegradation, photo-degradation, sorption, etc.) support the removal of erythromycin.

The fate of clofribic acid at different stages of WTP is shown in Figure 5. In the influent, to WTP it varied from 0.13-0.26 µg/L, and in the finally treated effluent, it ranged from 0.04-0.12 µg/L. The removal efficiency observed was in the range of 46-77%. Not many researchers have studied the removal or mechanisms of the removal of clofibric acid. Dordio *et al*. [37] studied the removal of clofibric acid in winter (12 °C) and summer (26 °C) in planted microcosm constructed wetland and observed the removal of 45% and 75%, respectively. Clofibric acid is water soluble, has a moderate value of log K_{ow} (2.57) and very high water solubility (582.5 mg/L). Based on the value of log K_{ow} and solubility, the possibility of biodegradation is high.

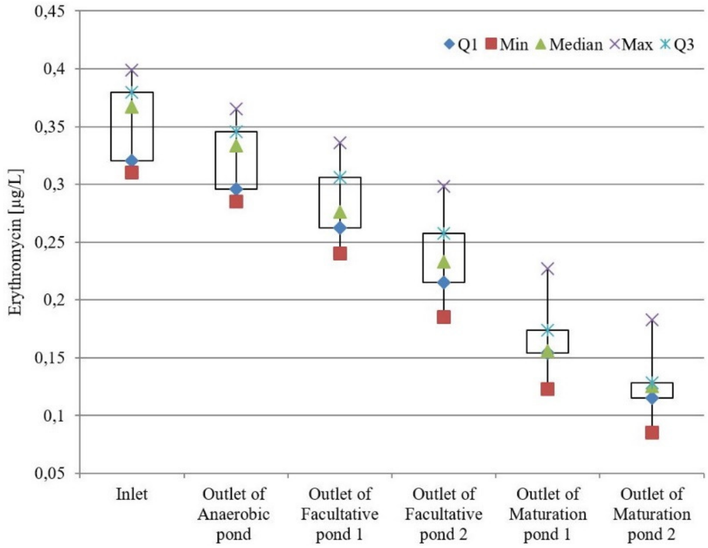

Figure 4. The fate of erythromycin at different stages of WSP based WTP

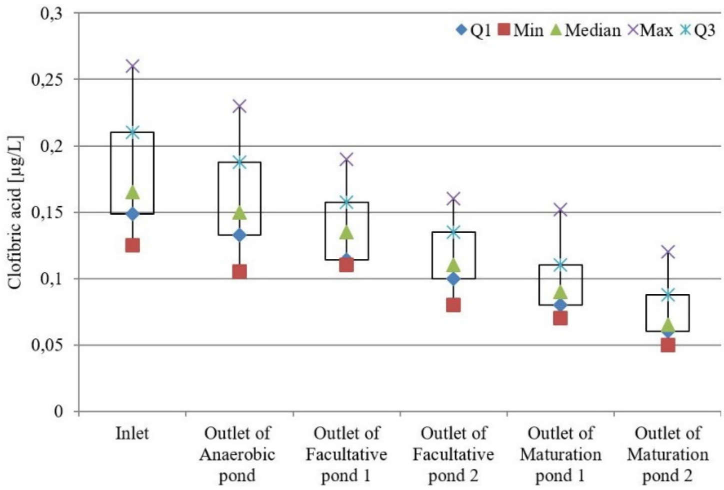

Figure 5. The fate of clofribic acid at different stages of WSP based WTP

Occurrence and removal of Endocrine Disruptors in Wastewater Stabilisation Ponds

EDs possess the capability to cause disruptions to the endocrine system of humans and animals. Due to this, extensive studies on the removal of ED have been carried out in developed countries.

The fate of 17beta-estradiol at different stages of WTP is shown in Figure 6. The removal efficiency observed was in the range of 45-59%. As shown in Figure 6, 17beta-estradiol was mainly removed in the anaerobic and facultative ponds. Joss *et al*. [38] reported that oxidation of estradiol ($150 < K_{bio} < 1,000$) was higher under anaerobic and anoxic condition. Lee and Liu [25] tried to identify the mechanisms of aerobic and anaerobic degradation of EDs in WTPs. They reported that degradation of 17beta-estradiol commences with its oxidation into estrone, which is further oxidised into CO_2 and water. Gomez *et al*. [39] found that the long HRTs of 78 and 43 days in two French WSPs resulted in twice the removal efficiency compared to a WTP consisting of a trickling filter followed by post-tertiary treatment with 20 days HRT. Servos *et al*. [40]

studied 18 municipal WTPs and found that lagoons with high HRT and sludge retention time were more efficient in reducing the level of EDs. Shi *et al*. [21] carried lab scale studies using three ponds in series with 20 days HRT using mixed microalgae species. They observed the removal efficiency of 84%. Different studies [21, 39, 40] show that due to the longer HRT, WSPs were more effective in the removal of EDs, including 17beta-estradiol compared to conventional WTPs having lower HRT.

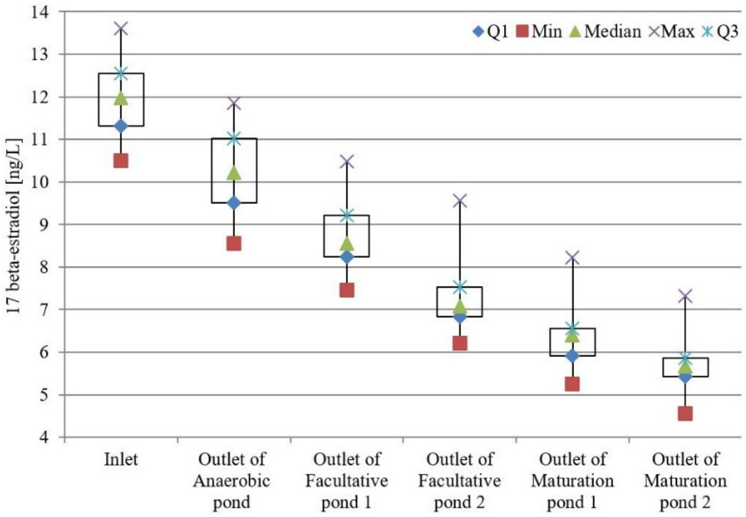

Figure 6. The fate of 17beta-estradiol at different stages of WSP based WTP

Occurrence and removal of pesticides in Wastewater Stabilisation Ponds

Out of the six pesticides detected, Dichlorodiphenyltrichloroethane (DDT), Hexachlorocyclohexane (HCH), aldrin and endosulfan fall into the category of organo-chlorines. This class of pesticides is one of the most hazardous classes and hence, is banned in most of the countries. Due to the recalcitrant structure of organo-chlorines, only a specific class of bacterial and fungal species possesses the capability of degrading them [41].

The fate of DDT at different stages of WTP is shown in Figure 7. The removal efficiency observed was in the range of 22-41%. The major removal of DDT occurred in the anaerobic and facultative ponds. DDT has very high log K_{ow} (6.91), which make it highly hydrophobic. It has very low water solubility. Yang *et al*. [42] showed that it has a high persistence (0.1-4 ng/m^2) and high biomagnification in the food chain. It also has a very high half-life. High log K_{ow}, very low water solubility and high half-life indicate that biodegradation of DDT is difficult and possibly sorption and photo-degradation are the chief removal processes.

Figure 8 shows the removal of HCH at different stages of WTP. The overall removal efficiency ranged from 22-44%. HCH is an organochlorine pesticide with high persistence in nature. HCH has been classified as moderately hazardous by WHO and is a potent carcinogen. India is among the top consumers of HCH in the world with most of it being found in the rivers which pass through the agricultural areas [43]. Figure 8 indicates that the major removal occurs in the first three ponds only. It also possesses a high log K_{ow} (5.28), thus making it hydrophobic and insoluble in the water. The removal of HCH is likely to take place through photo-degradation and sorption in WSPs.

The fate of endosulfan at different stages of WTP is shown in Figure 9. The removal efficiency observed was in the range of 18-37%. Matamoros and Rodriguez [44] conducted a study using microalgae from HRAP with dominant species as *scenedesmus obliquus* and *chlorella vulgaris*. They showed that the main mechanism for the removal of endosulfan from agricultural run-off was biodegradation and photo-degradation.

They also state that removal of endosulfan can also take place by alkaline chemical hydrolysis. It was also found that the removal efficiency of endosulfan can be increased by 20% by increasing the HRT from 2 to 8 days.

Figure 10 shows the fate of aldrin at different stages of WTP. The removal efficiency observed was in the range of 29-55%. The removal of aldrin in this study was noticed to be uniformly distributed among different stages of WTP. The aldrin possesses high log K_{ow} (6.5), which makes it highly hydrophobic. Aldrin is extremely persistence organochlorine pesticide with a high half-life of 266 days. All these factors suggest that the removal of aldrin is likely to take place through photo-degradation and sorption in WSPs.

The fate of carbaryl at different stages of WTP is shown in Figure 11. The removal efficiency observed was in the range of 88-97%. Major removal of carbaryl occured in the anaerobic and facultative ponds. Carbaryl has higher water solubility than organochlorine pesticides indicating its easy degradation in WSPs.

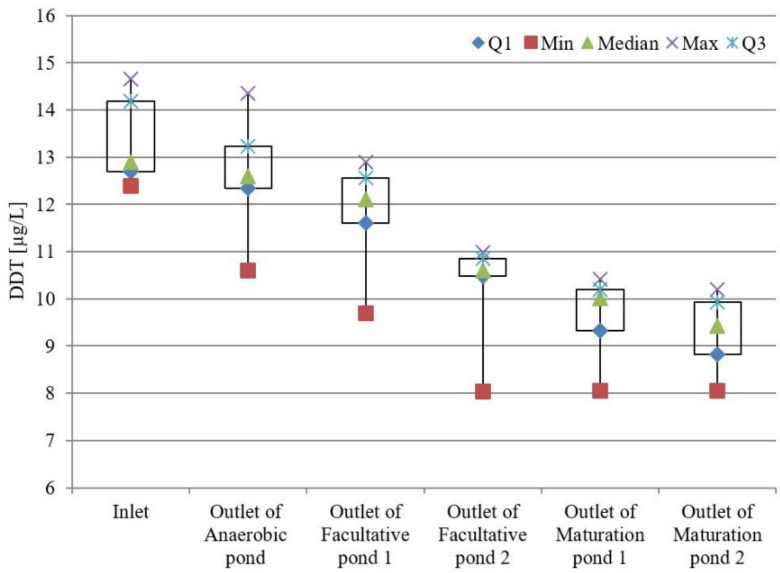

Figure 7. The fate of DDT at different stages of WSP based WTP

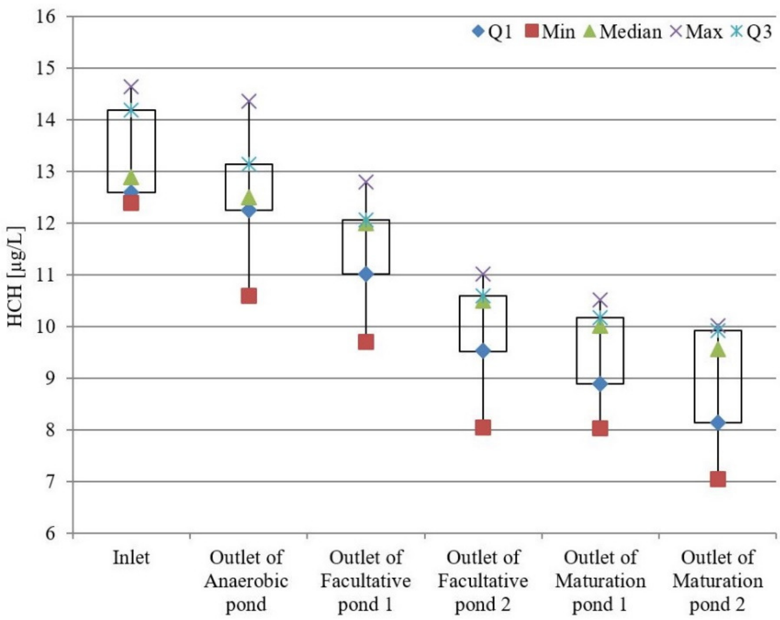

Figure 8. The fate of HCH at different stages of WSP based WTP

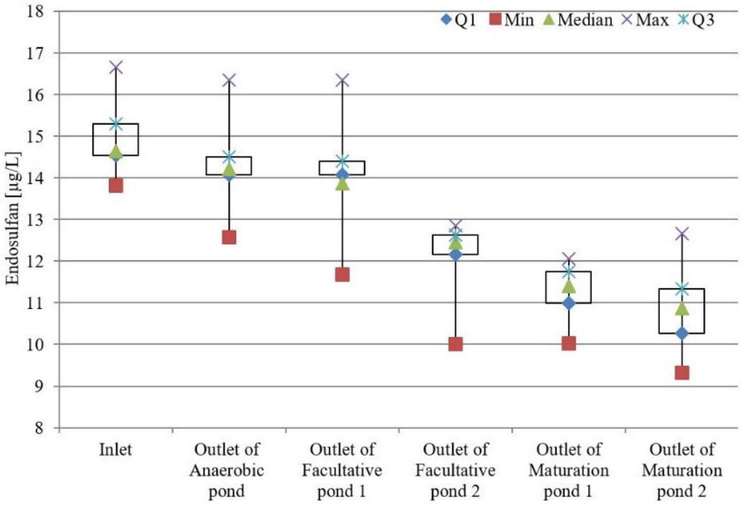

Figure 9. The fate of endosulfan at different stages of WSP based WTP

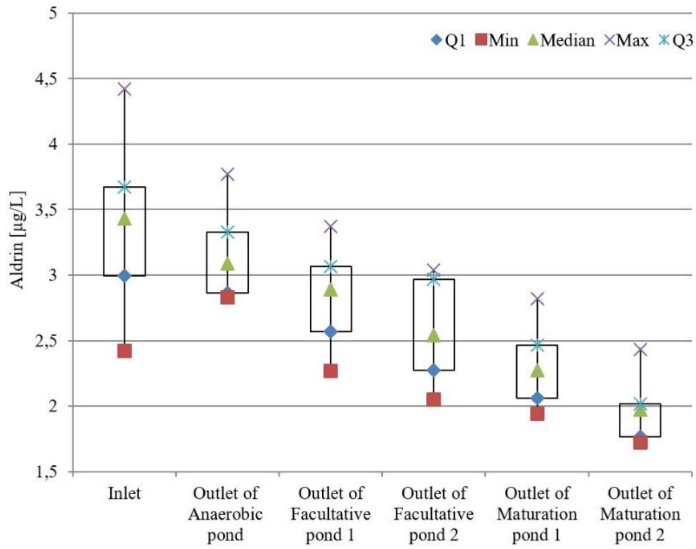

Figure 10. The fate of aldrin at different stages of WSP based WTP

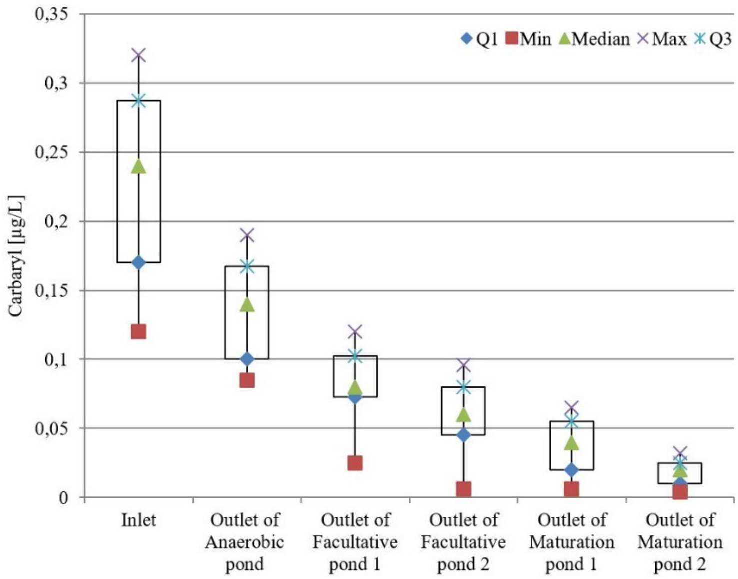

Figure 11. The fate of carbaryl at different stages of WSP based WTP

The fate of malathion at different stages of WTP is shown in Figure 12. The removal efficiency observed was in the range of 52-79%. Malathion has moderate log K_{ow} (2.36) and low half-life of 0.07-1.5 days. It has been found biodegradable under co-metabolic conditions [45]. Matamoros and Rodriguez [44] carried a batch study in 2 L flask in which microalgae species *scenedesmus obliquus* and *chlorella vulgaris* were incubated with agricultural runoff. They showed that the main mechanism for the removal of malathion from agricultural run-off was biodegradation and photo-degradation.

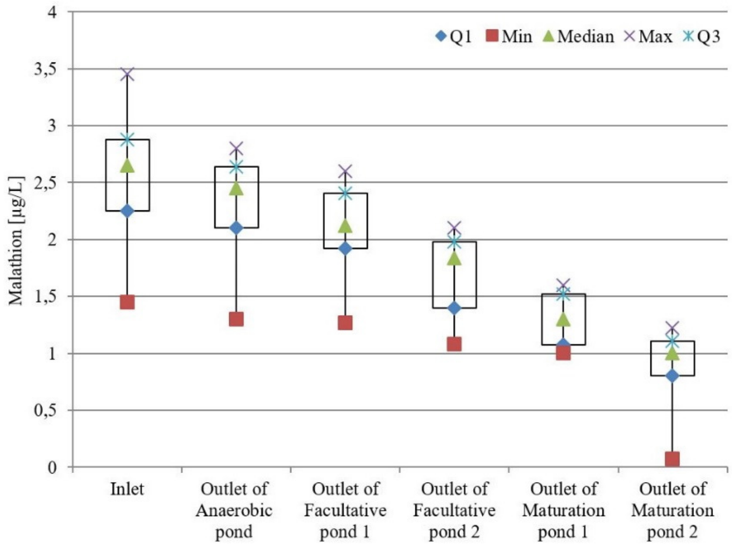

Figure 12. The fate of malathion at different stages of WSP based WTP

CONCLUSION

It was found that WSPs are capable of removing a range of ECs from the wastewater with different removal efficiencies. High removal (> 75%) was observed in the case of paracetamol and carbaryl. Moderate removal efficiencies (50-75%) were found for malathion, erythromycin, clofibric acid and 17beta-estradiol while low (< 50%) removal efficiencies were witnessed in the case of aldrin, endosulfan, DDT, HCH and diclofenac. Removal efficiencies depend on many factors, e.g. their nature: water soluble/insoluble, hydrophilic/hydrophobic, half-life, log K_{ow}, to name a few. Despite their dependence on physic-chemical factors, it is not possible to correlate a particular mechanism of removal with physicochemical properties of an individual EC. Results indicated that most of the removal takes place at the initial stages, i.e. in anaerobic and facultative ponds, whereas maturation ponds act for the polishing of the effluent only. The removal of ECs in WSPs, in general, can be attributed to three processes, namely, biodegradation, photo-degradation and sorption. Study to identify predominant removal mechanism for a particular EC in WSPs is in progress. However, the effluent of WSPs requires further treatment as the water of River Ganga is used for drinking in many downstream cities, e.g. New Delhi, Ghaziabad, Noida, Greater Noida, Agra, etc. to name a few.

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