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Study on the Phytoremediation Potential of Pharmaceutical Wastewater Spiked with Nutrients through Municipal Wastewater – A Case Study in Indian Context

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Abstract

Phytoremediation being a low cost treatment system has been attempted to mitigate effluent from a specific pharmaceutical industry manufacturing sodium oxalate. The effluent being too high in organic content (COD≈91264 mg/l) is chemically treated first with calcium oxide (CaO), so that organics in the wastewater contributing high COD forms salts and precipitates out. The optimum dosing of calcium oxide is found to be 2g/100 ml of the raw sample. COD reduction through chemical treatment is found to be approximately 19.35%. The chemically treated effluent having COD value 73,600 mg/l is subjected to anaerobic biological treatment and the COD value comes down to 12800 mg/l after 29 days. The fact that the plant species simply die, if they come in touch with this raw wastewater sample signifying excessive toxic effect of the ingredients of the wastewater to the plant, necessitates dilution of the anaerobically treated effluent 40 and 80 times by mixing municipal wastewater with it in the ratio 1:39 and 1:79 respectively, These dilutions are selected after some trial experiments ensuring sustenance of the aquatic macrophytes (Pistia stratiotes) meant for phytoremediation study, which has been conducted for 10 days. The plant sustains and grows in the test samples (both dilutions). The quantities of biomass at the beginning are 29.26g and 31.31g in 40 times and 80 times diluted test samples respectively and after 10 days the biomass have increased to 60.62g and 58.10 g respectively in the two dilutions. So it is examined that even in 40 times dilution (COD≈600 mg/l), the plant can survive and helps removal of organics (81.61%) after 10 days of phytoremediation, after which the plant starts decaying gradually. Hence this experiment cannot be continued beyond 10 days. The COD value still remains close to 100 mg/l, which needs further polishing before disposal.

Keywords: Pharmaceutical wastewater, municipal wastewater, high organic carbon, chemical treatment, anaerobic biological treatment, phytoremediation, *Pistia stratiotes*,

Introduction

Land and surface water are the convenient places of disposing industrial wastes. While disposing pharmaceutical effluents, a new range of chemically stable and persisting contaminants from pharmaceuticals accumulate potentially in ground and surface water. It becomes an urgent necessity to make the effluent free from these chemicals in order to dispose it to the environment in a safe manner. The industries at their present state cannot cope with the huge cost involved in the current practice of chemical treatment and membrane filtration.

While examining surface water and drinking water in Berlin (Germany) in the year 1991, presence of some pharmaceuticals e.g. clofibric acid and others have been detected[1]. Germany and Switzerland have started investigations of pharmaceuticals in surface and wastewater in the early 1990's[2]. In 1999, researchers within the United States undertook a nationwide reconnaissance of 95 pharmaceutical and other organic wastewater contaminants in water resources, including anti-bacterial agents, hormones, personal care products, cleaners and others[3]. In 1999, Ternes et al.[4,5] reported on the occurrence of estrogens in water from municipal sewage treatment plants of Germany, Canada and Brazil, documenting detectable levels of natural and synthetic hormones.

WWTPs (Wastewater Treatment Plants) have varying effectiveness at removing pharmaceuticals from wastewater, as noted by the presence of these compounds in effluent, receiving waters, and even drinking water[6]. Designed to be stable for increased shelf- and biological-life, excreted pharmaceuticals are often still biologically active as metabolism in man or animals may be incomplete or results in an altered form that can become active again under certain conditions[7].

Effluent from pharmaceutical industries usually contains organic matter. The current practice of removing organics from the effluents is chemical treatment and membrane filtration.

This involves huge cost which, the industries are reluctant to bear as this cost does not add to their profit. Chemical treatment plants are found to be difficult to operate in most of the cases. Low cost treatment system involving microorganism may be a solution in this respect. Presently phytoremediation of pharmaceutical wastewater is also attempted. The main problem associated with this phytoremediation is lack of nutrients present in pharmaceutical wastewater. This problem can be overcome if municipal wastewater containing nitrogen and phosphorus (nutrients) is mixed with pharmaceutical wastewater to make it suitable for treatment by phytoremediation technology.

Material and Methods

Experimental Design: The experiment has been conducted in the Environmental Engineering Laboratory of Department of Civil Engineering, Jadavpur University. The wastewater sample has been collected from a pharmaceutical industry situated at Kolkata, India and the municipal wastewater sample has been collected from KMDA treatment plant situated near Baghajatin Railway Station.

The pharmaceutical wastewater samples have been tested for their basic characteristic features. Simultaneously, municipal wastewater has also been tested for organic carbon and nutrients.

The pharmaceutical wastewater has been chemically treated with calcium oxide (CaO) used @ 2g/100ml of raw wastewater. The wastewater has been stirred thoroughly with the calcium oxide and then kept overnight only to get precipitate of calcium oxalate, as the wastewater contains high concentration of oxalic acid.

Chemically treated wastewater has been decanted after 24 hours and prepared for anaerobic treatment with 300 ml sludge (obtained from an anaerobic experimental set up currently running in the same laboratory) and 200 ml micronutrient solution in a 5-litre aspirator bottle and kept under 24-hr stirred condition at around 40˚C for about 1 month. Sampling is done at 3 days regular interval and analysed in the laboratory.

After the anaerobic treatment the treated pharmaceutical wastewater has been mixed with municipal wastewater in two sets, one is in the proportion of 1:39 and another is in the proportion of 1:79 for phytoremediation study. The plant sample, *Pistia stratiotes* used for phytoremediation study, has been collected from Dhakuria Lake, Kolkata. The initial weights of the plants are 29.26g and 31.31g in first and second set respectively. The wastewater samples have been collected from each set at one day interval for study of the variation of different chemical parameters with time. Side by side control experiments are also run for each set in order to ascertain the efficacy of plant system in removing carbon and nutrients.

The water samples collected from the control and test are filtered and the parameters like chemical oxygen demand (COD), soluble phosphorus (P), ammoniacal nitrogen (NH_3-N) and nitrate nitrogen (NO_3-N) values are determined by the methods laid down in Standard Methods of Examination of Water and Wastewater (APHA 21st Edition).

Figure-1
Test Set up (first day)

Figure-2
Control Set up (first day)

Figure-3
Test Set up (after 10 days)

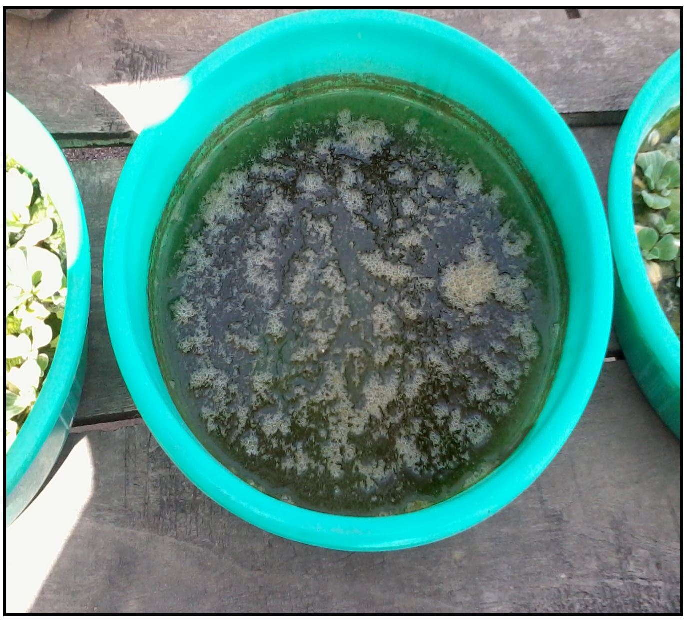

Figure-4
Control Set up (after 10 days)

Results and Discussion

Wastewater Characterization: Table-1 shows the results of chemical analysis of the raw pharmaceutical wastewater sample. pH value (≈3.5) shows that the wastewater is highly acidic. Total solids content of the wastewater is also high. The values of organics (volatile) and inorganic (fixed) solids are almost close to each other and both are high. COD (91264 mg/l) and BOD (39593 mg/l) values show high concentration of dissolved organic matters in the wastewater sample. The pharmaceutical wastewater has been found to be highly rich in organics and the colour of the sample is deep brown.

Table-1
Chemical Analysis of the Raw Pharmaceutical Wastewater Sample

Sr. No.	Parameter	Quantity
1	pH	3.5
2.	Total Solids	364.54 gm/lit
3.	Volatile solids	179.51 gm/lit
4.	Fixed solids	185.04 gm/lit
5.	COD	91264 mg/lit
6.	BOD	39593 mg/lit

The analysis report of municipal wastewater (table-2) shows moderate values of COD (249 mg/l) and BOD (108 mg/l) and low to moderate values for TKN (30 mg/l), NH_4-N (20 mg/l), NO_2-N (0.5 mg/l), NO_3-N (3.4 mg/l) and P (6 mg/l). Conductivity and TDS values show higher concentration of dissolved solids in municipal wastewater.

Table-2
Chemical Analysis of the Raw Municipal Wastewater Sample

Sl. No.	Parameter	Unit	Concentration
1.	pH	-	6.9
2.	Conductivity	uS/cm	3835
3.	BOD	mg/l	108
4.	COD	mg/l	249
5.	TKN	mg/l	30
6.	PO_4-P	mg/l	6
7.	NH_4-N	mg/l	20
8.	NO3-N	mg/l	3.4
9.	NO2-N	mg/l	0.5
10.	TDS	mg/l	2224
11.	TSS	mg/l	213

Chemical Treatment: No colour reduction of the pharmaceutical wastewater sample has been visually observed even after chemical treatment. pH value increases from acidic to alkaline condition. After chemical treatment COD value has reduced from 91264 mg/l to 73,600 mg/l and the percent reduction is found to be approximately 19.35 (table-3).

Table-3
COD Reduction of Pharmaceutical Wastewater Sample by Chemical Treatment

COD value (mg/l)		
Before Chemical Treatment	After Chemical Treatment	% reduction
91264	73600	19.35

Anaerobic Biological Treatment: After mixing with sludge taken from a lab-scale anaerobic treatment unit running simultaneously in the same laboratory and requisite nutrient solution, the COD value becomes 63296 mg/l, which is the initial COD value in the present study of anaerobic treatment.

Care is taken to maintain alkaline condition all through to facilitate growth of anaerobic bacteria.

Initially for the first few days, reduction in COD value has been found to be low due to the acclimatisation stage of the anaerobic bacteria with the organic content of the wastewater.

At the later stage the COD reduction becomes faster and after 29 days of observation COD value has come down to 12,800 mg/l and the percent reduction is about 86 (figure- 5).

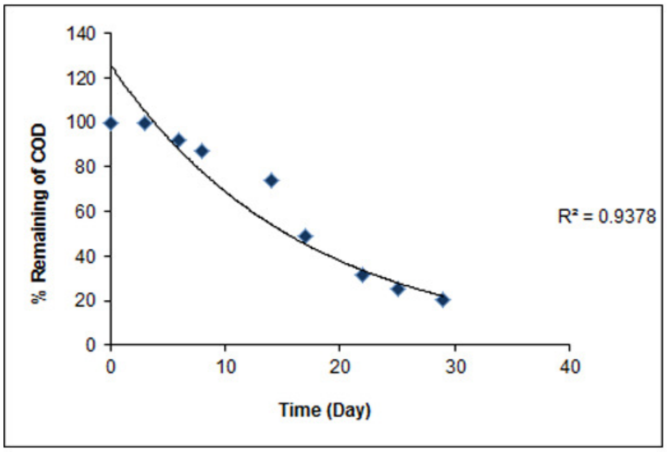

Figure-5
Change of COD with Time in Anaerobic Treatment

Phytoremediation: The anaerobically treated wastewater has been diluted to 40 and 80 times with municipal wastewater to bring down initial COD value to 597.84 and 312.08 respectively in the two sets of experiment. These dilutions have been fixed up simply on trial basis for phytoremediation with *Pistia sp.*

Table-4
Initial Concentration of Various Parameters of the 40 times and 80 times Diluted Test and Control Samples

Concentration						
Parameters	Temp	pH	COD	NH_4-N	NO_3-N	PO_4-P
Test and Control 40 times diluted	35	8.9	597.84	14.6	3.845	2.92
Test and Control 40 times diluted	34	7.8	312.08	11.1	1.925	2.96

Temperature and pH: On analysis of the samples taken from the two experimental set ups, temperature in the control is always found to be higher than that of test, as the test set up is mostly covered by plants and the direct sunbeam cannot enter into it. The pH value gradually reduces primarily due to dissolution of carbon dioxide formed during bacterial degradation of organics in the wastewater.

Table-5
Variation of Temperature

	Temperature			
Date	P+M (Test) 1:39	P+M (Control) 1:39	P+M (Test) 1:79	P+M (Control) 1:79
Initial	35	35	31	31
2^{nd} Day	37	38	33	34
4^{th} Day	39	40	36	38
6^{th} Day	41	42	40	42
8^{th} Day	39	40	38	39
10^{th} Day	40	41	41	42

N.B: P- Pharmaceutical wastewater, M- Municipal wastewater

Table-6
Variation of pH

	pH			
Date	P+M (Test) 1:39	P+M (Control) 1:39	P+M (Test) 1:79	P+M (Control) 1:79
Initial	8.9	8.9	7.8	7.8
2^{nd} Day	8.5	8.6	7.7	7.7
4^{th} Day	8.3	8.2	7.6	7.7
6^{th} Day	8.1	8.0	7.5	7.5
8^{th} Day	8.1	7.6	7.4	7.6
10^{th} Day	8.0	7.5	7.2	7.5

N.B: P- Pharmaceutical wastewater, M- Municipal wastewater

Table-7
Removal Percentage of Different Parameters after 10 Days of Phytoremediation

Percentage Reduction After 10 Days					
Sl. No.	Parameters	T-40	C-40	T-80	C-80
1.	COD	81.61	61.71	75.33	54.5
2.	NH4N	65.75	40.41	63.06	22.52
3.	NO3N	15.22	8.97	20.78	10.65
4.	PO4P	67.24	43.1	81	36.82

N.B: T-40- Test sample 40 times diluted, C-40- Control sample 40 times diluted, T-80-Test sample 80 times diluted, C-80- Control sample 80 times diluted.

Organic Carbon: In the first set (40 times dilution) at the end of 10 days of phytoremediation, COD reduction is 81.61 % in the test sample running with plants, where as in the control, COD reduction is 61.71 %. In the second set (80 times dilution), COD reduction is 75.33% in the test sample running with plants, where as in the control, COD reduction is 54.50% (table-4).

It has been observed that in the control set up, the percent remaining of COD is less than that in the test set up (for both the dilutions) up to 2 to 3 days and after that the situation becomes reverse i.e. percent remaining of COD in test set up is less than that in control set up (figure- 6,7).

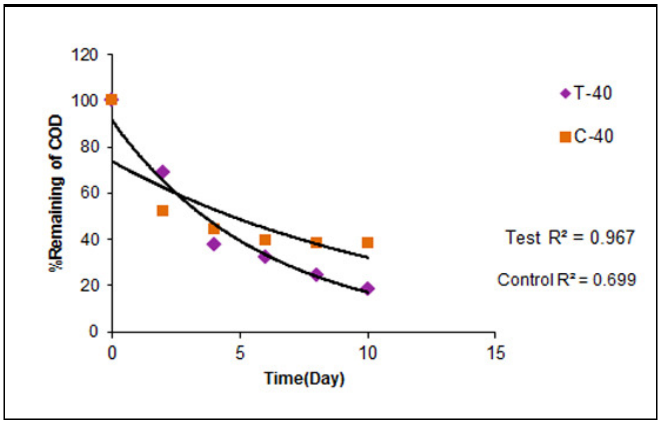

Figure-6
Change of COD Value with Time in 40 Times Diluted Test and Control Samples

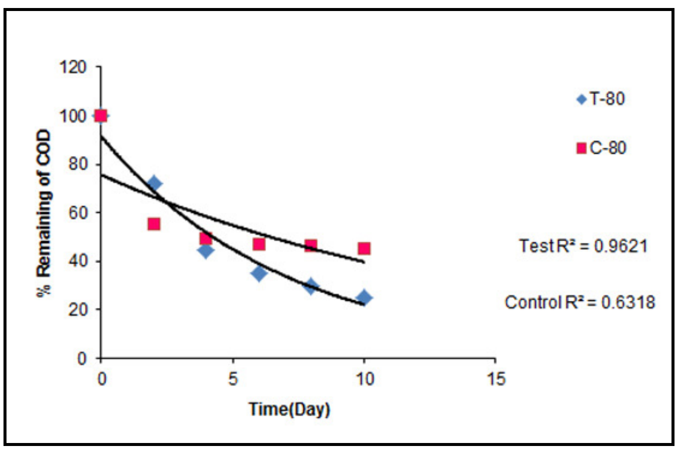

Figure-7
Change of COD Value with Time in 80 Times Diluted Test and Control samples

The reason behind initial higher removal of COD in control set up may be attributed to the condition of the control set up, where the container is exposed fully to the atmosphere and susceptible to precipitation of dust particles, which while settling adsorb the dissolved organic materials causing removal of COD. The situation is different for test set up where the wastewater sample is mostly covered with plants and the above phenomena is not discernible to any extent. Side by side bacterial degradation of organics occur in both the set ups. In the control set up algae-bacteria symbiosis cause removal of organics and in the plant set up, removal of the same take place due to different mechanisms involved in phytoremediation. Moreover, as temperature is higher in control setup compared to test condition, biochemical reaction rate is observed to be more at the initial stage. Hence, higher percent removal of COD in control set up during 2 to 3 days is mostly due to adsorption by dust particles and slight increase in biochemical reaction rate. After about 3 days the phytoremediation of organics has become predominant in test set up and percent reduction exceed that in control set up (figure-6,7).

Nutrient Reduction: In the first set (40 times dilution) percent reductions of NH_4-N, NO_3-N, and PO_4-P are 65.75, 15.22 and 67.24 respectively in the test sample running with plants, where as in the control, percent reductions of NH_4-N, NO_3-N, and PO_4-P are 40.41, 8.97 and 43.10 respectively (figure-8,9,10).

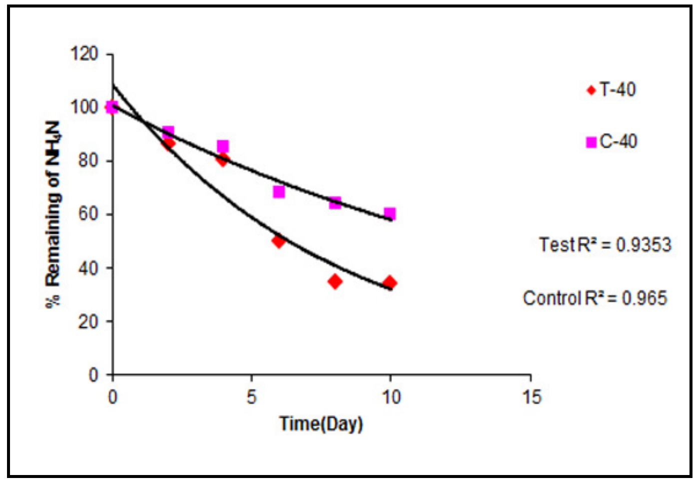

Figure-8
Change of NH_4-N Value with Time in 40 Times Diluted Test and Control Samples

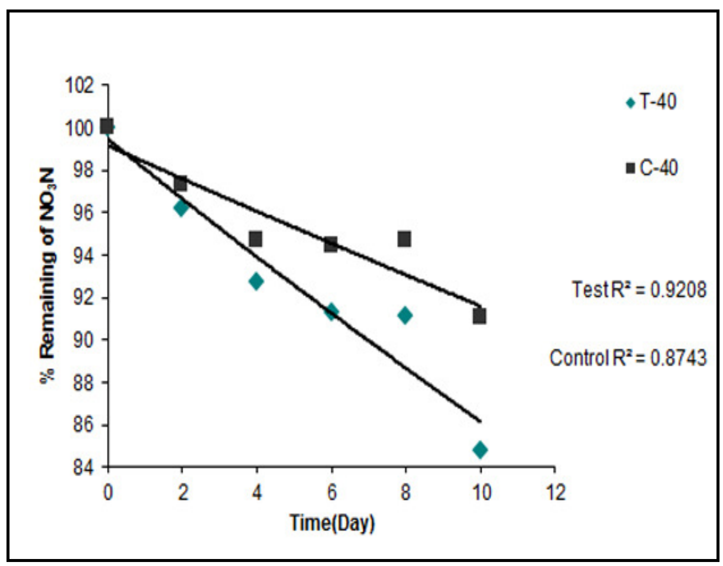

Figure-9
Change of NO_3-N Value with Time in 40 Times Diluted Test and Control Samples

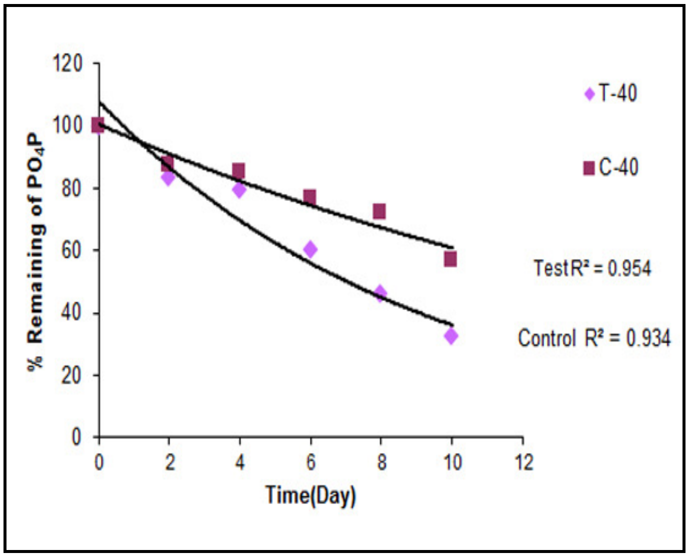

Figure-10
Change of PO_4-P Value with Time in 40 Times Diluted Test and Control Samples

In the second set (80 times dilution), percent reductions of NH_4-N, NO_3-N, and PO_4-P are 63.06, 20.78 and 81.00 respectively in the test sample running with plants, where as in the control, percent reductions of NH_4-N, NO_3-N, and PO_4-P are 22.52, 10.65 and 36.82 respectively (figure-11,12,13).

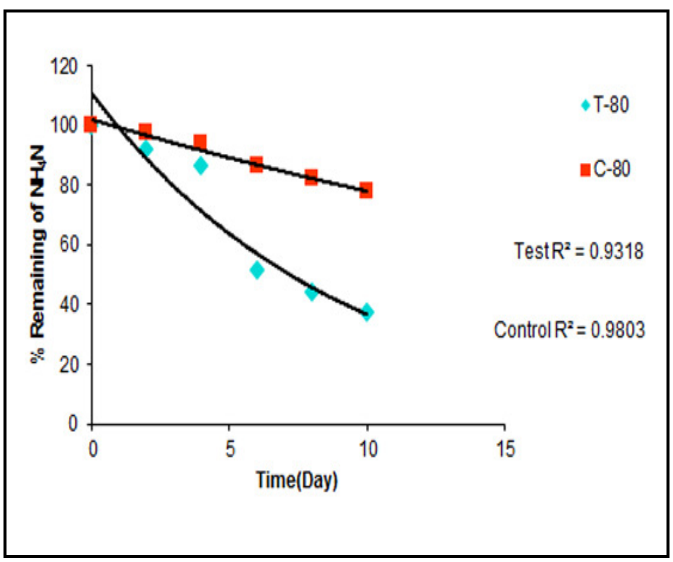

Figure-11
Change of NH_4-N Value with Time in 80 Times Diluted Test and Control Samples

Though it is observed that during Nitrogen removal, early precipitation of nutrients at the bottom of the controlled sets occur and for that reason initially nitrogen removal is little higher than the treatment set ups. Later it is seen that plant in the test, takes up NH_4-N, NO_3-N, and PO_4-P better than algae found to be present in control.

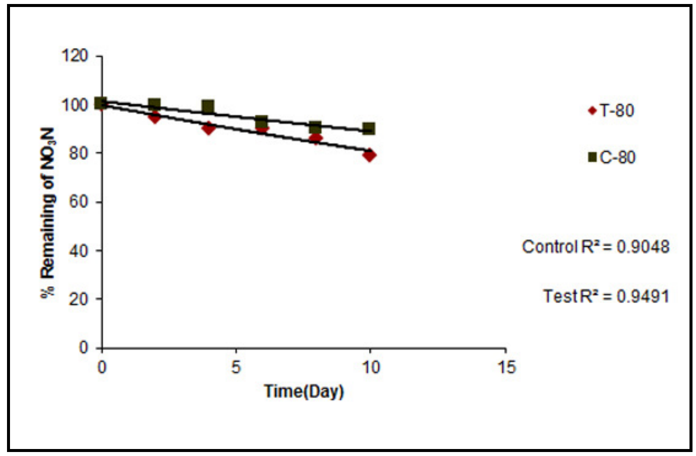

Figure-12
Change of NO_3-N Value with Time in 80 Times Diluted Test and Control Samples

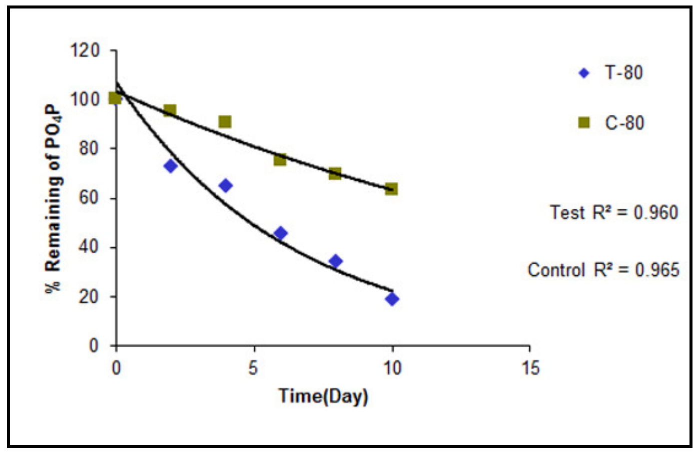

Figure-13
Change of PO_4-P Value with Time in 80 Times Diluted Test and Control Samples

Conclusion

The pharmaceutical wastewater selected under present study contains huge amount of organics, mainly oxalic acid (COD≈91264 mg/l). Plant species simply dies if they come in touch with this raw wastewater sample.

This sample is chemically treated first with calcium oxide (CaO), so that oxalic acid forms calcium oxalate and precipitates out. The optimum dosing of calcium oxide is found to be 2g/100 ml of the sample. COD reduction is found to be approximately 19.35%.

After chemical treatment COD value still remains close to 73,600 mg/l, which value is found to be unsuitable for either aerobic biological treatment or phytoremediation. Hence this sample is subjected to anaerobic biological treatment. Through this anaerobic treatment the COD value comes down to 12,800 mg/l after 29 days.

But this value too does not provide congenial environment for plant growth. The sample needs to be diluted. This dilution is done with municipal wastewater, which will provide nutrients, both nitrogen and phosphorus, for plant growth as the pharmaceutical wastewater does not have such nutrients. After some trial study, the dilution of the pharmaceutical wastewater has been fixed as 40 and 80 times.

Phytoremediation study has been conducted for 10 days. The plant grows in the test samples (both dilutions). The quantities of biomass at the beginning are 29.26g and 31.31g in 40 times and 80 times diluted test samples and after 10 days the quantities have been increased to 60.62g and 58.10 g respectively in the two dilutions. So it is concluded that even in 40 times dilution (COD≈600 mg/l), the plant can survive and helps removal of organics 81.61% after 10 days of phytoremediation. After 10 days the plant starts decaying gradually. Hence this experiment can not be continued beyond 10 days. The COD value still remains close to 100 mg/l, which needs further polishing.

It is finally concluded that for treatment of such pharmaceutical wastewater having high COD, sequentially chemical followed by anaerobic biological and finally either aerobic biological treatment or phytoremediation may be suggested. Aerobic biological treatment being costly both from the consideration of installation and of maintenance, phytoremediation may be considered as viable alternative for treatment of the wastewater under present study.

The pharmaceutical wastewater being highly rich in organics will be required to undergo a series of treatments like chemical, anaerobic biological before being subjected to phytoremediation. As this wastewater does not contain nutrients, spiking of nutrients is essential to make the same suitable for phytoremediation. Dilution of pharmaceutical wastewater through municipal wastewater will serve two fold purposes. First of all, nutrients will be added and secondly, dilution will reduce the organic concentration to a great extent. The aquatic macrophytes (*Pistia stratiotes*) are quite capable of removing nutrients and root zone mechanism of bacterial degradation of organics is quite effective in this system. Phytoremediation obviously shows its supremacy over algae-bacteria symbiosis in the control system.

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