Full Scale Treatment of Herbal Pharmaceutical Industry Wastewater

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Abstract

Herbal pharmaceutical industries generate moderately concentrated wastewater in huge volumes in terms of COD, BOD, and SS in the range of 21960-26000 mg/L, 12200-15660 mg/L and 5460-7370 mg/L respectively. It is not feasible to treat this wastewater in a single stage to meet the stipulated standards instead a combination of suitable treatments is required. Physicochemical treatment studies were carried out using various conventional coagulants individually and in combination with six polyelectrolytes of three different charges. Among ten combinations, Alum 300 mg/L + Oxyfloc-FL-11 was found to be the best combination with respect to COD, BOD, and SS removals of 6266 mg/L (64.00%), 2867 mg/L (69.40%) and 637 mg/L (80.82%) respectively. Further this treated effluent was selected for secondary biological Activated Sludge Process (ASP) using optimal parameters like organic/ hydraulic loadings. Removals of organics in terms of absolute value of COD, BOD, and SS were found in the range with an absolute value of 896-944 mg/L, 156-174 mg/L and 66-74 mg/L respectively. Finally ASP treated effluent was subjected to tertiary Fenton's oxidation process where the removals of COD, BOD, SS, and TOC were found to be efficient with 138 mg/L (85.19%), 20 mg/L (88.10%), 21 mg/L (70.00%), and 98 mg/L (78.22%) respectively on optimum conditions, which is well below the prescribed standards. This article discusses in details the results obtained on Primary physico-chemical, secondary biological and advanced oxidation treatment.

Key words: Activated Sludge, Fenton's reagent, Herbal medicine, Herbal pharmaceutical wastewater.

Introduction

Herbal medicines are being used by about 80% of the world population primarily in the developing countries. Herbal medicines include herbs, herbal materials, herbal preparations and finished herbal products that contain as active ingredients from plants or other plant materials. Of all the sciences, India possesses the longest and most glorious tradition in the field of herbal medicine. Ayurveda, the science of long life, body and mind is said to have divine origin. It uses mostly medicinal plants and minerals in diseases to bring back the body equilibrium.

The sages of India mastered an unparalleled knowledge of medicinal plants. Over the years, the traditional practice of using herbal medicines gained popularity due to their safety, efficacy, cultural acceptability and lesser side effects. The chemical constituents present in the herbal medicines are part of the physiological functions of living flora and hence they are believed to have better compatibility with the human body. Ancient literature also mentions herbal medicines for age related diseases namely memory loss, osteoporosis, diabetic wounds, immune and liver disorders etc (Rajashekharan, 2002). Centuries ago, the herbal medicines were a household practice. But as the importance of the medicine was understood, the production of herbal medicines increased by leaps and bounds. The population increase was also one of the factors. During the manufacture of herbal medicines, a large volume of wastewater generation takes place. This wastewater due to its highly biodegradable nature cannot be discharged directly into the surface water, as they putrefy very fast leading to environmental disorders.

The global market for herbal drugs is growing rapidly. The global market for herbal medicines currently stands at over $60 billion annually. The sale of herbal medicines is expected to get higher at 6.4% an average annual growth rate (Inamdar et al., 2008). Due to the contribution of numerous significant factors, the market of herbal medicines has grown at an expressive rate worldwide (Calixto, 2000). According to World Health Organization (WHO), herbal medicines are lucrative globally and they represent a market value of about US$ 43 billion a year. According to an estimate in 1991, the herbal medicine market in the European countries was about $ 6 billion, with Germany accounting for $ 3 billion, France $ 1.6 billion and Italy $ 0.6 billion while in other countries was 0.8 billion. In 1996, the herbal medicine market in the European countries was about $ 10 billion, in USA about $ 4 million, in India about $ 1.0 billion and in other countries was $ 5.0 billion. In 1997, the European market alone reached about $ 7.0 billion. The German market corresponds to about 50% of the European market, about $ 3.5 billion. This market is followed by France, $ 1.8 billion; Italy, $ 700 million; the United Kingdom, $ 400 million; Spain, $300 million; the Netherlands, about $ 100 million (Calixto, 2000).

According to WHO, up to 80% of the population in Africa depends on traditional medicine for primary health care and in China, herbal medicines account for 30–50% of total medicinal consumption. In Europe, North America and other industrialized regions over 50% of the population have used complementary or alternative medicine at least once (Jaggi, 1984).

In India, around 7000 large, small and medium scale industries manufacturing herbal pharmaceutical products alone in India, which are distributed in all the segments of the country. According to WHO, in both developed and developing countries, a considerable percentage of people use medicinal plant remedies and the number is on the increase, especially among younger generation (Nandy et al., 1998). Herbal pharmaceutical wastewater is moderately strong with COD and BOD concentration in the range of 21960-26000 mg l^{-1} and 1200-15660 mg l^{-1} respectively and equally high concentration of SS of 5460-7370 mgl^{-1}.

The countrywide scenario of herbal pharmaceutical industries reveals that the products are produced on batch basis. The process involves the cleaning of herbs (like flowers, stem, bark, nuts, fruits, resins, seeds, roots, leaves etc.) to remove dust and soil adhered to the material. They are thoroughly dried and passed through cutters or ball mills as per the requirement and are further subjected to extraction, fermentation, distillation, decoction preparation, percolation as per the requirement. Though the product is based on herbs, synthetic chemicals are also used in the manufacturing process. Chemicals that are used include alcohol, sugar, gelatin, lactose, mineral salts, clays and different organic solvents.

Due to variation in the types of medicines produced, raw materials used and based on market demands, the wastewater flow and its characteristics differ widely. During the biological processes, the system gets hampered due to this fluctuating load and the system malfunctions. Since stringent effluent requirements have to be met during operation of the biological treatment system, an alternative treatment scheme has to be arrived at. So as to reduce the pollution load on the secondary treatment, a primary treatment in the form of physicochemical treatment process has been tried. This can be used either independently or in tandem with the conventional treatment units as a pretreatment and also as a tertiary polishing process.

Few papers on the treatment of herbal pharmaceutical wastewater by anaerobic fixed film, fixed bed have been reported (Mukti, 1993 and Jain, 2001). One of the treatment technologies, which seemed viable for the reduction of organic load in the herbal pharmaceutical wastewater, is physico-chemical treatment using conventional coagulants in combination with anionic/cationic/non-ionic polyelectrolyte.

Literature survey reveals only few papers on the physicochemical treatment of herbal pharmaceutical wastewater, but the reported work has been carried out using grab samples with very high doses of polymers (Gregary et al., 1990). Hence an attempt has been made to study in detail the treatment of the herbal wastewater using conventional coagulants individually, in combination and also with addition of anionic/cationic/ non-ionic polyelectrolyte. Results are very encouraging and have been discussed in detail (Vanerkar et al., 2005).

This paper discusses in details about the complete treatability study of herbal pharmaceutical wastewater by suitable combination of primary physicochemical, secondary, biological aerobic suspended-growth activated-sludge process, and tertiary advance oxidation process.

Materials And Methods

Large scale herbal pharmaceutical medicines manufacturing industry, producing approximately 700 types of various formulations was selected for the characterization and treatability of herbal pharmaceutical effluent, composite samples were collected and characterized according to the procedures given in standard method (Franson et al., 1998). Detailed treatability studies are as follows.

Primary Physicochemical Treatment

Physico-chemical treatment is applied as a primary treatment using jar test apparatus (Phipps & Birds, USA) to reduce the organic load for further secondary biological process. To obtained optimum dose experiments were carried out using different conventional coagulants like Lime, Alum, Ferric chloride and Ferrous sulphate, (in the range of 50-600 mg/L) individually and also in combination with six polyelectrolytes of three different charges (i.e. anionic, cationic and nonionic) from Pidilite industries ltd., Baroda, India and Baroda Minerals Chemicals (in the range of 0.1-0.6 mg/L) for enhancing the flocculation and coagulation process.

Stock solution of coagulants were prepared and used for the complete set of each test. The physicochemical treatability studies were carried out at ambient temperature using conventional Jar-test apparatus. Initially rapid mixing at 100 rpm for one minute then at 40 rpm for half an hour followed by settling for 30 minutes was carried out. After half an hour of settling, samples were withdrawn and subjected to various physicochemical analyses as per the standard procedures. Optimum dose of coagulants and polyelectrolyte were evaluated by repeated experiments.

Secondary Biological Treatment

Bench scale secondary, biological aerobic suspended-growth activated-sludge process was carried out to determine the treatability of physicochemically treated wastewaters by completely mixed activated sludge process. The bench scale unit was operated with activated sludge acclimated to the wastewater. The required nutrients normally, Nitrogen and Phosphorus were provided in the form of Di-ammonium hydrogen orthophosphate for maintaining the nutrient to microorganisms in the proportion of BOD: N: P = 100: 5: 1. In order to evaluate the performance of the unit at different F/M ratio (in the range of 0.2 to 1.2), the unit was fed constantly with physicochemically treated wastewater at selected HRT using peristaltic pump. Different eight sets of HRT in the range of 6 to 48 hours were tried for each F/M ratio and for two different MLSS concentration of 3000 mg/L and 4000 mg/L. Oxygen level was maintained (in the form of compressed air) at the rate of 0.5 mg/L in the ASP system. Once the system stabilized as indicated by the reduction in COD, BOD and SS, samples were withdrawn and analyzed for various parameters including MLSS, and MLVSS concentrations.

Tertiary -Advance Oxidation

This new and effective technology of wastewater purification leading to complete mineralization of organic pollutants in water and wastewater by generating highly reactive Hydroxyl radical (OH^*) in the system, which is remarkably unstable but provided with very high oxidative potential of 2.8 E_0 (V) as compare to any other oxidant except Fluorine. In the advanced oxidation process, Fenton's reagent was tried for oxidation of pollutants using jar test apparatus of biologically treated herbal pharmaceutical wastewater. Fenton's oxidation process was carried out at ambient temperature and pressure, as the literature reveals that, thermodynamically this process is exothermic in nature hence, high temperature have negative impact on H_2O_2 stability, which favored the maximum removal of organics. The oxidation condition was optimized by varying different parameters viz. pH (1.5 - 5.0), CRT (15 – 120 minutes.), amount of $FeSO_4$ (25 – 450 mg/L) and amount of H_2O_2 is varying in the range of 01- 10 mg/L.

Results and Discussion

Characterization of wastewater from herbal pharmaceutical industry is shown in Table 1, reveals that the pollution load of the effluent in terms of COD, BOD and SS is in the range of 21960 -26000 mg L^{-1}, 11200 -15660 mg L^{-1} and 5460 -7370 mg L^{-1} respectively. Apart from organics, the in-organics namely heavy metals, Sulphates, total Phosphates, total Nitrogen and oil and grease have been found in higher concentration range. The load of the wastewater is due to the host of the several herbs, organic and inorganic compounds and minerals/clays used in the process of various herbal formulations. The ratio of BOD to COD for herbal pharmaceutical wastewater has been found in the range of 0.51-0.60, which shows the biodegradable nature of the wastewater (Metcalf Eddy, 1999 and Stoddard et al., 2002).

Table 1. Characterization of herbal pharmaceutical wastewater.

Parameters	*Raw Wastewater**	Neutralized wastewater*
pH	3.9 - 4.0	6.8 - 7.4
Colour (Visual)	Dark yellow	Black
Total Acidity	3000	-
Total Suspended Solids	5460 - 7370	3320 - 4864
Total Dissolved Solids	2564 - 3660	2680 - 4474
Total Solids	8024 - 11030	6230 - 9340
Chemical Oxygen Demand (COD)	21960 - 26000	17400 - 20000
Biological Oxygen Demand (BOD, 5day - 20°C)	11200 - 15660	9370 - 11910
Sulfide as (S^{-2})	42 - 54	38 - 42
Sulphates as (SO_4^{-2})	82 - 88	68 - 72
Total Phosphates as (PO_4^{-2})	260 - 280	220 - 242
Total Nitrogen as N	389 - 498	336 - 378
Oil and Grease	140 - 182	75 -98
Sodium as Na^+	155 - 266	144 - 250
Potassium as K^+	128 - 140	118 –132

Heavy Metals		
Iron	65.6 - 65.7	26.2 - 41.4
Copper	0.649 - 1.67	0.081- 1.42
Manganese	6.41 - 8.47	3.22-5.87
Nickel	0.892 - 2.35	0.107- 1.49
Zinc	0.583 - 0.608	0.215- 0.414
Chromium	0.057-1.11	0.051- 0.456
Lead	0.559 - 6.53	0.460- 4.08
Cadmium	0.036 - 0.484	0.032- 0.339
Selenium	0.428 - 0.666	0.121- 0.397
Arsenic	0.0049 - 0.0076	0.0023-0.0040

*All values are expressed in mg L^{-1} except pH and colour.

The high organic load observed in terms of COD, BOD, SS and other parameters is also attributed to certain harmful organic impurities, which may come out from extraction of natural ingredients and formulations of various dosage forms of herbal medicines (Lenng, 1980). The report of Central Pollution Control Board (CPCB), New Delhi, India also attributed that considerable amount of pollutants may generate from extraction of herbs and natural materials (CPCB, June- 1989).

Primary Physicochemical Treatment

The physicochemical studies were of two-stage treatment, i.e. initial treatment by Lime to raise the pH of wastewater from initial pH of 4.2 to 7.0 pH, and then the second stage use of different coagulants were studied. Conventional coagulants used were Lime, Alum, Ferric chloride, and Ferrous soleplate on neutralized wastewater. Initially Lime being the cheapest and cost effective chemical was tried. During first stage of treatment the Lime required to neutralize the wastewater was 4.2 mg L-1. Later neutralized wastewater was used for the experiments and individual coagulants were tried. Detail studies on the effectiveness of different anionic, nonionic and cationic polyelectrolyte on the conventional coagulants in organic removals were carried out.

Cationic polyelectrolyte (Oxyfloc-FL-11) dose of 0.25 mg L^{-1} with optimum Alum dose of 300 mg/L resulted in COD, BOD, and SS removals of 64.00%, 69.40% and 80.82%, which shows the highest removals in organics by physicochemical treatability study. This is due to the fact that herbal pharmaceutical wastewater comprises natural organic matters, which are anionic in nature, and hence its behavior with cationic polyelectrolyte addition resulted in best removals in organics. This trend has also been reported in literature (Bolto and Braun, 1999). Details studies on the effectiveness of different conventional coagulants individually and with different synthetic polyelectrolytes were carried out and results are shown in Table 2**.** In general the physicochemical studies carried out indicate that the pharmaceutical wastewater is amenable to this treatment. It may be applied as a primary treatment before subjecting the wastewater to secondary biological treatment. This will help in efficient working of biological system by reducing the organic load.

Table 2. Percent Removals of COD, BOD and SS at optimum doses of various conventional coagulants individually and in combination with synthetic polyelectrolyte doses.

Conventional Coagulants + Synthetic Polyelectrolyte Doses	Optimum Doses of Conventional Coagulants and Synthetic Polyelectrolyte (mg L^{-1})	*Removal Efficiency*					
		COD in mg L^{-1}	% R in COD	BOD in mg L^{-1}	% R in BOD	SS in mg L^{-1}	% R in SS
Lime	300	10684	38.60	5227	44.22	1494	55.00
Alum	300	12389	28.80	6390	31.80	1882	43.30
Lime + Alum	(300+150)	9814	43.60	4948	47.20	1706	48.60
Ferrous sulphate	100	11310	35.00	5471	41.61	1555	53.30
Ferric chloride	150	11971	31.20	5788	38.23	1743	47.50
Lime + Magnafloc – E-207	(300+0.20)	8839	49.20	4198	55.20	1136	65.78
Lime +Magnafloc – 1011	(300 +0.20)	8770	49.60	4104	56.20	1138	65.71
Lime + Zetag –7563	(300 +0.25)	7586	56.40	3729	60.20	1036	68.77
Lime + Zetag –7650	(300 + 0.25)	7517	56.80	3636	61.20	1146	65.48
Lime + Oxyfloc -FL-11	(300 + 0.20)	7378	57.60	3270	65.10	864	74.00
Alum + Magnafloc – E-207	(300 + 0.25)	7656	56.00	3636	61.20	1018	69.33
Alum + Magnafloc – 1011	(300 +0.20)	7795	55.20	3729	60.20	1022	69.21
Alum + Zetag – 7563	(300 + 0.25)	7238	58.40	3448	63.20	940	71.67
Alum + Zetag – 7650	(300 +0.25)	6890	60.40	3373	64.00	892	73.13
Alum + Oxyfloc-FL-11	(300 + 0.25)*	6266	64.00	2867	69.40	637	80.82

***Optimum dose of conventional coagulant (i.e. Alum) in combination with synthetic cationic polyelectrolyte (Oxyfloc –FL-11) in mg L^{-1}.

Secondary Biological ASP

Under this study physicochemically treated herbal pharmaceutical wastewater was subjected to bench scale aerobic-biological- activated sludge treatment on different F/M ratio (0.1 to 0.7), different HRTs (24 to 54 hours) and two different MLSS concentrations of 3000 mg L^{-1} and 4000 mg L^{-1}.

The results shown in Table 3 indicated that COD, BOD, and SS removals on 4000 mg L^{-1} MLSS concentrations were found to be in the range of 896-944 mg L^{-1} (84.93% to 85.63%), 156 -174 mg L^{-1} (93.93% to 94.51%) and 66-74 mg L^{-1} (88.40% to 89.49%) respectively on HRT of 42.00 hours with 0.18 F/M ratio.

Table 3. **Performance of bench – scale aerobic activated sludge system using wastewater from herbal pharmaceutical industry. (F/M = 0.18; MLSS = 4000 mg L^{-1}; Influent Flow = 1.250 Liter D^{-1})**

Set	Sample	HRT in Hrs.	pH	COD in mg L^{-1}	% R in COD	BOD in mg L^{-1}	% R in BOD	SS in mg L^{-1}	% R in SS	MLSS in mg L^{-1}	MLVSS in mg L^{-1}
I	Influent	--	6.7	6266	--	2865	--	638	--	--	--
	Effluent	24	6.8	1944	68.98	663	76.90	162	74.61	3900	2760
		30	6.8	1580	74.78	456	84.08	128	79.94	3930	2780
		36	6.9	1276	79.64	300	89.53	102	84.01	3950	2810
		42*	7.0*	944*	84.93*	174*	93.93*	74*	88.40*	4000*	2870*
		48	7.0	752	87.99	123	95.71	50	92.16	4040	2920
		54	7.1	572	90.87	87	96.96	30	95.30	4080	2950
II	Influent	--	6.7	6236	--	2844	--	628	--	--	--
	Effluent	24	6.8	1896	69.60	642	77.43	150	76.11	3890	2760
		30	6.9	1544	75.24	429	84.92	112	82.17	3920	2780
		36	6.9	1248	79.99	282	90.08	94	85.03	3960	2820
		42*	7.0*	896*	85.63*	156*	94.51*	66*	89.49*	4010*	2880*
		48	7.1	716	88.52	114	95.99	46	92.68	4050	2910
		54	7.1	560	91.02	78	97.26	28	95.54	4100	2940

***Related optimum values with optimum reduction**

It can be inferred from the results that an optimum HRT of 42 hours and 0.18 F/M ratio is a feasible combination where absolute concentrations of COD, BOD, and SS of 896-944 mg L^{-1}, 156-174 mg L^{-1} and 66-74 mg L^{-1} respectively were achieved. The values indicated that the treated effluent is not suitable for discharge or reuse, as it does not comply with stipulated standards for discharge of environmental pollutants (liquid effluents) prescribed by regulatory body i.e. CPCB, New Delhi, India under Schedule VI of Environment Protection Third Amendment Rules, 1993 even after two stage of ASP (CPCB, June- 1995). This concentration is suitable for tertiary advance oxidation studies.

Tertiary - Fenton's Oxidation

Lower strength of wastewaters are generally treated aerobically where as high strength wastewaters are pretreated an-aerobically, physicochemical treatment methods or by advanced oxidation process such as ozonation, Fenton's oxidation and photo-catalytic oxidation (Balciog and Otker, 2003). This new and effective technology of wastewater purification leading to complete mineralization of organic pollutants in water and wastewater by generating highly reactive Hydroxyl radical (OH^*) in the system, which is remarkably unstable but provided with very high oxidative potential of 2.8 E_0 (V) as compare to any other oxidant except Fluorine. In the advanced oxidation process, Fenton's reagent was tried for oxidation of the non-biodegradable organics as an advanced tertiary treatment and the same was tried to treat the secondary/biologically treated herbal pharmaceutical wastewater. Literature survey reveals that this is the simplest way to generate the Hydroxyl radicals (Meyers, 1998), which are responsible to mineralize/degrade the non-biodegradable organics.

This process was applied to the biologically treated herbal pharmaceutical wastewater, obtained from bench scale activated sludge process (with 0.18 F/M ratio, 42.00 hours of HRT and 4000 mg L^{-1} of MLSS concentration) having COD, BOD, SS, and TOC concentrations of 932 mg L^{-1}, 168 mg L^{-1}, 70 mg L^{-1}, and 450 mg L^{-1} respectively. This effluent was selected, based on the optimum removals achieved.

Literature survey reveals that inadequate or excess addition of H2O2 may leads to the dangerous heat evolution as thermodynamically this process is exothermic in nature (Herber and Weiss, 1934). Our work supports the work of previous workers who have suggested the pH rang of 2.0 to 4.0 for experiments on removal of organics using Fenton's reagent**.** [38] Therefore optimize all the important parameters. Thus after achieving all the optimal conditions viz. pH, CRT, dose of $FeSO_4$ and H_2O_2, biologically treated wastewater was further subjected to Fenton's oxidation as a tertiary treatment. The results on all the optimized conditions are given in Table 4.

Table 4. **Performance on optimized conditions using wastewater from herbal pharmaceutical industry.**

Sr. No.	Optimized Conditions	COD (932*)		BOD (168*)		SS (70*)		TOC (450*)	
		mg L^{-1}	% R	mg L^{-1}	% R	mg L^{-1}	% R	mg L^{-1}	% R
1	pH of Wastewater- 3.5; Contact Reaction Time - 60 min; Dose of $FeSO_4$ - 200 mg/L; and Dose of H_2O_2 - 6.0 ml/L.	128	86.27	18	89.29	18	74.29	94	79.11
2		156	83.26	24	85.79	26	62.86	104	76.89
3		152	83.69	21	87.50	26	62.86	104	76.89
4		132	85.84	18	89.29	20	71.43	96	78.67
5		128	86.27	18	89.29	18	74.29	92	79.56
6		140	84.98	21	87.50	22	68.57	98	78.22
7		132	85.84	18	89.29	18	74.29	96	78.67
8		136	85.40	24	85.79	20	71.43	98	78.22
Avg.		138	85.19	20	88.10	21	70.00	98	78.22

*** Absolute value of influent in mg L^{-1}**

The results show that, under the optimum conditions i.e. pH of 3.5, CRT of 60 minutes, dose of $FeSO_4$ of 200 mg L^{-1} and dose of H_2O_2 of 6.0 ml L^{-1}, the average optimum removals of organics in terms of COD, BOD, SS, and TOC were found to be 138 mg L^{-1} (85.19%), 20 mg L^{-1} (88.10%), 21 mg L^{-1} (70.00%), and 98 mg L^{-1} (78.22%) respectively, which is well below the standards prescribed by regulatory body CPCB, New Delhi, India for discharging the wastewater in to inland water or surface water.

Conclusions

The characterization of herbal pharmaceutical wastewater shows that the wastewater from this type of industries is of moderate strength. Physicochemical treatability studies of herbal pharmaceutical wastewater show amenability to physicochemical treatment and Alum as a coagulant in combination with cationic synthetic polyelectrolyte found efficient and economically viable combination. The wastewater from herbal pharmaceutical industry requires a single stage activated sludge process with optimized parameters viz. HRT of 42 hours, F/M ratio of 0.18 and MLSS concentration of 4000 mg L^{-1}. Though these removals are the maximum but not at par with the national standards promulgated by regulatory body. Hence it is inferred that tertiary (advance) treatment is essential for this wastewater. The tertiary Fenton's oxidation process is amenable to remove the non biodegradable organics and thus achieves the optimum removal of organics as promulgated by regulatory agency. As compared to radiation induced hydroxyl radical generation processes, the Fenton's oxidation has been found highly suitable to treat the herbal pharmaceutical wastewater. In this process, Hydroxyl radicals can be introduced in to the wastewater mixture in any concentration, at any rate, simply by varying the quantity of H_2O_2 and other catalyst; thus making it a much more versatile tool.

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