http://www.pjbs.org

PJBS

ISSN 1028-8880

Pakistan Journal of Biological Sciences

ANSInet
Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Pakistan Journal of Biological Sciences, 2 (4): 1263-1267, 1999 Research Article

Chemical processing of Pharmaceutical wastewater for Pollution control

Imran Hashmi, S. Nazrul Hasnain*, Moazzam Ali Khan and M. Altaf Khan
Institute of Environmental Studies, University of Karachi, Karachi-75270,
* Department of Biochemistry, University of Karachi, Karachi-75270, Pakistan.

Abstract

The present research investigation was aimed at determining the behavior of TSS, BOD_5, COD, Oil and grease, phenols and ammonia of pharmaceutical wastewater under varied concentrations of polymers (alum and chlorine), in order to determine the effectiveness of polymers as coagulant aids. Wastewater samples were collected from the holding tank in plastic containers. Total suspended solids were removed from the wastewater by alum treatment and it was found that alum dose of 200 mg L^{-1} was sufficient to remove TSS from 458 to 23 mg L^{-1} (95% removal). Similarly BOD_5 was also readily removed by the alum treatment, showing that alum dose of 300 mg L^{-1} was optimum, in achieving 89 percent removal. Although removal of COD was not easily obtained due to the complex chemical composition of the wastewater. Therefore, variable results in terms of COD removal were obtained. It was observed that COD removal efficiency was as low as 13-45 percent for 100 mg L^{-1} and for 200 mg L^{-1} lit was between 26-77 percent and for 300 mg L^{-1} it was found out to be 28-88 percent. Different volumes of chlorine (diluted bleach, 50:50, 25:75 and 15:85) were used in order to find out the optimum chlorine dose for further reduction of COD. The residual COD removal efficiency of 15 percent bleach at 30 ml/100 ml dose was found to be 71 percent. Similarly for 25 percent and 50 percent bleach it was found out to be 89 percent and 86 percent respectively (Based on average of six results). Similarly alum dose of 300 mg L^{-1} it was sufficient to remove 65 percent phenol within a contact time of 30 minutes depending upon the phenol concentration in the original sample. Similarly the effect of chlorine on alum treated wastewater was observed for residual phenol and ammonia removal and it was found that 25 percent bleach at 10 ml, 20 ml and 30 ml was effective in bringing phenol level down to acceptable level of 0.1 mg L^{-1} or less.

Introduction

Polymer application in industrial wastewater treatment has become very important in recent years due to the increased pollutant removal efficiencies, easier sludge disposal, economy in chemical consumption, etc. Polymers may either be used as coagulant or as coagulant aids for the aggregation of colloidal particles (Billmeyer, 1984).

Coagulants most often used in the wastewater treatment include alum ($Al_2(SO_4)_3.14H_20$), ferric chloride ($FeCl_3.6H_20$), ferrous sulphate ($FeSO_4.7H_20$) and some polyelectrolytes. The materials that find utilization as 'coagulant aids' are for the most part polyelectrolytes, by applying these substances higher density flocs may be obtained.

The polyelectrolytes, when serving as coagulant aids act to reduce the stability of colloidal systems and facilitate their coagulation. Their effectiveness in water and wastewater treatment has been shown in many applications (Robinson, 1979).

In coagulation, chemicals are added to the wastewater (or water) to reduce the forces that keep the colloidal particles apart. Flocculation of a polymer-sol system of like charges results only if an appropriate concentration of a salt is present in the solution. However, floculation usually occurs at electrolytes concentrations much smaller than those necessary in the absence of polymers (Stumn and Morgan, 1976).

Chlorine is widely used for disinfection of wastewater in many parts of the world. It is a strong oxidizing agent and its application for wastewater disinfection is likely to modify the chemical and biological nature of wastewater, most notably its organic characteristics.

Several studies in the literature have examined the history and credibility of wastewater chlorination practices and questioned the benefits of chlorination against the deleterious effects that arise from chlorine residuals and byproducts on aquatic ecosystems (GAO, 1977; Buxton and Ross, 1979).

A variety of inorganic and organic constituents of secondary effluents can chemically reduce aqueous chlorine resulting in chlorine demand. Of these constituents, ammonia plays an important role in determining chlorine demand of secondary effluents. Nitrified effluents with NH_3-N less than 2 mg L^{-1} tend to have higher chlorine demand compared to non-nitrified or less nitrified effluents (Dhaliwal and Baker, 1983; Venosa, 1983; Gosser, 1984; Gordon, 1985). The increased chlorine demand at very low NH_3-N concentration is a result of the breakpoint chlorination reaction. At extremely low levels of NH_3-N ($\leq$0.1 mg L^{-1}). NO_2-N in concentrations $\geq$1.0 mg L^{-1} was found to greatly reduce chlorine disinfection ability at dosages upto 50 mg L^{-1} and 180 minutes contact time (Gosser, 1984).

The effect of chlorination on the bulk organic content of wastewater measured as TSS, BOD_5, COD, NH_3 and phenol was investigated, and the general impression is that chlorination slightly reduces these parameters and provides some treatment advantage. Similar conclusion were also observed in India in 1985 (Mayadeo and Pandit, 1985) on wastewater of different treatment levels.

Setting an acceptable level of risk is highly subjective and frequently variable (Rodricks *et al*., 1987; Munro and Travis, 1986). Risk based actions levels may be set differently for different industries or for voluntary and involuntary exposures (NCRP, 1987).

The present research investigation was aimed to compute tentative cost estimates pertaining to the use of chemicals (alum and bleach) and to further determine the effects of alum and bleach on the TSS, BOD_5, COD, NH_3-N and phenol removal from the pharmaceutical wastewater and to confirm that treatment with bleach for a contact time of 2-hours, further improves the efficacy of COD, NH_3-N and phenol removal.

Materials and methods

Sampling Procedure

Site of sample collection: The source for the collection of wastewater samples throughout the present studies was the pharmaceutical industry.

Collection of wastewater sample: Whenever the wastewater sample was required it was usually collected in the morning hours. For the collection of wastewater a pump was allowed to run for 1-2 minutes in-order to avoid the collection of previously present wastewater in the pump line. After the run for 1.2 minutes the wastewater sample was collected.

Sample Processing: 10-Litres of wastewater sample was passed through a sieve in order to avoid collection of debris, papers, twigs as well as silt. Small floating materials were removed. The wastewater must be homogenous in consistency before it is processed. Imhoff graduated cones were set in series each containing 1-litre of wastewater sample.

Treatment of wastewater sample

Settleable solids: One cone was reserved for determining settleable solids. Observation for settleable solids was made after one hour and reported as settleable solids mlL^{-1}.

Alum treatment: To the remaining 3-cones, 100 mg, 200 mg and 300 mg alum was added. The required quantity of alum was weighed and dissolved in small quantity of distilled water and then added to the respective cones. Soon after adding the content the cones were throughly stirred and floc's were allowed to form which later on settled at the bottom of the cones. After settling time of 30 minutes the sludge quantity was measured in mlL^{-1}. About 400 ml alum treated supernatant was carefully taken out and filtered. Small quantity of the filtered sample was separated for TSS, BOD_5, COD, oil and grease, phenol and ammonia determination.

Chlorine treatment: Three 250 ml flasks were set in series each containing 100 ml alum treated filtered sample. The filtered samples in these flasks were treated with 10 ml, 20 ml and 30 ml appropriately diluted liquid bleach.

Similarly three flask each containing 100 ml filtered sample were treated with 10 ml, 20 ml and 30 ml 25:75 diluted sample of liquid bleach. Likewise 15:85 and 50:50 diluted bleach was also used for this purpose.

The chlorine treated wastewater sample in flasks were allowed a contact period of two hours. After this a small quantity was taken out for COD, phenol and ammonia determination.

Chlorine treated effluent samples were not tested for TSS and BOD_5 removal as their levels had already come down after alum treatment.

Analysis of Sample: The samples were analyzed for the following parameters.

pH: It was determined by an Orion pH-meter.

Total Suspended Solids (TSS): TSS in raw and alum treated samples were determined according to the method described in the Standard Method for the Examination of Water and Wastewater (AWWA, APHA and WPCF, 1985).

Biochemical Oxygen Demand (BOD_5): BOD_5 was determined by using Azide modification method as described in the Standard Method for the Examination of Water and Wastewater (AWWA, APHA and WPCF, 1985).

Chemical Oxygen Demand (COD): It was determined by the potassium dichromate reflux method using HACH COD analyzer as per method described in the Standard Methods for the Examination of Water and Wastewater (AWWA, APHA and WPCF, 1985).

Oil and Grease (n-Hexane extract): Oil and grease was determined by the Standard Methods for the Examination of Water and Wastewater (AWWA, APHA and WPCF, 1985).

Ammonia-Nitrogen (NH_3-N): Ammonia was determined by the Nesslerization method as described in Standard Methods for the Examination of Water and Wastewater (AWWA, APHA and WPCF, 1985).

Phenol: Phenol was determined by distillation using direct photometric measurement as described in Standard Methods for the Examination of Water and Wastewater (AWWA, APHA and WPCF, 1985).

Results and Discussion

Effect of Alum Treament: The effect of 100, 200 and 300 mg of alum per litre of wastewater was studied on the removal of the following parameters in order to find out the minimum/optimum doses of alum which could be practically applied for the removal of these parameters.

Table 1: Effect of Alum Treatment on TSS, BOD_5, 0 & G, Phenol and Ammonia

Parameters (mg/L)	Alum Dose (mg/L)						
	Raw (mg/L)	100	% Rem	200	% Rem	300	% Rem
TSS	458	173	62	23	95	30	93
BODS	166	74	55	42	75	19	89
0 & G	21	8	62	4	81	-	-
Phenol	4.66	3.362	28	2.457	47	1.628	65
Ammonia	7.46	6.28	16	2.3	69	1.63	78

Table 2: Effect of Alum Treatment on COD-Removal

COD (mg/L)	Alum Dose (mg/L)						
	Raw (mg/L)	100	% Rem	200	% Rem	300	% Rem
1	1600	880	45	680	58	520	68
2	2720	1520	44	1360	50	880	68
3	1040	760	27	640	38	600	42
4	1040	900	13	750	28	505	51
5	1120	690	43	480	57	320	71
6	2720	1520	44	1040	62	520	81
7	1040	720	31	560	46	240	77
8	1040	560	46	240	77	120	88
9	1120	1066	5	826	26	800	28
10	1920	1080	44	760	60	420	78

Table 3a: Effect of chlorine (15 ml bleach + 85 ml distilled water) on COD Ammonia and Phenol Removal

Parameters (mg/L)	Chlorine Dose m1/100 ml								
	Raw (mg/L)	Alum Treated	% Rem	10%	% Rem	20 %	% Rem	30%	% Rem
COD	350	250	29	220	37	160	54	100	71
Ammonia	2.64	1.324	50	0.23	91	<0.1	96	<0.1	96
Phenol	1.34	<0.1	96	<0.1	96	<0.1	96	<0.1	96

b: Effect of chlorine (15 ml bleach + 75 ml distilled water) on COD Ammonia and Phenol Removal

Parameters (mg/L)	Chlorine Dose ml/100 ml								
	Raw (mg/L)	Alum Treated	% Rem	10%	% Rem	20 .96	% Rem	30%	% Rem
COD	720	560	22	320	56	240	67	80	89
Ammonia	2.64	1.324	50	0.18	98	<0.1	96	<0.1	96
Phenol	1.34	<0.1	96	<0.1	96	<0.1	96	<0.1	96

c: Effect of chlorine (50 ml bleach + 50 ml distilled water) on COD Ammonia and Phenol Removal

Parameters (mg/L)	Chlorine Dose ml/100 ml								
	Raw (mg/L)	Alum Treated	% Rem	10%	% Rem	20%	% Rem	30%	% Rem
COD	560	300	96	320	43	120	79	80	86
Ammonia	9.32	6.85	26	0.91	90	0.4	96	0	100
Phenol	5.19	5.18	0.2	3.88	25	1.39	73	0.75	86

Table 4: Ost benefit analysis of chemical treatment

(Tentative)

Tentative cost of chemicals used in the chemical treatment of effluent.

Daily effluent generation		50,000 L
Alum dose application rate		300 mg/L
Total quantity of alum required		
(50,000 x 300)		15,000,000 mg
	Or	15 Kg
Total cost of alum at Rs.5.5/Kg		Rs. 82.5
15% bleach application rate		30 ml/100 ml
	Or	30 ml/L
Total volume of 15% bleach required		
(50,000 x 300)		15,000.000 ml
	Or	15,000L(3260 gallons)
For making 1L solution bleach required		150 ml
For making 15,000 L solution bleach required		
(15,000 x 150)		2,250,000 ml
	Or	2250 L
Total bleach required in Kg		
(1.25 L bleach = 1 Kg)		2813 Kg
Cost of 2813 Kg bleach at Rs.10/Kg		Rs. 28,130
Total recurring cost of chemicals used for the treatment of 50,000 gallons.		
Cost of alum		Rs. 82.5
Cost of bleach		Rs. 28,130
	Total:	Rs. 28,212.5

Cost of recovered water should also be considered for working out full economic analysis

Table 5: Estimated performance of Alum (300 mg/L) and Bleach Treatment of pharmaceutical wastewater

Wastewater parameters	Raw values	% Efficiency (removal rate)	Expected residual values (mg/L)	NEQS mg/L
TSS	upto 2000	93-100	Max 80	150
BOO_5	200-300	84-91	30-40	80
0 & G	400-1000	71-83	68-170	150
Phenol	2-4	92-96	0.08-0.16	0.1
Ammonia	2-8	92-96	Almost nil	40

Note:

a. Minimum time for alum treatment & sedimentation = 30 minutes

b. Minimum time for chlorine treatment = 2 hours

c. If sedimentation time and chlorine contact time is increased the residual level of diterment pollutants may further decrease.

Total Suspended Solids (TSS) removal: TSS were easily removed from the wastewater by alum treatment. Many samples of wastewater having different values for TSS were treated with 100, 200 and 300 mg L^{-1}. Alum dose of 200 mg L^{-1} was found to be very good as it caused removal of TSS from 458 mg L^{-1} (Raw) to 23 mg L^{-1} (95 percent removal). The experiment for TSS removal was repeated many times and it was found that 200 mg L^{-1} alum was optimum for TSS removal. After treatment with 200 mgL alum almost all the suspended matter formed floc's and finally settled down at the bottom of the Imhoff cones (Table 1).

Biochemical Oxygen Demand (BOD_5) removal: Most of the BOD_5 was found to be in the suspended solids. increase in TSS also increases BOD_5 load, like TSS, BOD_5 was also readily removed by alum treatments. Alum dose of 200 mgL was found to be optimum and was capable of removing BOD_5 upto 89 percent (Table 1). Although alum dose of 200 mg L^{-1} is also effective but it may be risky to use this dose in case of BOD_5 values greater than 200 mg L^{-1}. However, filtration or sedimentation after 100 mg L^{-1} alum treatment may prove to be safer and effective.

Chemical Oxygen Demand (COD) removal: It was difficult to remove COD from the wastewater by using alum alone because of the seemingly complex chemical composition of the wastewater. Variable results in terms of COD-removal were obtained. A series of experiments were performed in order to determine optimum alum dose for the removal of maximum COD. It was observed that COD removal efficiency was found to be between 28-88 percent using 300 mgL^{-1} alum (Table 2). For 100 mgL^{-1} alum dose the COD-removal efficiency was 13-46 percent and for 200

mgL^{-1} it was between 26-77 percent (Table 2). The COD removal efficiency using same alum dose was different in different batches indicating variable chemical composition of the effluent. It also indicates the presence of some soluble chemicals that are not precipitated out by the alum treatment alone. On the basis of these results it was decided to select 300 mgL^{-1} alum dose for maximum removal of COD followed by chlorine treatment for further COD-removal. Different rate of COD removal was observed using different doses of alum depending upon the COD values of the raw wastewater (Table 2). As alum treatment alone brought TSS and BOD_5 values within NEQS limits the effect of chlorine was not done on these parameters (Table 5).

Phenol and Ammonia removal: Wastewater was treated with various concentration of alum, for phenol and ammonia removal. Phenol is a common hazardous chemical in both industrial and domestic wastewater. In pharmaceutical industries it is principally contributed by activity related to sanitation. Being soluble it is not readily removed by plain alum treatment or any other floculating agent. It is either removed by chlorination or by microbial decomposition. Alum dose of 300 mgL^{-1} removed 65 percent phenol and 78 percent of ammonia within a contact time of 30 minutes depending upon the phenol and ammonia concentration in the original sample (Table 1).

Effect of Chlorine (Bleach)

Chemical Oxygen Demand (COD) removal: 300 mgL^{-1} alum treated wastewater was used throughout for determining the effect of chlorine on COD removal. Different volumes of chlorine diluted bleach 15:85, 25:75, 50:50) were used in order to find out the optimum chlorine dose for further reduction of COD (Table 3). Chlorine treatment proved to be effective for further reduction of COD. Although 50, 25 and 15 percent bleach in 30 ml/100 ml were all promising in that they removed residual COD after alum treatment to an acceptable level. On the basis of the results obtained we therefore are inclined to favour the use of 15-25 percent bleach at the dose level of 30 ml/100 ml with a minimum contact time of 2-hours. If the contact time is increased much better results may be obtained for COD removal. The residual COD removal efficiency of 15 percent bleach at 30 ml/100 ml dose was found to be 71 percent. Similarly for 25 percent and 50 percent bleach it was found out to be 89 percent and 86 percent respectively (Based on average of six results). It was revealed during this study that lower concentration of chlorine was more effective in removing COD from the alum treated wastewater (Table 4).

Phenol and Ammonia removal: Alum treated wastewater was treated with various concentration of bleach for residual phenol and ammonia removal. 15 percent bleach at 10 ml, 20 ml and 30 ml/100 ml was effective in bringing phenol level down to acceptable level of 0.1 mgL^{-1} or less (Table 3). Since for COD removal it was found that 15-25 percent bleach at 30 ml/100 ml dose was optimum in bringing down various levels of COD to the acceptable limit it is therefore concluded that phenol and ammonia would also be reduced to an acceptable level. Chlorine treatment also brought about 96 percent removal of ammonia which is very much expected as chlorine forms mono, di and tri chlorine with ammonia. The efficiency of alum and chlorine in remaining pollutants both suspended and soluble depends largely upon their original contents in the wastewater. The greater the amount of TSS, BOD_5, COD, Oil & grease phenol, ammonia etc. The greater would be the residual amount left after treatment. The concentration of these pollutants should not be allowed to go beyond a certain range, and extra care result be taken to avoid shock load. In case of shock load and abnormal introduction of BOD_5, COD, oil and grease, phenol, ammonia etc. Equalization process should therefore, be considered before chemical treatment.

References

AWWA., APHA. and WPCF., 1985. Standard Methods for the Examination of Water and Wastewater. 15th Edn., American Water Works Association (AWWA), American Public Health Association (APHA), Water Pollution Control Federation (WPCF), Washington. D.C., USA.

Billmeyer, F.W., 1984. Textbook of Polymer Science. Wiley Inter Science Publication, John Wiley and Sons, Canada.

Buxton, G.V. and S.A. Ross, 1979. Wastewater disinfection-toward a rational policy. J. Water Pollut. Control Fed., 51: 2023-2032.

Dhaliwal, B.S. and R.A. Baker, 1983. Role of ammonia-N in secondary effluent chlorination. J. Water Pollut. Control Fed., 55: 454-456.

GAO., 1977. Unnecessary and harmful levels of domestic sewage chlorination should be stopped. General Accounting Office, Washington, D.C., USA.

Gordon, J.H., 1985. The effect of ammonia in effluent chlorination. J. Water Pollut. Control Fed., 57: 101-102.

Gosser, J.A., 1984. Disinfection of nitrified effluents. J. Wat Pollut. Control Fed., 56: 386-387.

Mayadeo, M.S. and R.K. Pandit, 1985. Effect of chlorination on BOD of domestic wastewater. Asian Environment, 6: 8-10.

Munro, N.B. and C.C. Travis, 1986. Drinking water standards. Environment Sci. Technol., 20: 768-769.

NCRP., 1987. Recommendations on limits for exposure to ionizing radiation: Report No. 91. National Council of Radiation Protection and Measurements, Betlesda, Md.

Robinson, Jr., C.N., 1979. Cationic polyelectrolytes reduce organic matter in turbid surface waters (PDF). J. Am. Water Works Assoc., 71: 226-227.

Rodricks, J.V., S. Brett and G. Wrenn, 1987. Significant Risk Decisions in Federal Regulatory Agencies. Environment Corporation, Washington, D.C. USA.

Stumn, W. and J.J. Morgan, 1976. Aquatic Chemistry. John Wiley and Sons Inc., New York, USA.

Venosa, A.D., 1983. Current state-of-the-art of wastewater disinfection. J. Water Pollut. Control Fed., 55: 457-466.