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Biodegradability enhancement of purified terephthalic acid wastewater by coagulation–flocculation process as pretreatment

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Abstract

In this work, the coagulation–flocculation process was used as pretreatment for purified terephthalic acid (PTA) wastewater with the objective of improving its overall biodegradability. PTA production generates wastewaters with toxicants *p*-xylene [1,4-dimethyl-benzene (C_8H_{10})], a major raw material used in the production process, along with some of the intermediates, viz., *p*-toluic acid, benzoic acid, 4-carboxybenzaldehyde, phthalic acid and terephthalic acid. These compounds affect the bio-oxidation process of wastewater treatment; hence removal of these constituents is necessary, prior to conventional aerobic treatment. This paper addresses the application of coagulation–flocculation process using chemical coagulants, viz., aluminium sulphate (alum), polyaluminium chloride (PAC), ferrous sulphate and ferric chloride in combination with anionic polyelectrolyte. Polyaluminium chloride (PAC) in conjunction with lime and polyelectrolyte removed about 63.1% chemical oxygen demand (COD) and 45.2% biochemical oxygen demand (BOD) from PTA wastewater. Coagulation–flocculation process coupled with aerobic bio-oxidation treatment of PTA wastewater achieved, COD & BOD removals of 97.4% and 99.4%, respectively. The biodegradability enhancement evaluated in terms of the BOD_5/COD ratio, increased from 0.45 to 0.67 at the optimum conditions. The results obtained from these studies indicate that the coagulation–flocculation process could be a suitable pretreatment method in reducing toxicity of PTA wastewater whilst enhancing biodegradability for aerobic biological treatment scheme.

Keywords: Purified terephthalic acid; Treatment; Coagulation; Flocculation; Bio-oxidation

1. Introduction

Purified terephthalic acid (PTA) and dimethyl terephthalate (DMT) are the most important starting materials for making synthetic products. DMT and TA rank among the top 50 most abundantly produced chemicals worldwide [1]. The most well-known application of these compounds is the production of polyethylene terephthalate (PET) products, mainly bottles that are widely used for carbonated drinks. Other applications include polyester films used in audio–visual photography, packaging and textile fibers [2]. In recent years, the world PTA production has kept growing rapidly from 18.22 million tonnes in 1997 to 26.12 million tonnes in 2002, at average annual growth rate of 7.5%, whereas, China accounted to about 2.6 million tonnes in 2002, 72% more than 1997, with average annual growth rate of 9.2%. Currently, demands peaked to 12.14 million tonnes in 2005 contributing to 42% of total world demand (28.8 million tonnes) [3,4].

The production of purified terephthalic acid (PTA) is based on the well-established process developed by the American Amoco Group [5,6]. The process comprises of two steps, in the first step crude terephthalic acid (CTA) is produced by wet oxidation of *p*-xylene into acetic acid, and in the second stage CTA conversion into PTA through hydrogenation using palladium as a catalyst [2]. Scheme 1 presents the chemical reactions involved in the manufacture of PTA.

For each tonne of PTA manufactured, approx., 4–10 kg COD m^{-3} are generated with 5–20 g COD l^{-1}, and 3–4 m^3 wastewater [7]. In manufacturing facilities, wastewater is contaminated with this class of chemical compounds and it deserves advanced treatment before being discharged into the environment because of the ecological risk to animals and humans. Major aromatic compounds found in PTA wastewater are *p*-toluic acid (*p*-Tol), benzoic acid (BA), 4-carboxybenzaldehyde

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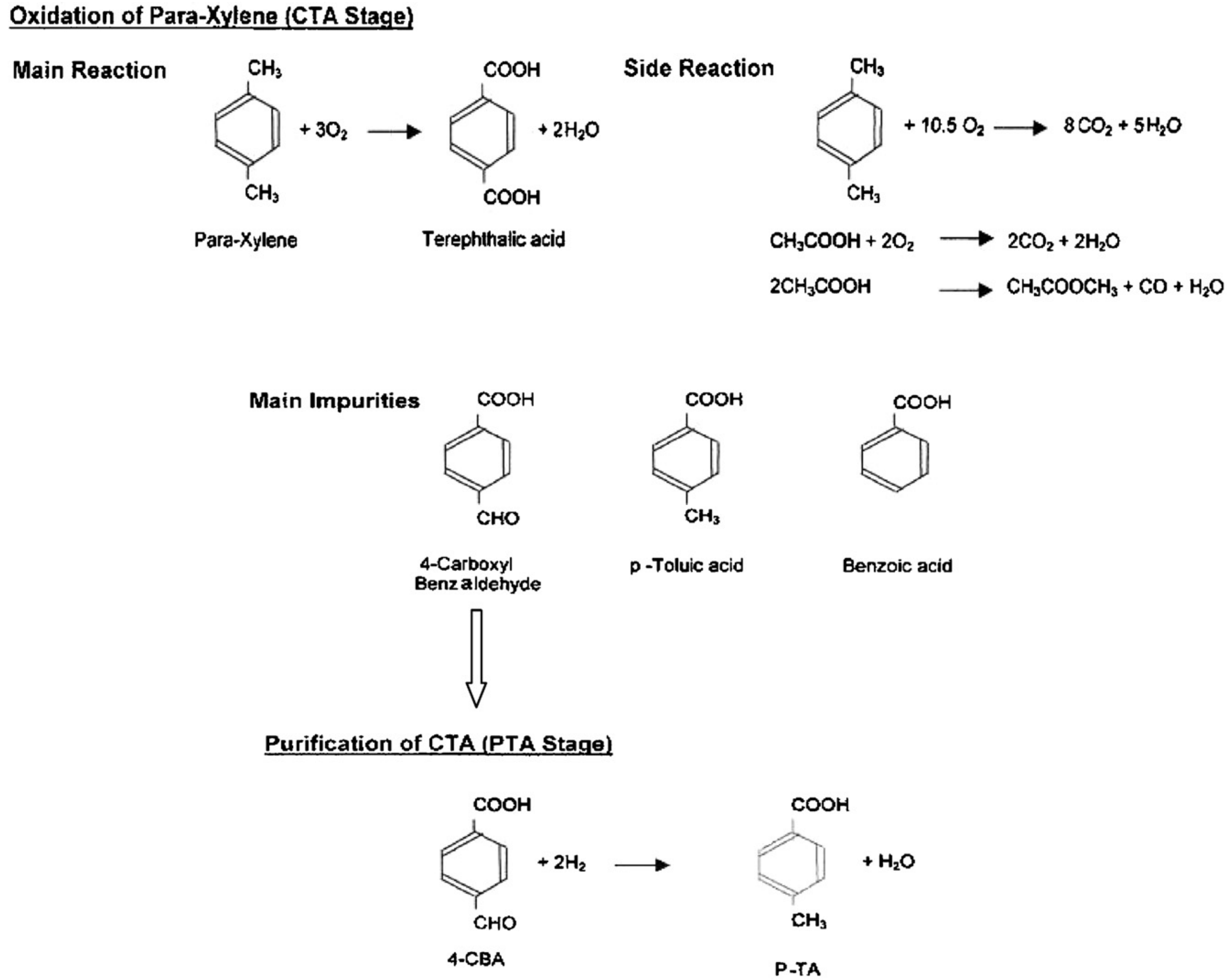


Scheme 1. Production and purification process of purified terephthalic acid.

(4-CBA), phthalic acid (PA) and terephthalic acid (TA) with minor concentrations of 4-formylbenzoic acid, methyl acetate and *p*-xylene [8–11]. The contribution of the five aromatics towards COD can be more than 75% in the wastewater. With increasing PET consumption, the treatment of PTA wastewater and contaminated environments has gained wide attention for the preservation of natural ecosystems and protection of the environment. PTA and its byproducts released into the environment are toxic to living organisms [12–15]. The pure chemical PTA has acute toxicity, sub-acute toxicity, chronic toxicity and molecular toxicity as reported [16–20]. Phthalate, its ester and degradation intermediates are suspected to cause cancer and renal damage, and as a result, the US Environmental Protection Agency has recently added this class of chemicals to the list of priority pollutants [21]. The toxic concentrations or doses of the pure chemical PTA were as high as over 1000 mg l^{-1}. But there are at least five kinds of benzoate pollutants existing in the PTA wastewater. Hence, the PTA wastewater toxicity is quiet different from that of the pure chemical PTA [22].

Recently, advanced oxidation processes (AOP), supercritical water oxidation, UV-assisted ozonation (UV/O_3), ozone-assisted photochemical oxidation (UV/O_3/H_2O_2), photo-fenton oxidation (UV/H_2O_2/$FeSO_4$), ozone-assisted photo-fenton oxidation (UV/O_3/H_2O_2/$FeSO_4$) and radiation treatment using gamma-ray have been used for the treatment of PTA wastewater [23–26]. Major limitations of all the methods are cost and generation of toxic intermediates and sludge leading to secondary pollution. In the past 20 years, research has been mainly directed in the area of biodegradation technology. Biodegradation is found to be environment friendly and cost effective treatment in comparison to chemical processes. Anaerobic or aerobic wastewater treatment is traditionally applied for treatment of medium to high strength wastewaters. However, the intermediates are poorly degradable [27–30]. Over 70% of the pollutants present in the PTA wastewater are benzoate chemicals, which is a major barrier in biodegradability enhancement. The low biodegradation rate increases the cost of treatment significantly. Therefore, it is necessary to develop innovative methods of treating PTA wastewater effectively and economically, especially for the biodegradation of aromatic compounds. In order to find out a way to cut down the energy consumed in aerobic degradation technologies have become a hot point in the wastewater treatment recent years. Physico-chemical treatment as an option for pretreatment of PTA wastewater to enhance the biodegradation rate has been reported [20,31–33]. Application of coagulation and flocculation is necessary for removal and settlement of colloidal, suspended particles and oily material present in the PTA wastewater. Merits of the physico-chemical method (coagulation–flocculation) employed for pretreatment of wastewater are mainly due to simplicity, low cost, good removal efficiency and easy onsite implementation.

The specific aim of this study is to evaluate suitability of the coagulants for pretreatment and to enhance biodegradability of PTA wastewater using coagulation–flocculation process. Based on the results obtained, the practical applicability of pretreatment concept to PTA wastewater followed by aerobic biological treatment is discussed.

2. Materials and methods

2.1. Chemicals

The commercial grade chemical coagulants, viz., lime, alum, ferrous sulphate, ferric chloride, polyaluminum chloride were used. All other chemical reagents purchased from Merck India Ltd. were of analytical grade.

2.2. Wastewater source

The wastewater for the studies was obtained from the effluent treatment plant of a PTA production unit at Haldia, West Bengal, India. The total volume of wastewater generated by this plant is estimated at 2500 $m^3\ d^{-1}$. An hourly wastewater sample was collected from mixing tank of the effluent treatment plant and a 24 h composite was prepared for the experimental studies. The effluent treatment plant failed to function at desired level of treatment due to the presence of toxic constituents in the effluents.

2.3. Analysis of physico-chemical parameters

Composite wastewater samples collected from the plant were analyzed for various physico-chemical parameters such as pH, COD, BOD, total ammonia nitrogen (TAN), total Kjeldahl nitrogen (TKN), total phosphate (TP), total solids (TS), total alkalinity (TA) and mixed liquor suspended solids (MLSS).

Changes in chemical oxygen demand (COD) were determined by means of the dichromate reflux standard method; biological oxygen demand (BOD) and pH were measured by procedures described in standard methods [34]. COD determinations, were carried out with samples (10 ml each) which was centrifuged and filtered through 0.45 μm millipore filter. Experiments were done in duplicate for the same set of conditions. The wastewater characterization and measurements were performed according to standard methods [34]. pH was determined by pH meter (WTW multiline P4). The variations were systematically observed within ±5% of the stated values.

2.4. Source of microorganisms

The microbial culture was bought from the existing working aerobic wastewater treatment plant at PTA production unit at Haldia, West Bengal, India. The sludge for biological degradation was collected from clarifier return activated sludge. Fresh activated sludge was grown at the lab using the return activated sludge with continuous feed of neutralized raw effluent. The sludge was aerated continuously and fed initially for 5 days using 5 g d^{-1} of commercial sucrose, 250 mg d^{-1} of nitrogen as NH_4Cl, and 50 mg d^{-1} of phosphorus as K_2HPO_4. This activated sludge was acclimatized by gradual introduction of the PTA wastewater in increasing COD concentrations (10%, 15%, 25%, 50%, 66%, 75%, 90–100%) every 3 days since the first introduction of 10% concentration. This activated sludge was used for further aerobic treatment studies.

2.5. Chemical coagulation and flocculation

Laboratory scale evaluation of chemical coagulation and flocculation is performed using a four-place jar test apparatus. Phipps & Bird (USA) jar testing apparatus was used for physico-chemical treatment of combined PTA wastewater to evaluate appropriate chemical coagulant and optimization of coagulant dosage for effective performance. The optimum concentrations of different coagulating agents with respect to percent removal of contaminants were determined through extensive jar test studies.

A standard 1000 mg l^{-1} solution is prepared from which the dilutions are made. The wastewater is treated in batch mode in 1 l jar at various coagulant doses and analyzed. Each litre of wastewater treated in the jar takes about approximately 45 min to complete the treatment after which the samples are analyzed for the specified parameters. The experimental process consisted of three subsequent stages: initial admixture was subjected to rapid (flash) mixing at 100 rotations per minute (rpm) for a minute, followed by a slow mixing at 30 rpm for 30 min. In the final stage the floc was allowed to settle for 90 min.

Four equal volumes of polyethylene beakers were used to examine the four different combinations of coagulant. Sample bottles are thoroughly shaken, for resuspension of settled solids and appropriate volume of sample is transferred to the corresponding jar test beakers.

The pH was adjusted to 7.0 through addition of lime (500 mg l^{-1}) to the effluent. The supernatant is then subjected to coagulation, flocculation and sedimentation using alum (200–1500 mg l^{-1}), polyaluminum chloride (PAC) (200–600 mg l^{-1}), ferric chloride (200–1800 mg l^{-1}) and ferrous sulphate (200–1800 mg l^{-1}).

2.6. Enhancing sludge settleability

Commercial grade anionic polyelectrolyte (Magnafloc LT: 31) was examined along with coagulants (PAC, Alum, $FeCl_3$ and $FeSO_4$) to improve sludge settleability. Addition of 1.5 g l^{-1} commercial grade polyelectrolyte along with effective chemical coagulant (PAC 500 mg l^{-1}) was mixed, to improve sludge settleability. After 30 min settling the supernatant was collected using a plastic syringe and analyzed for various parameters

2.7. Volumetric procedure using the Imhoff cone

The quantity of sludge generated during the studies was monitored. Once the experiment has been performed in the jar test, the contents of the glasses are transferred to Imhoff cone and the sludge production is determined by direct reading as ml of sludge per liter of wastewater.

2.8. Aerobic biological treatment

Treated effluent from physico-chemical treatment was further subjected to aerobic biological oxidation (activated sludge) process at various F/M ratios ranging from 0.3 to 0.8 kg BOD kg $MLSS^{-1}$ d^{-1} and at 3000–5500 mg l^{-1} MLSS. Aeration to the bioreactor was provided by compressed air through four diffusers at the bottom of the reactors. As the wastewater is nutrient deficient, NH_4Cl (50 mg l^{-1}) and K_2HPO_4 (10 mg l^{-1}) were added in requisite quantities to supplement nutrients during aerobic biological treatment to achieve optimum performance.

The MLSS content in the aerobic bioreactor was controlled through periodical removal of sludge through wasting as defined in the formula:

$$\text{sludge wasting rate}(\mathrm{l\,d^{-1}}) = \frac{V \times X}{\theta \times X_r}$$

where V is the volume of the reactor in litres, X & X_r the concentration of mixed liquor in the reactor and recycle sludge, respectively, θ is the sludge retention time. The concentrated sludge is recycled with a peristaltic pump. The wasted sludge is sent back to the sludge bank.

3. Results and discussions

3.1. Characteristics of PTA industrial wastewater

The wastewater is characterized by substantial organic mater. The characteristics (range) of combined PTA wastewater used in coagulation–flocculation experiments are presented in Table 1.

Table 1
Characteristics of combined PTA wastewater

Sr. no.	Parameters[a]	Concentration	
1	pH	4.7–6.2	5.3
2	Total alkalinity	250–984	690[b]
3	Total solids	5141–6868	6123[b]
4	COD	7402–10800	9222[b]
5	BOD_5, 20 °C	4050–6165	4150[b]
6	Total ammonia nitrogen	3.52–4.28	3.86[b]
7	Total Kjeldhal nitrogen	13.4–17.5	15.51[b]
8	Total phosphates	13.70–33.31	18.84[b]

[a] All parameters expressed in mg l^{-1} except pH.
[b] Combined PTA wastewaters used in coagulation–flocculation experiments values are average of five samples.

3.2. The comparison of efficiency of different coagulants

Numerous jar tests were carried out in order to establish a working coagulant and optimum dosage of coagulant in the treatment of PTA wastewater. Effect of single coagulant at different doses for reduction of pollutant parameters BOD and COD was evaluated. Coagulant doses vary widely to obtain the same removal efficiency of BOD and COD working dose of coagulants alum (1150–1300 mg l^{-1}), PAC (460–520 mg l^{-1}), ferrous sulphate (1300–1450 mg l^{-1}) and ferric chloride (1000–1150 mg l^{-1}) were obtained through the studies. The results of the study are presented in Fig. 1. The coagulant ferric chloride and ferrous sulphate did not show much variation in the study in terms of BOD and COD removal. A maximum COD removal was obtained by alum and polyaluminum chloride (39.5% and 41.2%, respectively) whereas the BOD removal (28.7% and 30.7% COD, respectively). However, PAC requirement was less than half of alum to meet the same efficiency of alum, $FeCl_3$ and $FeSO_4$. In case of ferric chloride and ferrous sulphate maximum removal efficiency of COD was 35.0% and 36.6% whereas BOD removal was 27.5% and 27.7%, respectively. Increasing dose of ferric chloride and ferrous sulphate produced persistent yellowish colour, which was observed after the biological treatment and is aesthetically objectionable and increases the oxygen requirement in biological treatment. Hence these two coagulants were discontinued in further studies. Addition of polyelectrolyte to increase sludge settleablity on these coagulants (ferric chloride and ferrous sulphate) did not show significant improvement in comparison to alum and PAC.

3.3. Effect of coagulant combination dose on coagulation

Lime was used mainly for neutralization as the combined PTA wastewater was acidic in nature, and is not directly applicable for biological treatment. To investigate the optimum coagulant dose, the pH value of the wastewater is maintained between 6.7 and 7.0 by addition of lime at various doses starting from 300 to 500 mg l^{-1}. The pH of the wastewater did not rapidly shift when the lime concentration was between 300 and 500 mg l^{-1}.

Hence, this concentration range was selected for neutralizing the wastewater. Whereas at concentration above and below, there was rapid shift of pH. This was just an observation and our major objective was to find out the optimum dosage of lime only.

The percent BOD and COD reduction of PTA wastewater at various mixture doses of lime as one coagulant and alum, PAC, ferric chloride and ferrous sulphate as the other coagulant (Figs. 2 and 3) were studied. The optimum alum dosage of 1300 mg l^{-1}, effectively removed a maximum of 34.9% COD and 42.4% COD from PTA wastewater. Increased alum dosage upto 1500 mg l^{-1}, resulted in an additional 0.31% BOD and 0.4% COD reduction. Table 2 presents the sludge volume at optimum dose of coagulants. The sludge generation at optimum alum dosage was around 140 ml l^{-1}. The maximum sludge generation was observed in alum followed by ferrous sulfate, ferric

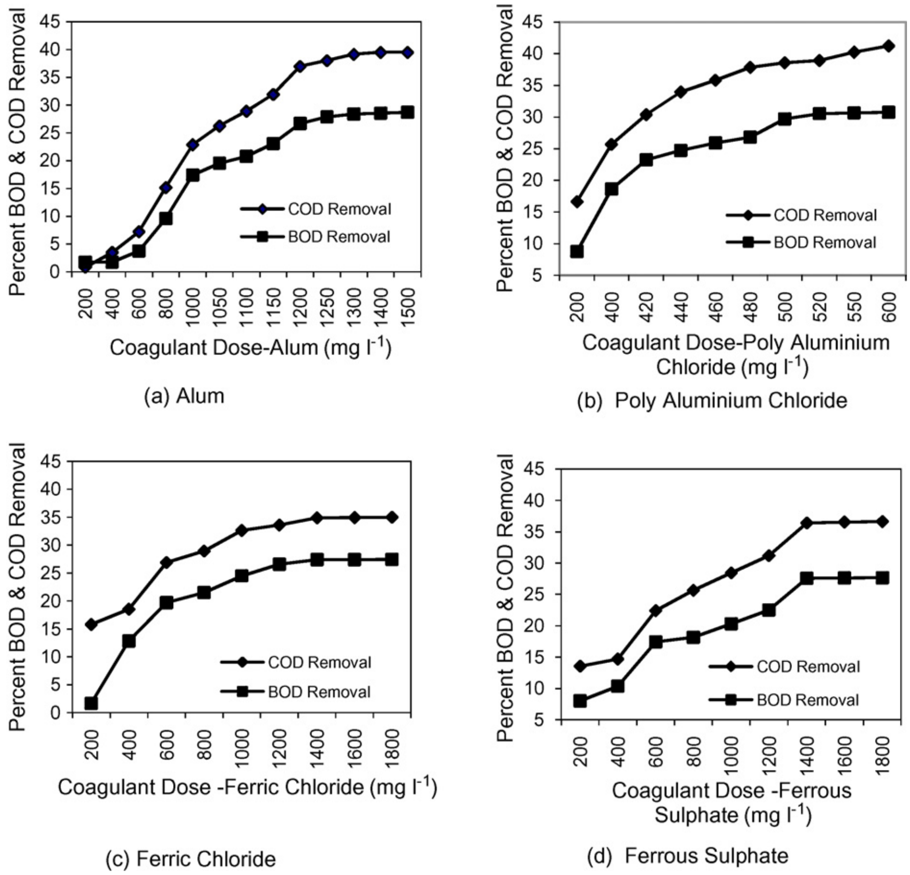


Fig. 1. Percent BOD and COD removal at various doses of coagulants; alum, polyaluminium chloride, ferrous sulphate and ferric chloride.

chloride and PAC. Alum dose of 1250 mg l^{-1} along with lime dose of 500 mg l^{-1} together removed about 35.3% BOD and 42.2% COD from combined wastewater. The pH of the treated effluent was observed to be 7.2, and sludge generation was 130 ml l^{-1}.

An optimum dosage of PAC (500 mg l^{-1}) achieved 46.7% BOD and 45.3% COD removals. An increased dosage of 600 mg l^{-1}, yielded marginal increases of 0.4% BOD and 4.1% COD reduction. The optimum PAC dosage produced 75 ml l^{-1} sludge. Percent BOD & COD reductions by PAC are about 46.7% and 45.3%, respectively. Beyond 500 mg l^{-1} (PAC) and 450 mg l^{-1} (lime) efficiency of BOD and COD reduction ceased to increase.

Ferric chloride dose was optimized at range 1100–1200 mg l^{-1} along with lime (450–500 mg l^{-1}); a maximum BOD and COD reduction of 31.64% and 39.6% was obtained at 1150 mg l^{-1} for lime 500 mg l^{-1} concentration. However, for 450 lime concentration at 1100 mg l^{-1} ferric chloride concentration reduction of 30.6% was obtained. A maximum BOD reduction of 39.56% was obtained at dose of 1150 mg l^{-1} against lime dosing of 500 mg l^{-1}. However, without lime COD removal was 35% and BOD removal was 27.54%.

Ferrous sulphate was optimized for working dose between 1300 and 1450 mg l^{-1} and the dose of 1350 mg l^{-1} was found to be optimum. A maximum COD removal (38.3%) and BOD (33.2%) was obtained at lime dose of 500 mg l^{-1} and ferrous sulphate 1350 mg l^{-1}.

Table 2
Treated effluent from chemical coagulation and activated sludge process

Sr. No.	Coagulant (optimum dose)	Sludge production (ml l^{-1})
1	PAC	75
2	$FeCl_3$	115
3	$FeSO_4$	130
4	Alum	140

3.4. Biodegradability enhancement of PTA wastewater by coagulation–flocculation process

The chemical oxygen demand (COD) and 5 day BOD were selected as major parameters to follow since the ratio BOD_5/COD indicates biodegradability of wastewater. Jar test experiments were employed in order to determine the optimum conditions for the removal of BOD and COD in terms of effective dosage, and pH control. Treatment with lime:PAC:PE in the ratio 450:500:1.5 (mg l^{-1}), respectively, proved to be effective at a pH 6.4. The sludge settleability was improved by using commercial grade anionic polyelectrolyte in combination with chemical coagulants. The amount of sludge generated with different coagulants in the studies is presented in Table 2.

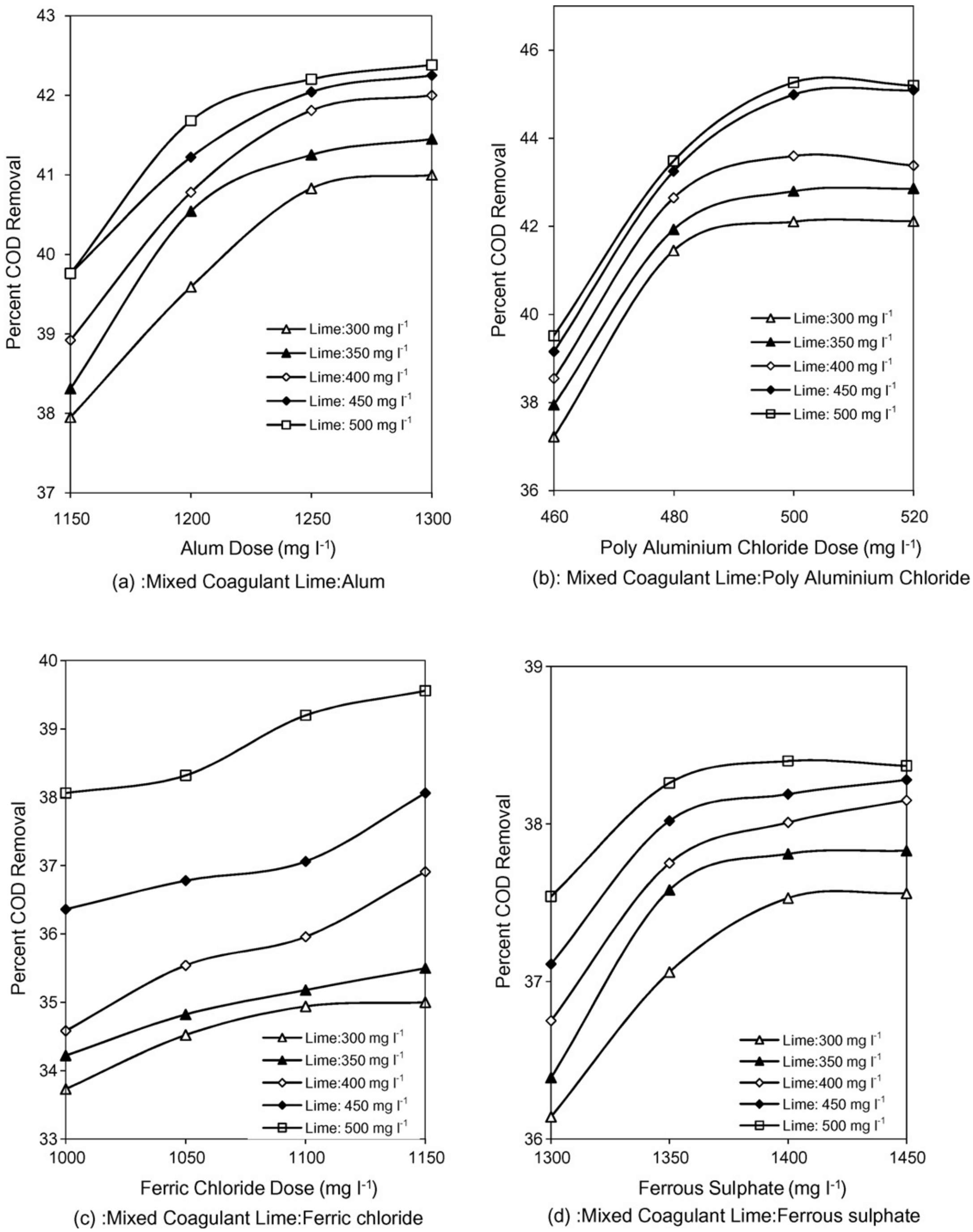


Fig. 2. Percent BOD removal at various doses of mixed coagulants; lime along with alum, polyaluminium chloride, ferrous sulphate and ferric chloride.

The use of polyelectrolyte (Magnafloc-LT-31) to enhance sludge settleability, at a dose of $1.5\,mg\,l^{-1}$, along with coagulant PAC at optimum dosage achieved a meager increase in 1.2% BOD and 2.3% COD reduction. The sludge generation was $115\,ml\,l^{-1}$, as compared to $75\,ml\,l^{-1}$ in case of using PAC alone. The sludge settling velocity, indicated improvement in settling velocity from 1.25 to $15\,cm\,h^{-1}$ on use of polyelectrolyte. Biodegradability, evaluated in terms of the BOD_5/COD ratio, was observed to enhance from 0.45 to 0.67. The pH of the treated effluent after addition of the polyelectrolyte was in the neutral range, which was favorable for aerobic biological treatment.

3.5. Bio-oxidation of pretreated PTA effluent by activated sludge process

Initially, the biodegradability of the PTA wastewater was evaluated through the evaluation of the BOD_5/COD ratio. The biological oxidation reactor for treatment of PTA wastewater is presented in Scheme 2. For untreated wastewater sample

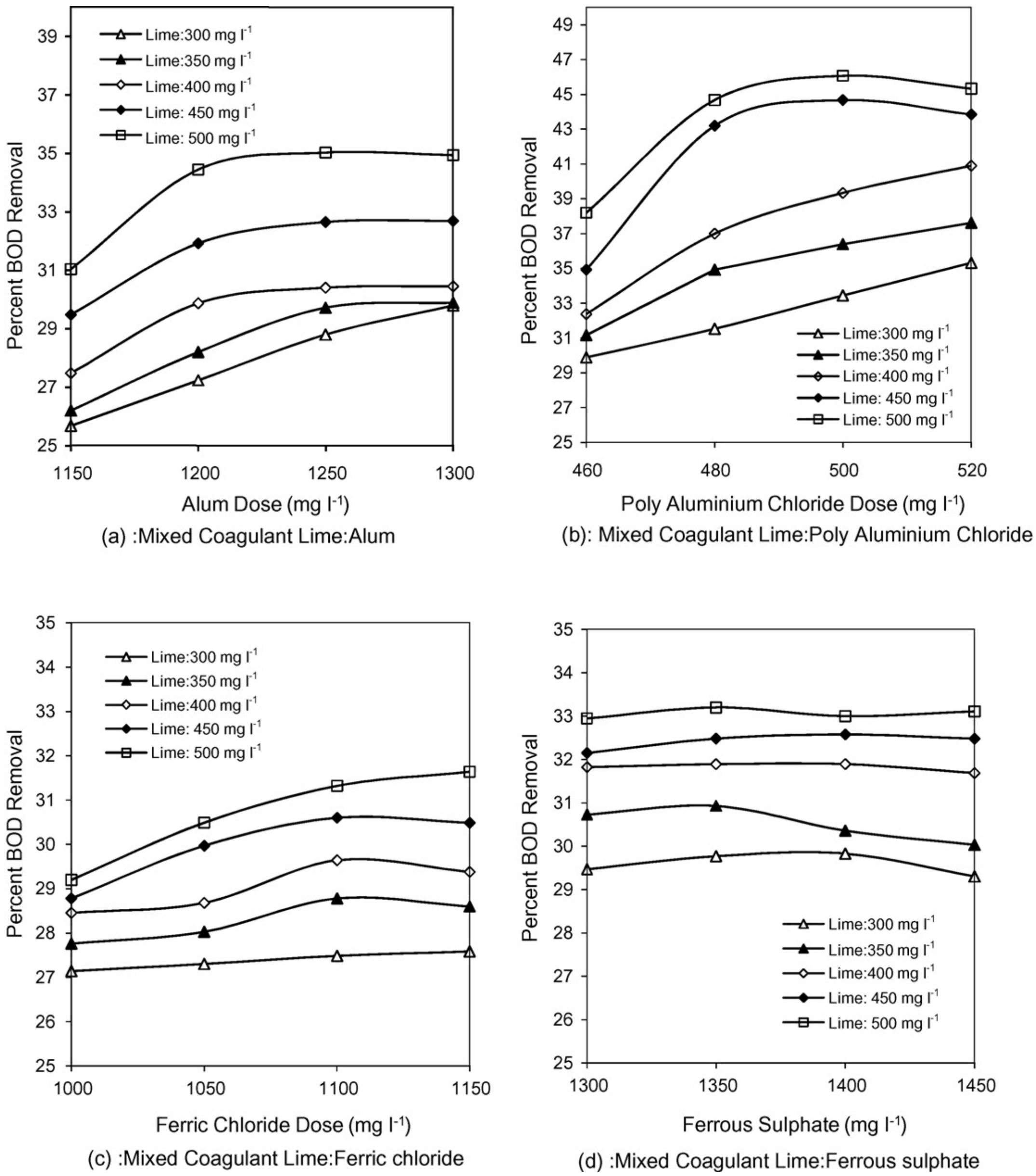
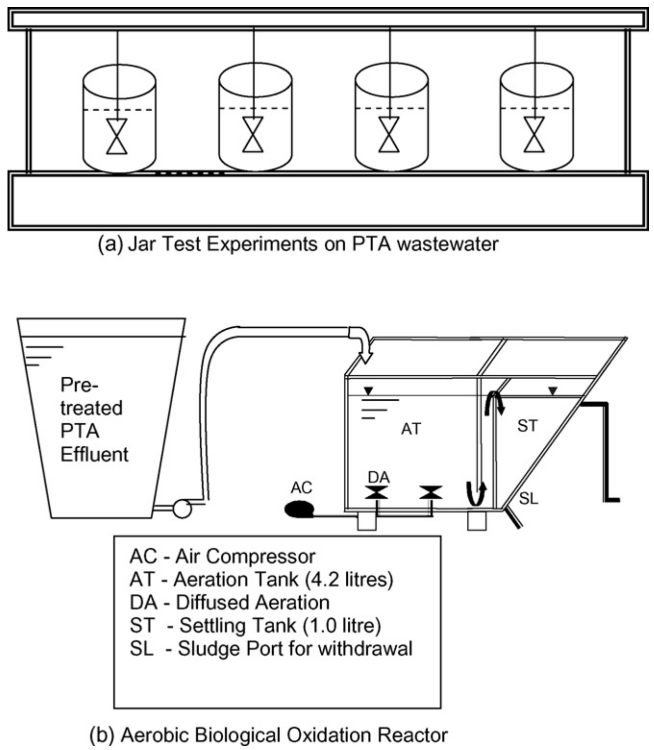


Fig. 3. Percent COD removal at various doses of mixed coagulants; lime along with alum, polyaluminium chloride, ferrous sulphate and ferric chloride.

Table 3
Volume of sludge production in the coagulation–flocculation studies

Parameters[a]	Raw composited PTA wastewater	Physico-chemical (Lime:PAC:PE[b], 450:500:1.50)	Treated effluent quality from activated sludge process (F/M (d^{-1}) = 0.4); MLSS ($mg\,l^{-1}$)				Standards prescribed by regulatory authority
			3000	3500	4000	4500	
pH	5.3	6.7	8.3	8.3	8.3	8.3	5.5–9.0
Total alkalinity	690	720	1370	1380	1390	1400	–
Total solids	6123	4265	3498	3522	3546	3710	–
COD	9222	3406	264	256	244	238	250
BOD_{5d}, 20 °C	4150	2275	40	34	25	22	30

[a] All values are expressed in $mg\,l^{-1}$ except pH.
[b] Magnafloc lt-31.



Scheme 2. Jar test apparatus for coagulation–flocculation studies and bench scale biological oxidation reactor.

of 9222 and 4150 mg l^{-1} initial COD and BOD concentration, respectively, this parameter attains values of about 0.45 while coagulation–flocculation treatment process increase this ratio to 0.67, which represent considerable enhancement in biodegradability. Percent BOD & COD removals from activated sludge process at various F/M ratios and MLSS concentrations are depicted in Fig. 4. The aerobic biological oxidation at MLSS concentration of 4000 mg l^{-1} at F/M ratio of 0.4 achieved 92.7% COD and 98.7% BOD reduction. The characteristics of final treated effluent obtained from oxidation process are presented along with the standards prescribed by the regulatory authorities Table 3. Results indicate that coagulation–flocculation process can trap the recalcitrant compounds with suspended solids. The studies for aerobic biological oxidation (activated sludge process) using the treated effluent from coagulation–flocculation process using PAC and polyelectrolyte were carried out at various F/M ratios ranging from 0.3 to 0.8 kg BOD kg MLSS^{-1} d^{-1} and MLSS between 3000 and 5500 mg l^{-1}.

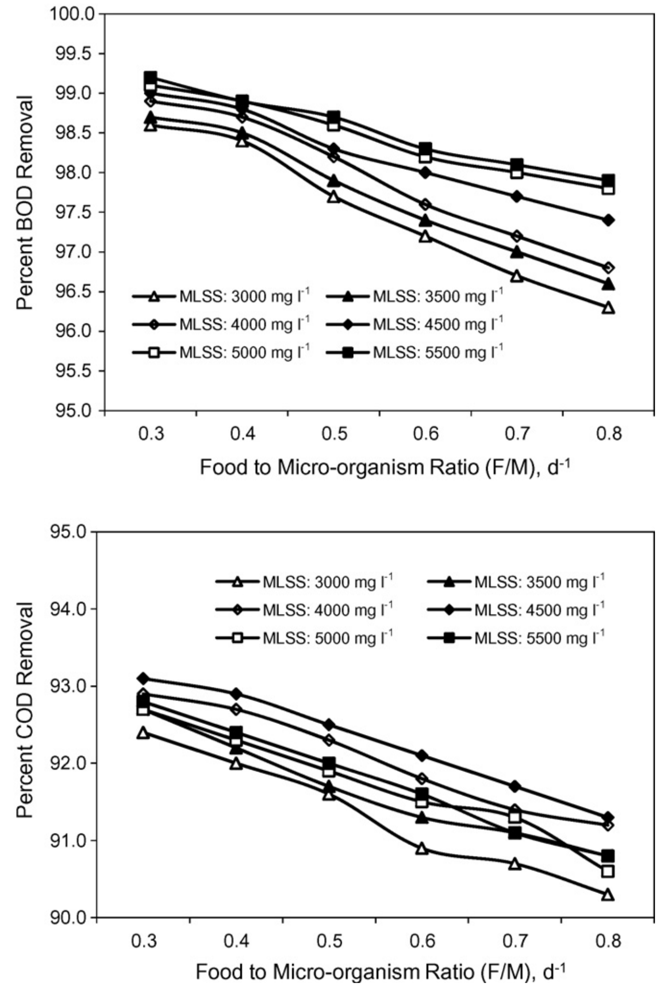


Fig. 4. Percent BOD & COD removals at various food to microorganism ratio (F/M) and MLSS concentrations at activated sludge process for the treatment of physico-chemically treated wastewater.

4. Discussions

In order to meet regulatory norms it is necessary to subject effluents to an appropriate treatment before discharge into environment. The BOD_5/COD ratios of certain wastewater indicate that biological treatment may not always be applicable for all cases and hence pretreatment is required [35,36] to enhance biodegradability.

The process wastewaters are treated individually or in combination with mechanical, chemical and biological methods. Among the currently employed chemical unit processes in the treatment of wastewaters, coagulation–flocculation has received considerable attention for enhancing the biodegradability index of wastewaters. Jar test experiments were employed in order to determine the optimum conditions for the reduction of BOD and COD from PTA wastewater. Treatment with lime:PAC:PE (450:500:1.5) combination proved to be effective in PTA wastewater treatment. The process was very effective in the reduction of COD and BOD at 36% and 45%, respectively. The pH of supernatant of chemical treatment was found to be in neutral, which is conducive for biological treatment. In coagulation–flocculation process, adsorptive micellar flocculation mechanism seems to contribute to the removal of organic matters with non-biodegradable toxic material.

The coarsely dispersed particles are easily removed by mechanical treatment although finely dispersed particles and colloidal particles remain. To remove them, coagulation methods are needed. The particles in a colloid system agglomerate to form larger particle aggregates, which are settled out and removed mechanically from the wastewater.

Coagulation and flocculation method is widely used for treating majority of industrial wastewaters [37,38]. Terephthalic acid is the main component in an alkali decrement wastewater, which was efficiently removed using ferric chloride in a high pH solution. About 90% removal of terephthalic acid is achieved at pH between 8 and 11 especially, the removal reached 94.3% at pH 11 [39]. The effectiveness of the coagulation treatment depends on many factors such as composition of the wastewater, the type of colloidal particles, their concentration and degree of dispersion, its temperature, the rate of mixing and the order in which coagulants and flocculants are introduced into the wastewater, the presence of electrolytes, and other substances in wastewater. Suspended particles acquire an electrostatic charge, which, is usually negative in water treatment. The charges produce repulsion between particles, which tends to stabilize the suspension. In colloidal suspensions, which have a maximum particle size of less than 2 μm, this repulsion effectively prevents settling. Coagulating agents are selected to have an opposite charge to that of the colloidal solids to effectively neutralize that charge. This process destabilizes the suspension and allows the particle to floc together. Flocculating agents form bridges between particles and lead to the formation of larger agglomerates, which can be removed by settlement or flotation.

Pretreatment through coagulation–flocculation process enhances the BOD_5/COD ratio of wastewater from 0.45 in raw wastewater to 0.67 for the treated wastewater. The optimum dosage of 450 mg l^{-1} lime, 500 mg l^{-1} of PAC and 1.5 mg l^{-1} polyelectrolyte removed 63.1% COD and 45.2% BOD. The biodegradability of the effluent after coagulation–flocculation process was significantly increased with the total BOD and COD removal of 97.4% and 99.5%, respectively, at 24 h HRT. The dissolved oxygen concentration in the aeration tank was observed to be 1.8–2.0 mg l^{-1}. BOD reduction was achieved in activated sludge process at 4000 mg MLSS l^{-1} and 0.4 kg BOD kg $MLSS^{-1}$ d^{-1} (F/M ratio) as compared to adopting bio-oxidation without chemical pretreatment which yielded 80% COD and 86% BOD reduction.

An investigation on anaerobic degradation mechanism and bio-kinetics for UASB has also been reported for easily biodegradable compounds, viz., acetic, benzoic and formic acids from PTA wastewater [40]. Compared with anaerobic process, an aerobic process has advantages of high degradation capacity, but the major disadvantages are high hydraulic retention time (HRT) and low elimination rates. Aerobic degradation of DMT was strongly inhibited by addition of terephthalic acid to the culture medium [41–43]. Pretreatment of wastewater containing terephthalic and dimethyl isophthalate can be achieved with microorganisms in engineering systems, resulting in high COD and BOD reduction only after removal of acetic, and benzoic acid produced during biodegradation of terephthalic acid from the DMT effluent [44].

5. Conclusions

The PTA production generates wastewater containing various organic and inorganic constituents that are resistant to biological degradation with low biodegradability ratio (BOD_5/COD = 0.45). These complex matrixes show a resistance towards conventional aerobic biological treatment process. In this work, the coagulation–flocculation process was initiated as a pretreatment method to increase biodegradability and reduce the toxicity of wastewater prior to aerobic biological treatment process. Pretreatment enhances the BOD_5/COD ratio of raw wastewater from 0.45 to 0.67. The characteristics of the treated effluent from coagulation–flocculation process coupled by aerobic biological sludge process conformed to the prescribed standards for discharge into inland surface waters. Determination of optimum concentration of coagulant agents has been delineated to achieve maximum process efficiency with minimum consumption of coagulant agents. Thus the pretreatment of the PTA effluent using coagulation–flocculation followed by aerobic treatment is a techno-economical and a viable alternative to treat non-biodegradable PTA wastewater. It is clear that a highly efficient system could be cultured for degradation of PTA wastewater using natural microbial flora.

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