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Removal of COD in Purified Terephthalic Acid (PTA) Effluent with Coagulation, Aqueous Oxidation and High Porosity Membrane

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Abstract. Present study was focused on purified terephthalic acid (PTA) industry wastewater treatment located at Port Qasim, Karachi. PTA wastewater containing high COD (100000 to 150000 mg/L) was treated with coagulate ferrous ion and then was oxidized independently with aqueous hydrogen peroxide using different doses at 45 °C for 1h. The resulting wastewater was passed through RO plant equipped with high porosity bio-ceramic membrane. It was observed that coagulation and oxidation processes have potential to reduce 87.9% COD but complete reduction up to 99.8% was achieved after passing the effluents from high RO plant equipped with high porosity ceramic membrane.

Keywords: COD reduction, coagulation, active oxidation, ceramic membrane, purified terephthalic acid

Introduction

Purified terephthalic acid (PTA) is a refractory organic material and an imperative industrial chemical used as precursor for manufacturing good quality multipurpose plastics like PBT (poly butyl terephthalate), PET (polyethylene terephthalate), and bio-plastic i.e., PTT (polytrimethylene terephthalate). It is also utilized for the production of chemical fibres, pesticides, dyes etc. Because of its wide-ranging applications, significant manufacturing and chemical distinctiveness, terephthalic acid and its related organic compounds have become omnipresent as environmental contaminants, and they have been found in soil, aquatic systems, and associated organisms (Zhang *et al*., 2013).

In 1993, PTA production was estimated to be 425 to 525 million tonnes world over. In 2002, its annual growth rate increased to 7.5% and accounted for about 26.12 million tonnes, with China growth rate attributed for about 2.6 million tonnes. PTA demand further increased to 28.8 million tonnes in the year 2005, in which China contributed 12.14 million tonnes that is 42% of the total world demand (CR, 2007). During production of every ton of PTA, about 3-4 m^3 of wastewater with 4-10 kg COD/m^3 is produced (Shafaei *et al*., 2010; Karthik *et al*., 2008; Franck and Stadelhofer, 1988). Major portion of PTA wastewater comprises of benzoic acid (BA), phthalic acid (PA), *p*-toluic acid (*p*-Tol), 4-carboxybenzaldehyde (4-CBA), and terephthalic acid (TA) with minor concentrations of the *p*-xylene, methyl acetate and 4-formylbenzoic acid (Kleerebezem *et al*., 1999). The contribution of these chemicals towards COD in the wastewater, at times become more than 85%.

US Environmental Protection Agency has recently added this class of chemicals to the list of priority pollutants (USEPA, 2007) because phthalate (its ester degradation intermediates) poses serious threat to human health causing acute, sub-acute, chronic and molecular toxicity. It is also reported that the exposure of pure chemical PTA causes impair renal damage, liver and testicular function, bladder cancer and inhibit microbial growth (Zhang *et al*., 2013; Chen *et al*., 2001; Qu *et al*., 2000). Therefore, treatment of PTA contamination is very essential not only to preserve and protect natural ecosystems but also to hinder its detrimental effect on human health (Pernille *et al*., 2007; Scholz, 2003; Qi *et al*., 2002).

Various methods are being used for the treatment of industrial wastewater to remove PTA world over like, supercritical water oxidation, ozone assisted photochemical oxidation ($UV/O_3/H_2O_2$), advanced oxidation processes (AOP), UV-assisted ozonation (UV/O_3), ozone-assisted photo-fenton oxidation ($UV/O_3/H_2O_2/FeSO_4$), photo-fenton oxidation ($UV/H_2O_2/FeSO_4$), and radiation treatment using gammaray, treated with powdered and

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granular activated carbon and biological treatment (Satish, 2013; Anbia *et al*., 2012; Saleem *et al*., 2011; Aygun and Yilmaz, 2010; Zhu *et al*., 2010; Barbusiñski, 2005). Although these procedures have been developed to treat industrial wastewater but there are some limitations which restrict to use them like high cost, generation of sludge and toxic intermediates that consequent to secondary pollution.

The alternate approach is to lowering down the COD (chemical oxygen demand) which measures the oxygen status of the component in the wastewater. The COD actually indicates the pollution level and sewage contents and also provides a gauge which relates to the impending environmental threats of a wastewater. High influx of chemicals in effluents commences chemical reaction that consume high quantity of oxygen (i.e., high COD) resulting lowering of oxygen amount required for biological life (WDNR, 2007). Therefore, it is very important to maintain COD for protecting and conserving aquatic environment. There are several methods available for COD removal from wastewater i.e., electrochemical Fenton process, flocculation and advanced oxidation processes, activated carbon and low cost adsorbent (Eslami *et al*., 2013; Lakdawala and Lakdawala, 2013; Hussain *et al*., 2013; Rakholiya and Puranik, 2012; Aluyor and Badmus, 2008; Zayas *et al*., 2007). The aim of this study was to reduce COD level by coagulation, oxidation and reverse osmosis with high porosity membrane (bio-ceramic) (Zheng, 2012). The results show that this method has remarkable potential to remove COD from PTA wastewater.

Materials and Methods

All analytical analysis and experiments were performed in duplicate.

Apparatus. A model 3510 pH meter Genway with glass electrodes was used for the pH, DR-4000, HACH Spectrophotometer was used for COD determination COD Reactor, HACH was used for digestion. Hot plate/electric stirror (HS 10_2, Torry Pines Scientific, USA) was used for stirring.

Chemicals and reagents. All chemicals employed in this study were of analytical grade (Merck, Darmstadt, Germany). All solutions were prepared in distilled/deionized water made on each experimental day. Glassware used for all experiments, was soaked with HNO_3 (~10%) for 24 h, and rinsed with distilled/de-ionized water prior to drying. Hydrogen per oxide used was of analytical grade as 30% w/v. The ferrous sulphate hepta hydrate ($FeSO_4.7H_2O$) was used as the coagulation process. Solutions of NaOH and HCl were used for pH adjustments.

Sample collection and pretreatment. Sampling and analysis of the raw wastewater coming from PTA industry was done by taking grab sample (WDNR, 2007). The wastewater samples were collected directly from main drain on a week basis for segregation purpose. After collection, first analysed the COD parameter to determine the quality of the incoming raw wastewater (Table 1). Segregation of effluent means separation as per effluent characteristics. It is a new concept for wastewater minimization and optimizes the operation cost (Tchobanoglous *et al*., 2003).

Analytical method. Standard Methods were used for determination of COD (APHA, 1998). The pH measurements were performed using a pH meter (3510 pH meter Genway).

The test was conducted on the standard potassium hydrogen phthalate (KHP) solution to evaluate the

Table 1. Physicochemical characteristics of PTA raw water

		NEQS limits (mg/L)		
Parameters	PTA effluent	into inland water	into sewage treatment	into sea
Temperature (°C)		≤3	≤3	≤3
pH	3.3	6 – 9	6 – 9	6 – 9
COD (mg/L)	108,000	150	400	400
BOD_5 (mg/L)	476	80	250	80
TSS (mg/L)	875	200	400	200
TDS (mg/L)	-	3500	3500	3500
Oil & grease (mg/L)	No traces	10	10	10
Sulphide (S) (mg/L)	No traces	1.0	1.0	1.0
Ammonia (NH_3) (mg/L)	147	40	40	40

technique and quality of reagents. At selected time interval, 5 mL of reaction mixture was taken and then analyzed for COD. The samples containing H_2O_2, which interfere with the COD measurements, were eliminated by the addition of MnO_2 powder. Before each analysis, samples were centrifuged to remove MnO_2 (Talinli and Anderson, 1992).

Methodology. Wastewater treatment was done in three phases such as coagulation, flocculation and oxidation using high porosity permeable membrane as shown in Fig. 1-2.

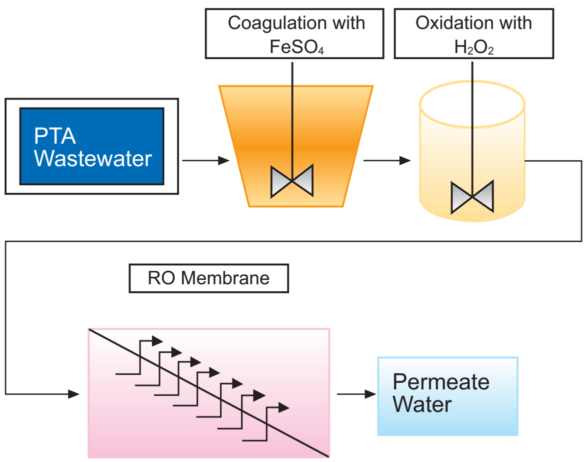

Fig. 1. PTA wastewater treatment flow diagram.

Raw wastewater samples were collected at random from industrial purified terephthalic acid (PTA) plant. This PTA plant manufactures a variety of multipurpose plastic products. The parameters like chemical oxygen demand (COD), biological oxygen demand for 5 days (BOD), total dissolved solids (TDS), total suspended solids (TSS), sulphides, ammonia, oil and grease, temperature and pH value of raw wastewater samples were performed before coagulation process.

Coagulation and flocculation. Coagulation and flocculation studies were performed in a standard jar-test apparatus (Jar Tester Model CZ150) comprises of six paddle rotors (24.5mm × 63.5mm) and equipped with 6 beakers of 2 L volume. The commonly used metal coagulants fall into two general categories: (1) based on aluminium and (2) based on iron. This paper deals with the iron based coagulants that is ferrous sulphate. $FeSO_4$ was applied on w/v basis i.e., 2, 4, 8, 10 and 12 g/2000 mL of PTA waste water.

Before coagulation process, wastewater sample was thoroughly shaken to avoid possibility of settling solids. The experimental process consisted of the initial rapid mixing stage that took place for 10 min at 100 rpm, the following slow mixing stage for 45 min at 50 rpm and the final settling step for 2 h. After 2 h settling period, samples were withdrawn from supernatant for analyses. Process performance was monitored by analysis of COD values.

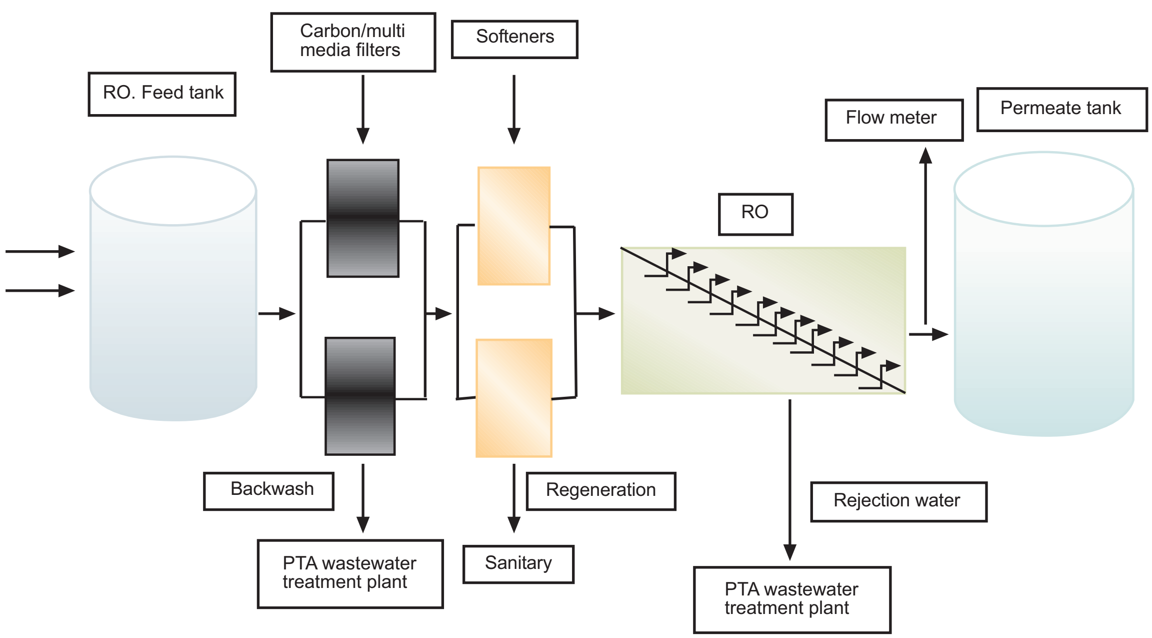

Fig. 2. RO flow diagram.

Oxidation by hydrogen per oxide. The oxidation of the organic compounds in the wastewater samples was carried out to further reduce the COD. This oxidative step was carried out using H_2O_2 (0.5% v/v) at pH 4.5 for 60 min. Coagulation supernatants were drawn in 1000 mL volume and labeled in six groups i.e., A, B, C, D, E and F. Hydrogen per oxide solution of known strength was prepared in de-ionized water in the range of concentration 4, 8, 12, 16, 18 and 20 mL and oxidized at 45 °C temperature.

Nano filtration through bio- ceramic membrane. After oxidation supernatant wastewater sample was passed through high porosity of bio- ceramic membrane (CSM, Model No.RE1812-88). COD was measured after passing from the membrane.

Results and Discussion

Present study was carried out to determine different parameters in analyzed samples. The average values of COD and BOD were found higher than the prescribed National Environmental Quality Standard (NEQS) limits. The results are expressed in Table 1. The results show high values of COD, BOD and removal of some or all of the contaminants making it fit for reuse or discharge back to the environment. Diseases have often been caused by discharging untreated or inadequately treated wastewater. Such discharges are called water pollution. The pollution of water has a serious impact on all living creatures, and properly treating wastewater assures that overall acceptable water quality is maintained.

Coagulation and flocculation process. Coagulation flocculation is also a common chemical water treatment process to treat industrial and domestic wastewater in order to remove suspended particles from the water. The raw wastewater produced by the industrial PTA plant a COD of 100,000-150,000 mg/L. During the course of coagulation-flocculation treatment selection of coagulant is the biggest problem to disperse the pollutants. In this process ferrous sulphate as a coagulant was assessed. Typically, results showed that this procedure is dependent on pH and concentration of ferrous sulphate, as a coagulant to remove COD and total suspended solids. When ferrous sulphate (10 mg/L) was added at pH =4.46, 65% of COD was removed. Hence, this shows that ferrous sulphate was more effective for PTA wastewater treatment. The results obtained from chemical coagulation to the raw PTA wastewater and iron coagulants ferrous sulphate at 10 g/2 L is listed in Table 2. The reduction of COD was observed in order of 7.7, 24.3, 37.5, 50.8, 65.0 and 65.0%.

Oxidation process. The results are summarized in Table 3. However, the presence of coagulant caused a reduction in COD up to 65%. Subsequent oxidation treatment caused a further decrease in COD. After irradiation of 60 min, COD had been reduced to 12987 mg/L with the maximum volume of H_2O_2 at 18 mL/L which correspond to COD reduction in order of 77, 82.4, 87.7, 87.8, 87.9 and 87.9%, respectively. In advanced oxidation processes, pH has a noteworthy effect on the removal efficiency of organic compounds. This study observed the effect of pH changes on the removal efficiency (Eslami *et al*., 2013; Lakdawala *et al*., 2013; Hussain *et al*., 2013), so the oxidative degradation processes were carried out at the initial pH of the PTA wastewater (5.1-6.8) and repeated at various other pH values (both acidic and alkaline).

Table 2. Effect of coagulation on COD

Adsorption dose (g)	pH	Concentration (mg/L)	Removal (%)
Fresh	3.3	108,000	-
2	3.7	99,700	7.7
4	4.1	81,300	24.3
6	4.5	67,500	37.5
8	4.7	53,100	50.8
10	4.9	37,800	65.0
12	5.1	37,800	65.0

Coagulation with ferrous sulphate at different adsorbent doses in weight by volume (volume = 2 L; contact time = 1 h; temperature = 25°C; mixing speed = 45-50 rpm).

Table 3. Effect of oxidation on COD

Oxidant dose (mL)	pH	Concentration (mg/L)	Removal (%)
After coagulation	5.1	37,800	65.0
4	5.4	24765	77.0
8	5.9	18959	82.4
12	6.3	13200	87.7
16	6.5	13167	87.8
18	6.7	12987	87.9
20	6.8	12987	87.9

Oxidized with hydrogen per oxide at different doses (volume = 1 L; contact time = 1 h; temperature = 45 °C; mixing speed = 120-130 rpm).

RO (Nano technology) process. In this study, coagulation-flocculation was examined as a pretreatment procedure for the treatment of PTA wastewater. The result of different organic and inorganic coagulants on the treatment of wastewater collected from flow coagulation of an effluent treatment and contaminated supplementary membrane was studied. Furthermore, PTA wastewater was treated and passed through nano based RO system with high porosity permeable membrane (bio-ceramic) (Pradeep *et al*., 2009, as shown in RO flow diagram (Fig. 2). Rejection of RO water dropped in the first stage i.e., mixing tank.

After this study, results obtained were compared with NEQS limits. At optimum conditions, COD of the waste water was reduced by high COD rejection values shows superior class of the permeate stream which correspond to COD reduction on the NEQS limit (148 mg/L) removed 99.8% shown in Table 4.

The graphically presented results (Fig. 3) reveal a comparison of COD removal in coagulation and flocculation (65%), in oxidation (87.9%) and in RO (99.8%).

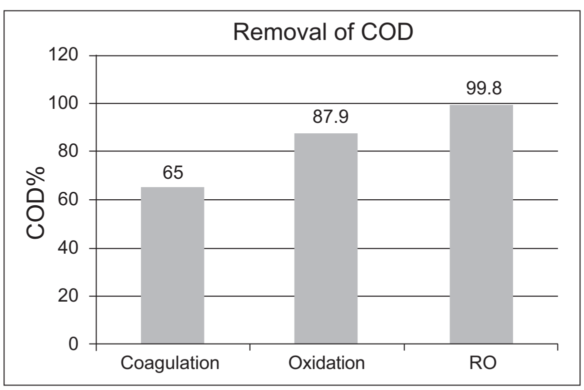

Fig. 3. Efficiency of COD reduction in PTA wastewater.

Table 4. Effect of application of advance RO on COD

Process	Concentration (mg/L)	(%)
After oxidation	12987	87.9
Pass out through RO (bio-ceramic membrane)	148	99.8

RO pressure at 350 psi.

Conclusion

It is concluded that this method is very efficient, economical and robust and can be reproduced at large scale level at PTA wastewater for the lowering of COD. The results of coagulation, oxidation and nano technology (RO) process show about 99.8% in COD reduction, which open a new process to reduce the organic and inorganic (ester and intermediate etc) load of wastewater. This process can be successfully implemented to many chemical/pharmaceutical manufacturing factories which will help in reducing water pollution in terms of COD.

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