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Integrated treatment of pharmaceutical effluents by chemical coagulation and ozonation

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ABSTRACT

The present study was aimed at treating pharmaceutical industry wastewater employing chemical coagulation and ozonation process. Coagulation was carried out by alum and lime. Parameters like coagulant type & dose, settling time and pH ranging from 0.5 to 1.0 g/L, 10 to 60 min and 4 to 10 respectively were investigated. Coagulation with alum proved to be effective with a dose of 0.75 g/L at pH 6 leading to 59% COD and 76.8% turbidity removal. Ozonation was carried out for 10–60 min. The COD abatement mechanism of ozonation is changed in unbuffered samples and is only 13.5% after 1 h ozonation. However, 93.4% color removal was reported at the same ozonation time. The treatment strategy is handy in treating pharmaceutical wastewaters.

1. Introduction

Pharmaceutical products are heterogeneous groups of chemicals which are used in veterinary medicine, human health and agrarian practice [41]. These are designed to have a precise method of action, so very low concentrations of pharmaceuticals are able to affect the aquatic organisms upon exposure [15]. There are 386 operational pharmaceutical units in Pakistan which discharge about 11,240 gallons of wastewater in the sewage system daily [37]. So, the discharged untreated pharmaceutical industrial effluent gets mixed with domestic wastewater [27,3,18], and pharmaceutical compounds are transported and distributed to the whole ecosystem [26,11]. Researchers have already detected some antibiotics in the effluent of pharmaceutical industrial units located in Lahore, Pakistan [18]. Thus, it is highly preferable to treat such a complex and potentially toxic wastewater to reduce ecological contamination.

Several techniques are used for the degradation of pharmaceuticals compounds [19,21]. The methods, commonly used for the treatments, include membrane filtration [40], the activated sludge biological method [29], advanced oxidation processes (AOPs) like ozone oxidation, photo-catalytic oxidation and Fenton processes [34]. However, most of these methods are either limited by their efficacy or due to cost ineffectiveness. The coagulation/flocculation process can be used as an alternative in pharmaceutical wastewater treatment scenarios due to their feasibility and cost effectiveness [24]. In this process, chemicals addition changes the physical state of dissolved and suspended solids, and promotes the elimination of these solids by precipitation [23]. Coagulation treatment has also been carried out for the reduction of turbidity and removal of color and pathogens [23,32] and is effective for the removal of organic matter [20,17].

The use of chemical oxidation based techniques like advanced oxidation processes (AOPs) are also feasible for the treatment of biologically resistant wastewater. Ozone oxidation transforms the non-biodegradable material into biodegradable form or CO_2 including the removal of taste, color [1], particles, chemical oxygen demand (COD), total organic carbon (TOC) [33,25] and increase the biodegradability of the wastewater [12,13].

Therefore, the efficiency of coagulation/flocculation and ozone oxidation processes in reducing the color, turbidity, and chemical oxygen demand of pharmaceutical industry wastewater to meet the existing legislative guidelines, was tested in this comparative study. The investigation was carried out to determine the suitable type of coagulant, coagulant dosage and also to evaluate the influence of pH on the coagulant efficiency because the coagulation mechanism is related to the pH conditions.

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2. Materials and methods

2.1. Sampling and characterization of wastewater

Composite samples were collected from the pharmaceutical plant located at Quaid-e-Azam Industrial State, Kot Lakhpat, Lahore, Pakistan when it was fully operational. Wastewater quality was monitored in terms of parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), conductivity, turbidity, dissolved oxygen (DO), total dissolved solids (TDS), total suspended solids (TSS), and total solids (TS) using Standard Methods (APHA, AWWA et al. [7]).

2.2. Chemical coagulation (jar test)

Coagulants, alum and lime, were used to treat the effluent. Optimal pH and dosages of both the coagulants were determined by jar test method [2]. A defined dose (0.5–1.0 g/L) of coagulant (lime/alum) was added to a series of six samples set each of 1L in reaction vessels and stirred at 80 rpm for 5 min to destabilize the pollutants and 40 rpm for 25 min to allow the collision between particles and their aggregation in bigger size. The experiments are performed at pH 6.9 (i.e. the actual pH of the effluent). After coagulation, the samples were allowed to settle down at room temperature.

2.3. Oxidation by ozone

Ozonation was carried out in bubble column reactor made of Perspex. The internal diameter of the reactor was 3.3 cm. A JQ-6M PURETECH model ozone generator, with a maximum ozone production capacity at the rate of 1.1 L/min was used [26]. The gas was nourished into the sample using diffuser stones to treat the 500 mL sample of pharmaceutical industry wastewater. The retention time (ozonation time) varied from 10 to 60 min. All experiments were performed at ambient temperature. The treated samples were withdrawn from the reactor at regular time intervals for analyses. The color absorption was measured at 254 nm.

2.4. Statistical analysis

Analysis of variance (ANOVA) between removal efficiencies of COD, turbidity and color in different treatments was evaluated using Microsoft office 2010.

3. Results and discussion

3.1. Wastewater properties

Wastewater discharged by the industries contains high level of COD, BOD and TDS and very low level of dissolved oxygen making the properties hazardous acceding the permissible discharging limits. On the basis of raw wastewater properties coagulation and ozonation are cost effective and better techniques to treat wastewater. Characterization of effluent of pharmaceutical industrial unit is given in Table below.

Table: characterization of pharmaceutical wastewater.

Temperature (°C)	24.1
pH	7.04
Conductivity (μS)	1561
Turbidity (FTU)	738
Dissolved oxygen (DO) (mg/L)	0.8
Total dissolved solids (TDS) (mg/L)	1012
Total suspended solids (TSS) (mg/L)	563
Chemical oxygen demand (COD) (mg/L)	560
Biochemical oxygen demand (BOD_5) (mg/L)	134

The efficiency of coagulant in the removal of turbidity and COD from pharmaceutical industry wastewater is important to achieve to discharge guidelines because both of them affect the performance of any treatment technology. The effluent with very low level of dissolved oxygen indicated that the industry is releasing organic substances that are high oxygen demanding wastes [14].

3.2. Coagulation process

The results of coagulation using alum as coagulant are shown in Figs. 1 and 2. An increasing in the dose of alum from 0.5 to 0.75 g/L decreased COD and turbidity with the increase in settling time. A slight low reduction *r* was observed thereafter. However, TDS and conductivity were increased due to the dissolution of alum into ionic species. COD was reduced by 30% at the dose of alum 0.5 g/L and settling time 10 min. Thereafter, increase in settling time showed non-significant effect on the removal of COD because all of the alum was consumed and settled down during the first 10 min of coagulation. COD and turbidity removal reached 59% and 76.8% respectively at settling time of 40 min for 0.75 g/L alum dose. It again dropped to 46% and 68.5 for 1 g/L dose at the same settling time. Hence the optimal dose of alum appeared to be 0.75 g/L. This behavior can be explained on the basis of pH dynamics of aqueous system. The pH of solution drops to acidic range with an increase in coagulant dose [6]. To overcome this problem, the effect of pH on alum coagulation was observed (Fig. 4). The pH was maintained in the range of 4–10 using acid (1 M H_2SO_4) or base (1 M NaOH) solutions. COD removal was increased from pH 4 to 6. And the maximum removal (59.3%) was observed at pH 6 which remained unchanged afterwards. Lin and Wang have also observed similar COD reduction trend in their work [22]. The pH effect in coagulation treatment process on organic pollutant removal is correlated with coagulant hydrolyzates. In acidic pH the polymerization of anionic species is inhibited to certain degree and the primary species are transformed to positive monomer/oligomer hydrolyzates [38,39,36,35,16]. These positively charged hydrolyzates are easy to counteract the external negative charge of organic pollutant materials and destabilize the colloids in waste water. When pH of wastewater approaches neutral, there are some

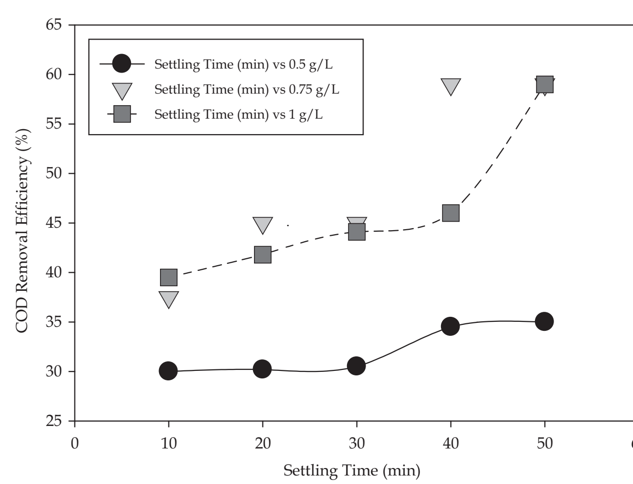

Fig. 1. COD removal (%) at different alum doses and settling times.

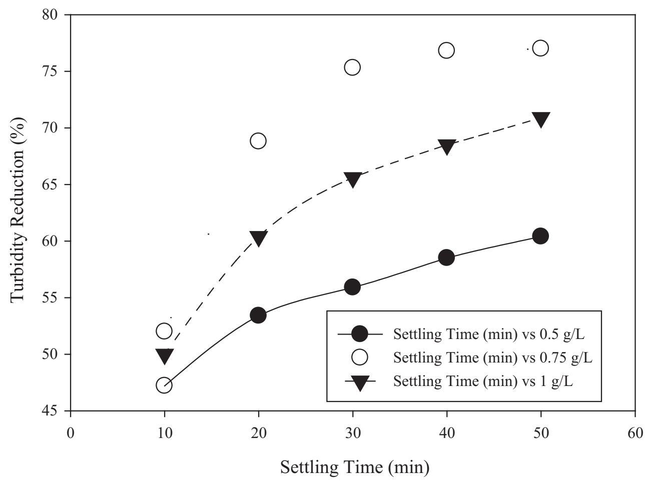

Fig. 2. Turbidty reduction (%) at different alum doses and settling times.

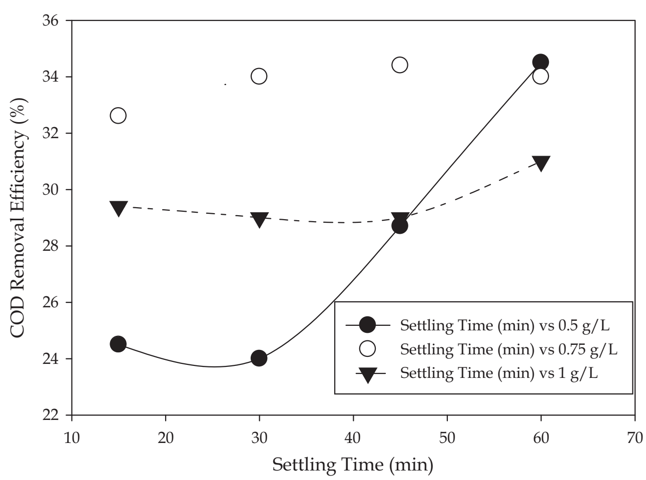

Fig. 3. COD removal efficiency (%) at different lime doses.

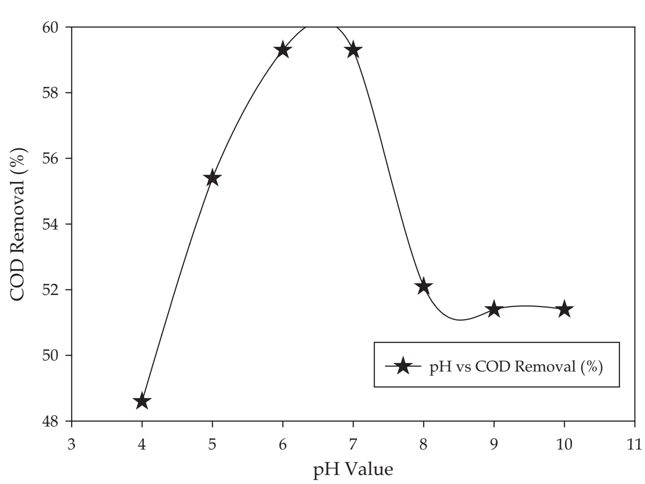

Fig. 4. Effect of pH on the performance of alum (alum dose 0.75 g/L).

high polymeric positive hydrolyzates in the solution and the colloids are easily adsorbed and precipitated. When pH enter in alkaline range the suspended material is difficult to be neutralized due to the transformation of hydrolyzates to cations [38,39,36,35,16].

Lime was also studied as coagulant. Fig. 3 represents the results of coagulation with lime (CaO). COD reduction increased with an increase in lime dose, whereas lime dose 0.75 g/L appeared as optimal. Calcium hydroxide ($Ca(OH)_2$), formed as a result of reaction between Lime and water, drifts the solution pH toward basic conditions. Ayeche, stated that with the gradual increase in lime dose ranging from 500 to 1000 mg/L, the pH will increase up to 11.5 [10]. Organic pollutants become negatively charged at high pH, which give weak charge neutralization effect and organic materials cannot be removed efficiently and prohibit the flocculation [4]. Settling time showed no significant effect on COD removal. Turbidity was increased with increasing the dose of lime because of the suspended particles of lime. Lime dose of 0.75 g/L gave optimal COD removal at 45 min settling time which was 34.4% resulted in an optimal treatment pH of 9. In primary treatment the COD removal efficiency of lime up to pH 9 increases from 30% to 35% of plain sedimentation up to 55–70% as reported by Barrella. It is also evident from the results that alum coagulation was much more effective than lime in the removal of COD and turbidity.

3.3. Ozonation process

The effect of ozone on the COD and color removal efficiency is shown in Fig. 5. Ozonation showed 93.4% reduction in color and 13.5% reduction in COD of un-buffered samples after 60 min. The ozonation was carried out at original pH of wastewater (pH 6.9). Ozonation is a pH and composition dependent reaction process. Generally ozonation carried out through direct molecular ozone reaction pathway in acidic pH and radical chain type reaction pathway in basic pH range. At the initial stage of ozonation at pH 6.9, ozone generated hydroxyl radical that react with double bond or functional group of organic compounds present in wastewater causing incomplete oxidation, generating ozone oxidation resistant intermediates resulting in high color removal because the oxidation potential of hydroxyl ion is greater than the molecular ozone. 77.5% color and 9% COD was removed within first 10 min and incremental improvement was observed afterwards. It was observed that ozone oxidation is favorable only for buffered samples. The pH of wastewater was not controlled and it was dropped (data not shown) in this type of oxidation [8]. Somensi et al., also observed a gradual decrease in wastewater pH due to the formation of transformed acidic reaction compounds like aliphatic acids, aldehydes and ketones [28]. The decrease in pH was an indication of shifting of reaction from hydroxyl radical to direct molecular ozone oxidation type of reaction. The hydroxyl radical oxidation is favored at basic pH and is stronger than molecular ozone oxidation. At low pH the

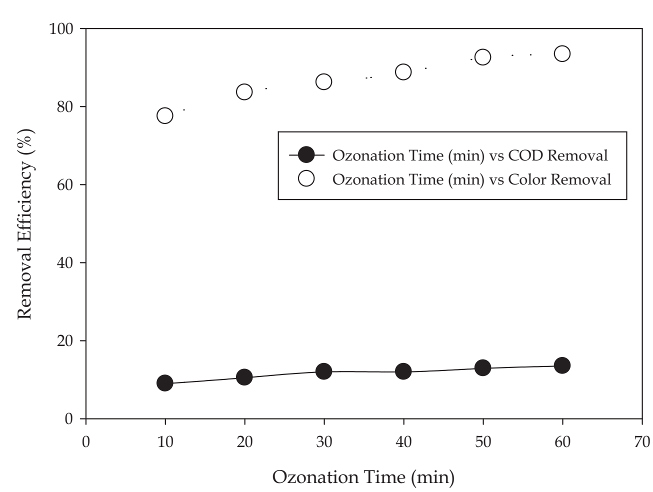

Fig. 5. Effect of ozonation time on COD and color removal.

hydroxyl ion generation is inhibited and molecular ozone react directly by an electrophilic attack leading to overall 93.4% color and 13.5% COD removal. Alaton et al., also reported that the COD removal efficiency is only10% at acidic pH due to the molecular ozone oxidation as mostly observed [5]. However, these transformed products, as a result of ozonation, are recalcitrant and thus, resist their degradation leading to lower COD removal [30,31]. The higher level of COD contributes to the prohibiting recalcitrant intermediates removal. Arslan and Balcioglu also reported that ozonation proved to be the best technique by removing 20% COD and almost 100% color for raw wastewater and 60% COD and 100% color removal of bio-treated wastewater [9].

4. Conclusion

The present study shows that the coagulation-flocculation can be suitable as a pre-treatment approach for pharmaceutical industry effluents. Coagulation with alum dose 0.75 g/L proved to be effective in COD and turbidity removal as compared with lime. However, it failed to lower COD level to meet the discharge guidelines. Alum gave better results at pH 6–7. COD removal (59%) was maximal at this pH. In addition there were no negative trends for conductivity and TDS. Alum is also a good clarifying agent and settled down the sludge rapidly. The problem associated with alum coagulation is only the high volume of residual alum in wastewater. It also increases conductivity and TDS.

Ozonation gives very low COD removals in unbuffered samples, however, proved to be effective for color removal. It is reflected from the literature that ozonation gives better result in basic pH.

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