Treatment of pesticide intermediate industrial wastewater using hybrid methodologies

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Abstract
Abatement of water pollution is being a major concern to be dealt with, as the scarcity of water for basic needs of human beings is increasing drastically. As a part of diminishing water pollution, treatment of industrial wastewater prior to disposal plays a paramount role. Due to the typical characteristics of pesticide, intermediate industrial waste water the treatment is also challenging issue. In this study three different sequential methodologies (Methodology-I: combined rotavapor distillation, fenton and anaerobic biological process, Methodology-II: combined rotavapor distillation, photo fenton and anaerobic biological process, Methodology-III combined coagulation, fenton, electro oxidation and anaerobic biological process) has been evaluated for the treatment of pesticide intermediate industrial wastewater. Among the three sequential methodologies opted in this study for the treatment of pesticide intermediate industrial wastewater, percentage removal of COD was 95% in methodology-1 (i.e. combined rotavapor distillation, fenton and anaerobic biological treatment).

Keywords Pesticide intermediate industrial wastewater · Chemical oxygen demand · Rotavapor distillation · Fenton process · Photo fenton · Anaerobic biological treatment

Introduction
Nowadays prevention of water resources from getting polluted is being a major concern. Surface water is being polluted by industrial untreated wastewater discharge into nearby water bodies, as they do not meet the dischargeable limits. Surface water bodies are also polluted by many other wastes as they are being easy dump yards for everyone to dispose their wastes generated. Finally, all the water bodies are transforming into toxic and hazardous water resources. In order to protect our water resources it is mandatory to reduce the water pollution by treating the wastes before disposal. Industrial wastewater treatment plays a major role in preventing pollution of water resources (Halone et al. 2018). Pesticides usage cannot be avoided as they are of major importance in agriculture for pest control, in order to improve food crop productivity (Smedt et al. 2015; Carlosa 2008). Inspite of their advantages, they also cause severe pollution which may become bio accumulative (Rhind 2002; Valickova et al. 2013) and even enter our food chain causing harm to human health. So there exists an alarming need to treat this pesticide intermediate industrial waste water properly before discharging them into nature.

Among various industrial wastewaters pesticides intermediate industrial wastewater has typical characteristics due to the presence of high amounts of organic and inorganic compounds. Generally, pesticide intermediates are chemically stable and they cannot be mineralized so easily. Due to their toxicity to microbes, pesticide intermediate wastewater cannot be treated biologically without undergoing any prior pre-treatment by physiochemical methods (Chen et al. 2007; Lapertot and Ebrahim 2007). The major challenges in treating the pesticide intermediate industrial waste water are its recalcitrant characteristics, toxicity to microbes, high COD, high TSS and highly acidic conditions (Wong 2004; Sadeghi et al. 2013). For treating this kind of waste water conventional processes like adsorption, coagulation, sedimentation are not sufficient as they produce lots of sludge, high operational costs, less removal and the generation of secondary pollutants (Zhang and Dong 2019). Direct conventional
biological treatment cannot be performed effectively due to toxicity to microbes.

Pesticide intermediate industrial waste water can be treated effectively by advanced oxidation processes as they are mainly based on hydroxyl radicals which are highly non selective to wide range of organics (Malato and Blanco 2002; Barbusiński 2015). Therefore, AOP’s can be preferred to treat various types of pesticide industrial wastewater. In recent studies, treatment of real industrial wastewater from petrochemical sector has been treated using hydrodynamic cavitation (HC) in combination with other AOPs at 70 L capacity. Combined operation of HC + Fenton + O₂ injection at H₂O₂ loading of 15 g/l and Fenton molar ratio of 1:20 was reported to result in 63% COD reduction during 180 min of treatment (Joshi and Gogate 2016). Photo fenton was used for the treatment of oil refinery waste water treatment with an initial COD of 3200 mg/l of which 75% was removed by photo fenton process (Mohadesi and Shokri 2019).

In recent past, the treatment of wastewater contaminated with fipronil pesticide has been carried out using electro oxidation in which graphite electrodes has been used. COD removal of 79%, was obtained at pH 9 and current density of 7.5 mA/cm², Thangamani et al. (2012). A scheme of treatments coagulation-flocculation-sedimentation (CFS) and Fenton has been used to treat the paper and pulp waste water. By using these coagulation-flocculation-sedimentation (CFS) and Fenton processes sequentially 61% of COD removal was obtained at an alum dosage of 750 mg/l, pH 3 and settling time of 60 min, Grötzner and Melchior (2018).

Vacuum evaporation followed by reverse osmosis process had been used to treat wastewater containing surfactant materials. By treating with vacuum distillation COD reduced from 8400 to 1100 mg/l, but as it was not below dischargeable limits further reverse osmosis was performed which could reduce the COD from 1100 to 100 mg/l (Haaz and Fozer 2019).

These were the recent studies in which AOP’s has been used individually to treat various kinds of pesticide and other industrial waste water, but not resulted in satisfactory results. In some studies individual EO itself yielded moderately high % of COD removal, but the effluents that have been treated in this study has very high COD (i.e. 90,000 mg/l) and recalcitrant in nature which led to the usage of combined treatment technologies to get high percentage removal of COD.

**Materials and methods**

**Waste water**

Pesticide intermediate industrial waste water sample has been collected from pesticide intermediates industry located at Hyderabad, Telangana, India. The physicochemical characterization of wastewater samples has been carried out using “standard methods for the examination of water and wastewater 21st addition-2005, APHA” (Jotin et al. 2012; Bhagawan et al. 2017). The initial characterization of the sample has been given in Table 1.

**Methodology**

Various combined methodologies had been opted for the treatment, as a single approach may not be effective for the wastewater treatment (Boczkaj et al. 2018).

**Methodology 1: combined Rotavapour distillation, fenton process and anaerobic biological treatment for the treatment of pesticide intermediate industrial waste water**

Rotavapour distillation of pesticide intermediate industrial wastewater was carried out by taking 250 ml sample in a round bottomed flask and attached to the reactor such that it immerses slightly in the water bath which was set at 100 °C and this flask with sample was rotated at an rpm of 45. At the receiver end another round bottomed flask was clamped to the reactor in order to collect the condensate. A vacuum pump was attached to the specified port and cooling water was also pumped into the condenser. Thus the 250 ml sample was distillated for 60 min. The slurry remained in the flask was collected and analysed. Thereafter the collected distillate or condensate was further treated by fenton. Batch mode experiments of fenton on this distilled sample had been carried out in a 500 ml reactor with the working volume of 250 ml, pH 3, reaction time was varied from 30 to 240 min (30, 60, 90, 120, 180 & 240 min) and the dosages of fenton reagents calculated theoretically for 250 ml of sample as FeSO₄.7H₂O of 0.027 g, H₂O₂ of 0.9 ml were added and kept in an orbital shaker at room temperature for 240 min by collecting samples at an interval of 30 min. As the pre treatment with physico chemical methods makes the effluent amenable for biological treatment (Chen et al. 2007; Zhang and Dong 2019; Lapertot and Ebrahimi 2007).

**Table 1 Initial characterization of pesticide intermediate industrial wastewater sample**

| S. no. | Parameters               | Concentrations |
|--------|--------------------------|----------------|
| 1      | Chemical oxygen demand (COD) | 90,000 mg/l   |
| 2      | pH                       | 1.29           |
| 3      | Electrical conductivity (EC) | 103.8 ms/cm   |
| 4      | Chlorides                | 36,159 mg/l   |
| 5      | Sulphates                | 1,685 mg/l    |
| 6      | Total Solids (TS)        | 75,500 mg/l   |
| 7      | Total suspended solids (TDS) | 55,000 mg/l  |
This effluent from combined rotavapor distillation and fenton process was further treated by biological treatment (anaerobic digestion) with contact time of 5 days to obtain a better efficiency. pH was adjusted to 6.5. Anaerobic sludge from the UASB reactor of a local municipal wastewater treatment plant located at HMWWS (Hyderabad Metropolitan Water Supply & Sewerage Board, Amberpet) was used as inoculum (Vijaya Krishna et al. 2017).

Methodology 2: combined Rotavapour distillation, photo fenton process and anaerobic biological treatment for the treatment of pesticide intermediate industrial waste water

In this methodology, after treating the sample with rotavapor distillation, the condensate obtained was further treated with photo fenton process. Photo fenton process was performed in a cylindrical photo-reactor with a total volume of 1 L in which working volume was 500 ml. The source used for UV-irradiation was a low pressure mercury vapour lamp of 250 watts with maximum emission at a wave length of 365 nm (Fig. 1). This lamp is enclosed within the quartz tube. A magnetic stirrer was placed at the bottom of reactor for the proper homogenization of sample.

During photo fenton process the pH of the sample was adjusted to 3 using 0.1 N/1.0 N HCl or 0.1 N/1.0 N NaOH solutions and the dosages of fenton reagents calculated theoretically as FeSO₄·7H₂O of 0.054 g, H₂O₂ of 1.8 ml were added to the sample. Then the reaction was carried out for 240 min by taking samples at an interval of 30 min (30, 60, 90, 120, 150, 180, 210 & 240 min).

The effluent from this Combined Rotavapour distillation and photo fenton process was further treated with biological treatment (anaerobic digestion) for a contact time of 5 day.

Methodology 3: combined coagulation, Fenton, electro oxidation and anaerobic biological treatment for the treatment of pesticide intermediate industrial waste water

The waste water sample was initially treated using coagulation with alum. Coagulation was carried out in a 1000 ml beaker with 500 ml as working volume and pH was adjusted to 7. After the addition of coagulant the beaker was placed in Jar test apparatus stirred at 150 rpm for 30 min, then sample was allowed settle for 60 min and then the supernatant was analysed. In this study dosages of alum are varied from 0.125 to 0.375 g to get an optimum coagulant dosage. This sample treated with optimum coagulant dosage was further treated with fenton by adding theoretically calculated fenton reagent dosages (FeSO₄·7H₂O of 0.04 g, H₂O₂ of 1.4 ml). The effluent from this combined coagulation and fenton treatment was further treated by electro oxidation, during this the operational conditions were, pH 7, working volume was 200 ml, SS-SS electrodes (100 mm × 50 mm × 2), constant voltage of 8 V, current was varied from 4 to 6 Amps and the reaction time was varied from 10 to 60 min (10, 20, 30, 40, 50 and 60 min). The sample treated at optimum reaction time was further treated with biological treatment (anaerobic digestion) for a contact time of 5 day.

Results and discussions

The initial characterisation of pesticide intermediate industrial wastewater sample was represented in Table 1.

Methodology 1: combined Rotavapour distillation, fenton process and anaerobic biological treatment for the treatment of pesticide intermediate industrial waste water

Initially, the sample with initial COD 90,000 mg/l, was treated with rotavapor distillation in which, 62% removal of COD was obtained, thereafter this effluent was treated by fenton in which COD removal of 70% was obtained at an optimum reaction time of 180 min (Figs. 2, 3). After 180 min the rate of removal of COD was very less hence in order to avoid excess costs the reaction time was optimised to 180 min. The overall percentage removal of COD was increased from 62% in rotavapour distillation to 88% in combined rotavapour distillation and fenton process.

Fig. 1 Schematic diagram of photo fenton reactor
Finally, the effluent from combined rotavapor distillation and fenton process was treated by using anaerobic biological treatment. The percentage removal of COD in biological process was 55%. The overall percentage removal of COD has been increased to 95%.

**Methodology 2: Combined Rotavapour distillation, photo fenton process and anaerobic biological treatment for the treatment of pesticide intermediate industrial waste water**

After treating the pesticide intermediate industrial wastewater with rotavapor distillation, further the distillate was treated by photo fenton process. In this photo fenton process after rotavapor distillation COD removal of 76% was obtained at an optimum reaction time of 180 min (Figs. 4, 5). The overall percentage removal of COD was increased from 62% in rotavapour distillation and photo fenton process.

The effluent from combined rotavapor distillation and photo fenton process was treated by using anaerobic biological treatment. The percentage removal of COD in biological process was 57%. The overall percentage removal of COD has been increased to 95%.

**Methodology 3: combined coagulation, Fenton, electro oxidation and anaerobic biological treatment for the treatment of pesticide intermediate industrial wastewater**

Initially, the sample with initial COD 90,000 mg/l, was treated with coagulation in which, optimum % removal of COD of 41% was obtained at an alum dosage of 0.25 g, thereafter this effluent was treated by fenton in which COD removal of 35.6% was obtained at an optimum reaction time of 180 min (Figs. 6, 7). The overall percentage removal of COD was increased from 41% in coagulation to 62% in combined coagulation and fenton process.
This combined coagulation and fenton treated sample was further treated by electro oxidation which resulted in a COD removal of 33% at an optimum reaction time of 50 min (Figs. 8, 9). The overall percentage removal of C.O.D. was increased from 62% in combined coagulation and Fenton process to 75% in combined coagulation, fenton process and electro oxidation.

Finally this effluent from combined coagulation, Fenton and electro oxidation process was treated by using anaerobic biological treatment. The percentage removal of COD in biological process was 12.44%. The overall percentage removal of COD has been increased to 78.88%.

**Comparison between above three methodologies**

From the Fig. 10, it was observed that the percentage removal of COD trend was methodology-2 (95.77%) followed by methodology-1 (95%). There exists only a slight difference in percentage removal of COD between methodology 1&2. As the photo fenton process in methodology-2
renders excess operational costs when compared to fenton process, methodology-1 can be preferred for the treatment of pesticide intermediate industrial wastewater.

**Kinetic analysis of C.O.D removal**

For fenton, photo fenton and electro oxidation processes, a plot has been drawn between the values of $\ln \left( \frac{C_0}{C_t} \right)$ and the reaction time. Least square regression was used to calculate the $k$ and $R^2$ values for each method (Pinto et al. 2018; Jotin et al. 2012; Lafi and Al-Qodah 2006) and the values thus obtained were mentioned in Table 2. As the values of $R^2$ obtained were high, it can be stated that the applied model fits successfully for the above methods (Alalma and Tawfika 2015). From the kinetic analysis it can be concluded that the reactions in above methods follows pseudo-first order kinetics.

The relation between the residual concentration of pollutant and the reaction time in pseudo first order equation (Alalma and Tawfika 2015) can be given by:

$$-\frac{dC}{dt} = k \cdot C$$

Upon integrating Eq. (1):

$$\ln \left( \frac{C_0}{C_t} \right) = k \cdot t$$

where $k =$ the constant reaction rate, $C_0 =$ the initial concentration of target pollutant in aqueous solution, and $C =$ the residual concentration of pollutant at time $t$.

**Conclusions**

1. Among the three sequential methodologies opted in this study for the treatment of pesticide intermediate industrial wastewater, methodology-2 (combined rotavapor distillation, photo fenton and anaerobic biological treatment) resulted in highest percentage removal of C.O.D (95.77%).

2. In methodology-1 (combined rotavapor distillation, fenton and anaerobic biological treatment) percentage removal of C.O.D was 95%, which was very slightly less than the percentage removal of C.O.D. in methodology-2.

3. Therefore in-order to avoid excess operational costs of photo fenton process when compared to fenton process, methodology—1(combined rotavapor distillation, fenton and anaerobic biological treatment) can be preferred for the treatment of pesticide intermediate industrial wastewater.

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**Compliance with ethical standards**

**Conflict of interest** All authors have seen and approved the manuscript being submitted. Hence, on behalf of all authors, the corresponding author states that there is no conflict of interest.

**Informed consent** Informed consent was obtained from all individual authors or persons involved in the study.

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