Treatability of Pharmaceutical Wastewater by Using Combined Ultrasound Cavitation and Persulfate Process

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Treatability of Pharmaceutical Wastewater by Using Combined Ultrasound Cavitation and Persulfate Process

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Abstract

In recent years industrialization caused, magnificent leaps to high profitable growth of pharmaceutical industries, however, simultaneously it has given rise to environmental pollution. Pharmaceutical processes like extraction, purification, formulation etc. generates huge volume of wastewater with high COD, biological oxygen demand, auxiliary chemicals, and different pharmaceuticals substance or their metabolites in the active or inactive form imparting intensive color, which necessitates its proper treatment before being discharged. This study focuses on the feasibility analysis of utilization of ultrasound cavitation assisted with persulfate oxidation approach for the treatment of such complex effluent. Process parameters like pH, amplitude intensity, oxidant dosage was optimized for COD removal applying response surface methodology-based Box Behnken design. The optimum value observed for pH, amplitude intensity, oxidant dosage is 5, 20%, 100 mg/L respectively with 39.5% removal of COD and 6.5% removal of TOC in 60 min of fixed processing time. Study confirms that acombination of ultrasound cavitation and persulfate is a viable option for the treatment of pharmaceutical

wastewater than individual treatment and it can be used as an intensification technique in existing treatment plants for achieving maximum COD removal.

Keywords–Ultrasound, Cavitation, Persulfate, Box -Behnken design, Optimization, Pharmaceutical wastewater.

INTRODUCTION

Environmental pollution is one of the global challenge of today's world (Spina et al., 2012; Singh & Prashant, 2017). Amongst that, industrial effluent and other hazardous discharge from industries is one of the prime concerns for developing countries like India. In India one-third portion of water pollution in the natural water bodies and marine pollution are induced by industrial wastewater (Kansal et al., 2013; R. Singh & Prashant, 2017), U.S EPA reported daily effluent produced from pharmaceutical unit as 1.0068×10^9 L (Adishkumar et al., 2012). Because of these effluents, containing highly biological active compound which is likely cause health harm to human and animals, and also promote the development and spreading of antibiotic resistance genes although the concentration of pharmaceutical residue present in effluent is less. This antibiotic resistance gene interrupt the ecological balance of aquatic environment by initiating irreversible transformation to aquatic fauna (Ng et al., 2014; Tiwari et al., 2020). Industrial wastewater quality is estimated based on the amount of organic matter present as COD (chemical oxygen demand), total carbon, biological oxygen demand, and other wastewater quality parameter and nowadays the high amount of pharmaceutical substances used for the protection and cure of diseases for humans and animals therefore, huge amount of wastewater generated in pharmaceutical industries (Mohapatra et al., 2014; Ghafoori et al., 2015). Over 60% of pharmaceutical sectors meet country's demand and is one of rapid expanding sectors of Indian economy. The produced wastewater from pharmaceutical sectors are complex and hazardous in nature, high COD, biological oxygen demand, solid Containing supplementary chemicals and presence of pharmaceuticals secondary metabolites leads the wastewater to be a under "red category" (Gadipelly et al., 2014; Martínez et al., 2018; Changotra et al., 2017, 2019). Pharmaceutical wastewater contains the majority of pollutants recalcitrant or bio-refractory substances which are very difficult to degrade (Grandclément et al., 2019). Thus it is necessary to treat pharmaceutical wastewater efficiently sooner than discharging it into any water bodies to avoid hazards to the environment and ecosystem (Gadipelly et al., 2014; Martínez et al., 2018; Changotra et al., 2017, 2019).

Conventional treatments cannot efficiently treat recalcitrant or bio-refractory molecules present in industrial effluent and sometimes it also get converted in another complex by-product as Fluoxetine and endocrine disruptors which has resulted multitude of undesirable problems like harm the reproduction, metabolism of aquatic organism and feminization of fish population (Ford & Fong, 2016; Huang et al., 2016) which are not easily biodegradable which further pollutes water bodies (Singh & Prashant, 2017). Treatments like biological oxidation required longer time because it is slower reaction rate (Crini & Lichtfouse, 2019) chemical coagulation is useful for removal of waste material in form of colloidal or suspended that do not settle very quickly it requires longer time & more sludge production (Verma et al., 2012) chemical oxidations target selective bio resistant compound it can be used as pretreatment (Mantzavinos & Psillakis, 2004) and adsorption reactors rapidly get clogged and its regeneration is costly and it decreases acceptance of certain type of metal ions (Crini & Lichtfouse, 2019), due to this demerits treatments are not efficient to remove all the hazardous compounds effectively from pharmaceutical wastewater (Jeworski & Heinzle, 2000; Ayare & Gogate, 2019). In recent times advance oxidation process (AOP) such as Fenton oxidation (Singh et al., 2013) ozonation

(Cortez et al., 2010) ultraviolet/hydrogen peroxide (Hu et al., 2011) ultrasound cavitation (Gągol et al., 2018) have been considered as a useful process for treatment of bio-refractory pollutants (Q. Yang et al., 2015). Among the AOP, ultrasound cavitation-based process has seen as a promising process for the oxidation of various pollutants in industrial wastewater. Principle behind ultrasonication process is pressure variation in liquid caused by inducing ultrasound which produces cavitation for the treatment of wastewater (Thanekar & Gogate, 2019). Cavitation occurs due to pressure difference in outer flow and inside the system pressure induced by sound waves as system pressure decrease or increase in flow velocity produce small cavities which starts to grow longer compare to higher system pressure (Dular et al., 2016). Furthermore, variation of pressure leads to cavity formation, growth, and its collapse over micro-scale duration. These three-stage occurs during ultrasound cavitation process which leads to generate free radicals and release a large amount of energy up to 5000K temperature and 1000 Atm pressure in wastewater known as "local hotspot" which can be extremely suitable for the oxidation of pollutants (Leighton, 1995; Thanekar & Gogate, 2019). The main advantage behind this treatment is it does not require any chemicals to promote oxidation, no sludge formation, no visible light require (Vega & Peñuela, 2018), break up agglomerates (Jordens et al., 2016; Dong et al., 2020). Ultrasound cavitation is useful for the treatment of active pharmaceutical compound like carbamazepine, diclofenac, ciprofloxacin (Beckett & Hua, 2001; Rayaroth et al., 2016). Ultrasound cavitation accelerates the degradation of pollutants in combination with other oxidation process like Fenton's regent (Zhang et al., 2016), hydrogen peroxide (Chandak et al., 2020), carbon tetrachloride and persulfate ions (Anipsitakis & Dionysiou, 2003) to generate radicals (Rayaroth et al., 2016). Among the various oxidant, per-sulfate ion enhance degradation of organic matter in the wastewater though the use of combined ultrasound - persulfate system has been less studied (Monteagudo et al., 2015, 2018; Wang & Zhou, 2016). Alternative of hydrogen peroxide, Persulfate ion has gained more attention in the interest of higher redox potential of sulfate radical (2.5 V – 3.1V) and expanded life time than hydroxyl radical for advanced oxidation treatment in recent time. Formation of sulfate radical occurs by breakage of O-O bond of Persulfate ions using different activation method like heat (Tan et al., 2012), transitional metals (Liu et al., 2016), UV (Xie et al., 2015). Among them, activation by ultrasound acts as an emerging method and typically used for pharmaceuticals(Zou et al., 2014; Yang et al., 2019).

In Combined process multiple operating parameters influences or affects the removal efficiency. For complex system governed by several parameters, generally usage of one parameter optimization at a time could provide mis-interpretation due to lack of interaction effect, thus design of experiment is effective tool for optimization, there are various DOE available for optimization of parameters by reducing the number of experiment and cost (Dopar et al., 2011) like box Behnken method of response surface methodology design (RSM) which is a powerful design tool for modeling complex conditions (Tak et al., 2015) and it estimate the relation between manageable input parameter and response variable (Khorram & Fallah, 2018).

This current study focuses on the combined effect of Ultrasound cavitation and Persulfate oxidation on the treatment of pharmaceutical wastewater. The optimization of process parameters like pH, Amplitude intensity, Persulfate Dosage by Box Behnken design as a response surface methodology for treatment of pharmaceutical wastewater using ultrasound – persulfate system was also carried out. Optimization can be potentially considered for scaling up purposes as an intensification technique for industrial wastewater treatment.

MATERIAL AND METHODOLOGY

Characterization of Untreated Pharmaceutical Industrial Wastewater

Pharmaceutical wastewater sample of 40 liters was collected from the pharmaceutical industry from Bharuch, Gujarat, India. Collected samples were stored in the refrigerator at 4°C to avoid further biodegradation. Characterization of the pharmaceutical wastewater was done as per the standard method (APHA, 2012) and given in Table 1. As given in Table 1, COD of the wastewater is as high as 13760 mg/L.

Chemicals

In this study chemicals of Analytical grade were used for the entire experimental process. The potassium persulfate purity 98% purity, potassium dichromate 99% purity, mercury sulphate 98% purity, silver sulphate 98% purity, ammonium ferrous sulphate 99% purity, manganous sulphate 98% purity, ferric chloride 98% purity, Di-potassium hydrogen phosphate 99% purity, potassium iodide 99% purity, potassium hydroxide 85% purity, sodium thiosulphate 98% purity were procured from M/s Merck India. Sulphuric acid of 98% purity, ferroin Indicator, calcium chloride 96% purity, magnesium sulphate 99% purity, starch as an indicator were procured from M/s Finar India. All the required reagents were prepared using double distilled water. For ultrasonic cavitation, probe-type sonicator was used with a microprocessor-based programmable probe (Model No: VCX 500 with 17 mm solid probe diameter) procured from Sonics Vibracell, USA.

Design of Experiment (DOE)

Design-expert software was used to prepare DOE. The removal of organic matter from pharmaceutical wastewater was optimized using Box- Behnke design as RSM. Table 2, represents coded and its real value for lower level (-1), mid-level (0), high level (+1) for removal of organic matter as COD another Table 3 provides detail total number of experimental runs to perform for factors pH (A), Amplitude Intensity % (B), Persulfate Dosage (C). Initially, while performing experiment process parameter pH (A) was varied from 2 to 8, Amplitude Intensity (B) was varied from 20 to 80 (%), Persulfate oxidant dosage (C) was varied from 100 mg /l to 400 mg/l to obtain better COD removal efficiency. The selection of real value for different levels decides based on the given literature review.

Experimental Procedure

All experiments were conducted in a cylindrical batch glass reactor with 250 mL of working volume (capacity of 500 mL). The schematic diagram of the experimental process reactor is shown in Figure 1. The temperature of the sample was maintained at 30°C and the pH was adjusted using nitric acid and sodium hydroxide. The Persulfate Dosage was added according to the real value of factors suggested by DOE. All 15 experimental runs were conducted according to DOE suggested value. Treated samples were withdrawn during the experiment at a time interval of 15, 30, and 60 min and analyzed for COD. COD of the sample was analyzed as per the Standard method using closed reflux method.

RESULT AND DISCUSSION

ANOVA Analysis

ANOVA Table 4, provides the details of various coefficient values of process parameters and other details for COD removal from pharmaceutical wastewater with ultrasound cavitation treatment. The table shows that the Model (Fischer test value) F value is 9.42 and it shows model value is significant as the p value is less than 0.0500 which implies the model is significant. The significance of p value fixes the error probability of regression co-efficient as significant. For optimized condition of parameter quadratic and some other interaction term are significant, the parameter pH (A) is slightly significant another parameter Persulfate Dosage (C) is significant, an interaction effect of Amplitude Intensity (B) and Persulfate Dosage (C), is also significant with respect to model terms. According to the analysis of variance (ANOVA) selected parameters P-value is less than 0.0500 ($P< 0.0500$) than selected parameters are significant for the process efficiency and the P-value of parameters is greater than 0.100 ($P>0.100$) than selected parameters is not significant for the process efficiency.

Mathematical representation of independent variable to the dependent response by coded terms shown by this Eqn. (1).

$$COD\ (mg/l) = 30 + 2197.7A + 19.62\ B - 6.013C - 3.55\ AB + 0.88AC + 0.256BC - 240.2\ A^2 - 0.620\ B^2 - 0.0319\ C^2 \ldots \quad (1)$$

From the above equation, it is noticed that the terms have a positive effect on yield or COD removal and persulfate concentration (C) has a negative impact on the yield. The quadratic terms with a negative sign show a negative impact on yield which means the percentage of COD yield will decrease with the increase in concentration of persulfate. Other interaction terms as AB, AC & BC shows a combined effect on the percentage of yield. The Persulfate Dosage (C) term shows a positive impact on yield as interaction term AC, BC & interaction term AB shows a negative impact on yield percentage.

For identification order of each process parameters and its effect while keeping the other process parameter constant indicated in perturbation plots Fig.2 (a) then factors sensitivity on COD removal is indicated by nature of the curve for each process parameter and the factor with more slope has more noticeable effects on COD removal (Muthukumaran et al., 2017; Milano et al., 2018). Hence, the plot shows that factor B has a prominent effect on COD removal followed by A and C similar to that reflected in the Table of ANOVA.

The individual effect of parameter effect plots shown in Fig.3(a),3(b), & 3(c) the plots are made by taking one factor as variable and the other two factors fixed at constant levels and the experimental results are shown at three different levels compare to predicated plots.

Effect of pH on COD removal

One of the important parameters that affect the process efficiency is pH, it plays a vital role in the generation of intermediate oxidants for the oxidation of various compounds it can also affect their state during the cavitation process (Keenan & Sedlak, 2008 ; Barik & Gogate, 2017; Thanekar & Gogate, 2019). Effect of pH on the degradation of organic pollutants were studied by varying pH from 2 to 8 with fix Amplitude as 50% and Persulfate Dosage of 250 mg/L. The plot shown in Fig. 3 (a) generated using Design of Expert shows the variation of pH from the lower level to a higher level and its effect on COD removal (mg/L). As shown in Fig. the maximum COD removal of 39.5% at pH 5 at a reaction time of 60 min was observed. Increasing pH from the lower level at pH 2 to mid-level pH 5 removal efficiency has also increased after achieving maximum removal at mid-level pH 5 with 50% of Amplitude Intensity and 250 mg/l dosage of Persulfate oxidant further increasing pH to a higher-level pH 8 reduced removal efficiency.

The plot Fig.4, shows the individual and combined effect of ultrasound cavitation and persulfate oxidation on COD removal. The individual effect of the ultrasound cavitation process under the optimum condition of pH 5 and Amplitude 20% shows the removal of 8.10% and Persulfate oxidation under 100 mg/l dosage show removal of 5%. Standalone effect of both processes for removal of COD is less significant compare to combine effect of Ultrasound cavitation with Persulfate process which was more significant (L. Yang et al., 2019) with the removal of 39.5% under the optimum condition of pH 5 Persulfate Dosage of 100 mg/l and Amplitude of 20%.

This was due to the production of synergistic effect which leads to higher amount of cavitation yield and effective generation of sulfate radicals by persulfate oxidant. Maintaining the mid-level value of factors Amplitude Intensity of 50% and Persulfate Dosage of 250 mg/l at pH 2 and pH 8 and the corresponding predicated removal efficiency was 19.5% and 20.6% respectively. Excessive loading of Persulfate Dosage above 250mg/l has proven as a scavenger for the process under acidic condition as given in Eqn. (2) (Peyton 1993; Wei et al. 2018). The observed results shows acidic condition as more effective compare to alkaline conditions for the degradation of pollutants under similar kind of analysis as shown in some literature (Thanekar & Gogate, 2019). Due to that removal was low at a higher level of pH 8. Especially, at mid-level pH 5 shows maximum removal efficiency rather than another highly acidic pH 2 due to a higher amount of cavitation yield and effective generation of sulfate radicals by persulfate oxidant. At pH 2 higher amount of proton present in form of H_3O^+ which decreases effective decomposition of persulfate oxidant while increasing pH, quantity of H_3O^+ ions decreases in solution which leads to effective generation of sulfate radicals from persulfate as in shown in given Eqn. (3) & (4) (Romero et al., 2010; Sarath et al., 2016).

$S_2O_8^{2-} \rightarrow 2SO_4^{2-}$ ……………. *(2)*

$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^{2-}$ ……….. *(3)*

$HS_2O_8^{2-} \rightarrow H^+ + SO_4^{\cdot} + SO_4^{2-}$ ……… *(4)*

Effect of Amplitude on COD removal

Effect of Power dissipation is one of the important influences in the ultrasound cavitation production rate, increasing amplitude generates more violent collapse of bubbles (Vega & Peñuela, 2018). In this study effect of power dissipation on COD removal was studied by varying Amplitude Intensity from 20 to 80% (Power dissipation – 18W to 78W) with fixed pH of 5 and Persulfate Dosage of 250 mg/l. The plot shown in Fig. 3 (b), shows the variation of Amplitude Intensity at different levels and its effect on COD removal. A maximum removal estimate at a lower level of 20% (18W) shows that generation of cavitation yield is higher at the lower amplitude and lower at higher amplitude (Feng et al., 2002). The trend of the plot shows that it is not much sensitive towards process efficiency from the lower level to higher level it shows slight curvature, therefore amplitude intensity variation shows least significant favorable by ANOVA as shows in Table 4. The COD removal at 50% and 80% of Amplitude intensity is 31.6% and 29.9% respectively. Higher power intensity at lower frequency decoupling effect occurs between sample solution and transducer, thus bubble cloud formation occurs at the surface of the horn or transducer resulting in a reduction of sound waves in the solution, hence at a lower frequency power cavitation becomes more effective (Sunartio et al., 2007).

Effect of Persulfate oxidant on COD removal

Persulfate ($S_2O_8^{2-}$) is one of the strong oxidizing agents (Yang et al., 2019) for the degradation of organic matter. It gets activated in the presence of metal (Liu et al., 2016), heat (Tan et al., 2012) or ultrasound (Yang et al., 2019) as in given below in Eqn. (5) and produces sulfate radicals $(\mathbf{SO_4^{\cdot}})$with an oxidation potential of 2.40 V. The persulfate radical is more stable radical compare to hydroxyl radical (Romero et al., 2010). Persulfate oxidation has strong oxidation ability and efficient performance in a wide range of pH (Amor et al. 2019).

$$\boldsymbol{S_2O_8^{2-} + activator(Heat, US, Metal, Heat) \rightarrow\ 2SO_4^{\cdot}} \qquad (\mathbf{5})$$

Organic compounds + $\mathbf{SO_4^{\cdot}}$→ Oxidation Product (6)

In this study effect of combined ultrasound activated and persulfate oxidation on COD removal was studied by varying Persulfate Dosage from 100 mg/l to 250 mg/l with fix factors pH 5 and amplitude of 50% as shown in Fig. 3 (c). Maximum COD removal of 32% was observed at a lower level of Persulfate Dosage of 100 mg/l. Predicted removal at mid-level of 250 mg/l dosage and higher-level of 400 mg/l dosage of persulfate was 31.3% and 21% respectively. Higher removal was reported at 100 mg/l dosage and with further increasing dosage from 250 mg/l to 400 mg/l removal efficiency starts decreasing which shows degradation rate is higher at 100 mg/L concentration of Persulfate Dosage. It shows that, increase in persulfate concentration lead to existence of excess persulfate in the system with which sulfate radicals in system react and produce sulfate ions and also extra sulfate radicals react itself, as given in Eqn. (7) and Eqn. (8) (Vu et al., 2004; Wei et al., 2018). The additional persulfate loading under particularly acidic solution reported as scavenger, thus rate of reaction slightly decreases with increase in dosage(Peyton 1993; Wei et al. 2018).

$$\boldsymbol{SO_4^{\cdot} + SO_4^{\cdot} \rightarrow S_2O_8^{2-} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)}$$

$$\boldsymbol{SO_4^{\cdot} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{2-\cdot} \ldots\ldots\ldots\ldots (8)}$$

Effect of pH and Amplitude on COD removal

The interaction effect of pH (A) and Amplitude (B) on COD removal is not significant approved by ANOVA as shown in Table 4, its P-value is higher than 0.005 ($P > 0.005$). Combined effect of pH and amplitude on COD removal was studied by maintain other parameters constant and the results are as shown in Fig. 6. The increasing amplitude at pH 2, removal of COD increased to 30.8% and on other hand middle level pH 5 with amplitude up to 50% removal efficiency increases further as a result of generation of effective cavitation and effective decomposition of persulfate (Sarath et al., 2016). Further increasing amplitude to 80% at pH 5, reduces removal due to reduced cavitational yield, thus increasing or decreasing amplitude beyond or below 50% under near acidic condition (Thanekar & Gogate, 2019).

Effect of Amplitude and Persulfate Dosage on yield Removal

Interaction effect of Amplitude (B) and Persulfate Dosage (C) on COD removal is a significant effect as indicated by ANOVA outputs shown in Table 4, its P-value is lower than 0.005 ($P > 0.005$). Fixing pH at 5, the interaction effect for Amplitude and dosage of persulfate on COD removal is shown in Fig. 7. For Amplitude of 20% and Persulfate Dosages of 100 mg/l shows much significant removal in COD due to amount of activation energy required for breakage of O-O bond and generation of sulfate radicals (Wacławek et al., 2017) was achieved under lower amplitude. Under higher amplitude of 50% and 80% persulfate amount of 250 mg/l and 400 mg/l became excessive loading for the system thus it reported as a scavenger for the process and it reduces the removal (Wei et al. 2018)compare to 20% amplitude and 100 mg/l of dosage.

Effect of pH and Persulfate Dosage on COD Removal

The interaction effect of pH (A) and Persulfate Dosage(B) on COD removal was not significant as indicated by ANOVA output as shown in Table 4, its P-value is higher than 0.005 ($P > 0.005$). Fixing amplitude at mid-level 50%, the interaction effect of pH and dosage of persulfate on COD removal is shown in Fig.8. Under acidic pH of 2 and 5 with 100 mg/l dosage, shows much significant COD removal efficiency when compared to removal achieved at 250 mg/l and 400 mg/l dosage. Excessive loading of persulfate leads to less utilization of persulfate ions under acidic conditions (Wei et al., 2018), persulfate loading above some extent proven scavenger under acidic condition (Peyton 1993; Wei et al. 2018). Increasing dosage under the alkaline condition has not shown significant removal in COD removal.

CONCLUSION

The optimized parametric condition of pH 5, Amplitude Intensity of 20% and Persulfate Dosage of 100 mg/l shows 5440 mg/L removal of COD and 6.6% removal of TOC at 60 min of reaction time. Observed result shows that process parameter pH and Persulfate oxidant dosage shows much significance on COD removal efficiency. Synergistic effect of ultrasound Cavitation and Persulfate oxidation was more efficient for the degradation of organic matter from pharmaceutical wastewater compare to stand-alone process effect under optimum condition. It can potentially consider for scaling up purposes as an intensification technique for industrial wastewater treatment.

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CRediT authorship contribution statement

Karan Pandya: Methodology, Formal analysis, Writing - original draft, Writing & editing.

T. S. Anantha Singh: Conceptualization, Methodology, Formal analysis, Supervision, Writing - original draft, Writing – review & editing.

Pravin Kodgire: Conceptualization, Methodology, Formal analysis, Supervision, Writing - original draft, Writing – review & editing.

Ethical approval: This study follows all ethical practices during writing.

Consent to participate: The author declares consent to participate.

Consent to publish: The author consents to publish this article in Environmental Science and Pollution Research.

Competing interests: The author declares that there are no conflicts of interest.

Transparency: The author confirms that the manuscript is an honest, accurate and transparent account of the study reported; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained.

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Figures

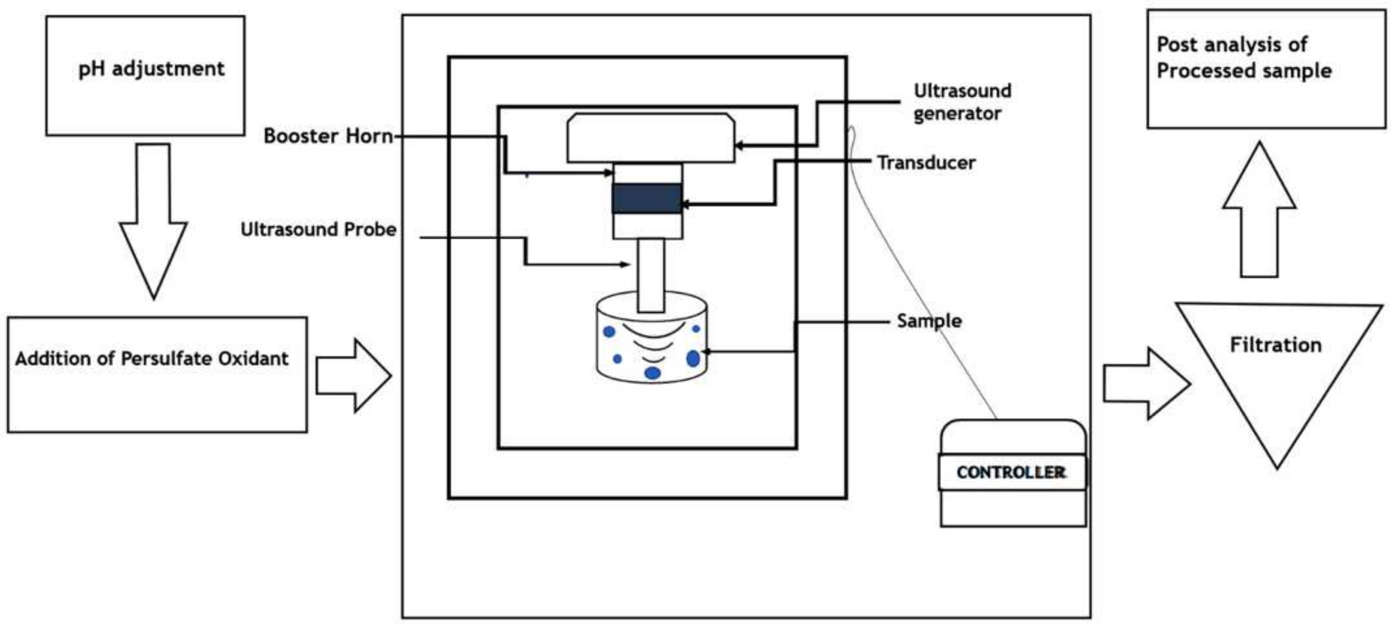
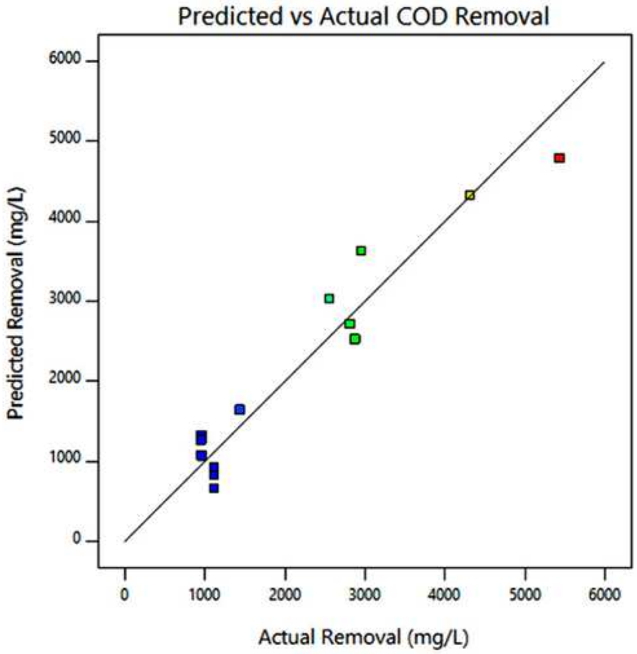
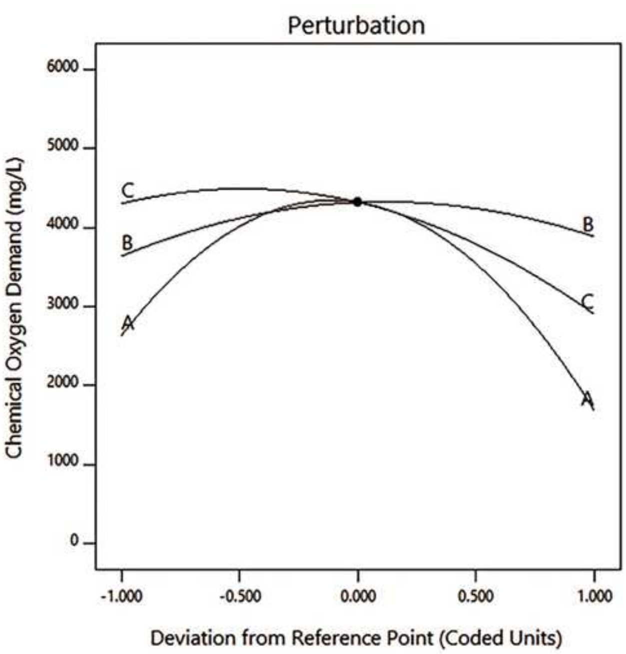


Figure 1

Schematic diagram of Experimental Process



A)



B)

Figure 2

(a) Comparison of Predicted COD removal (Box Behnken design) to Actual COD removal (b) Profile of Perturbation Plot showing significant parameter affecting COD removal with factors pH (A) 2 to 8, Amplitude (B) 20% to 80%, Persulfate Dosage 100 to 400 mg/l (C) with middle level values

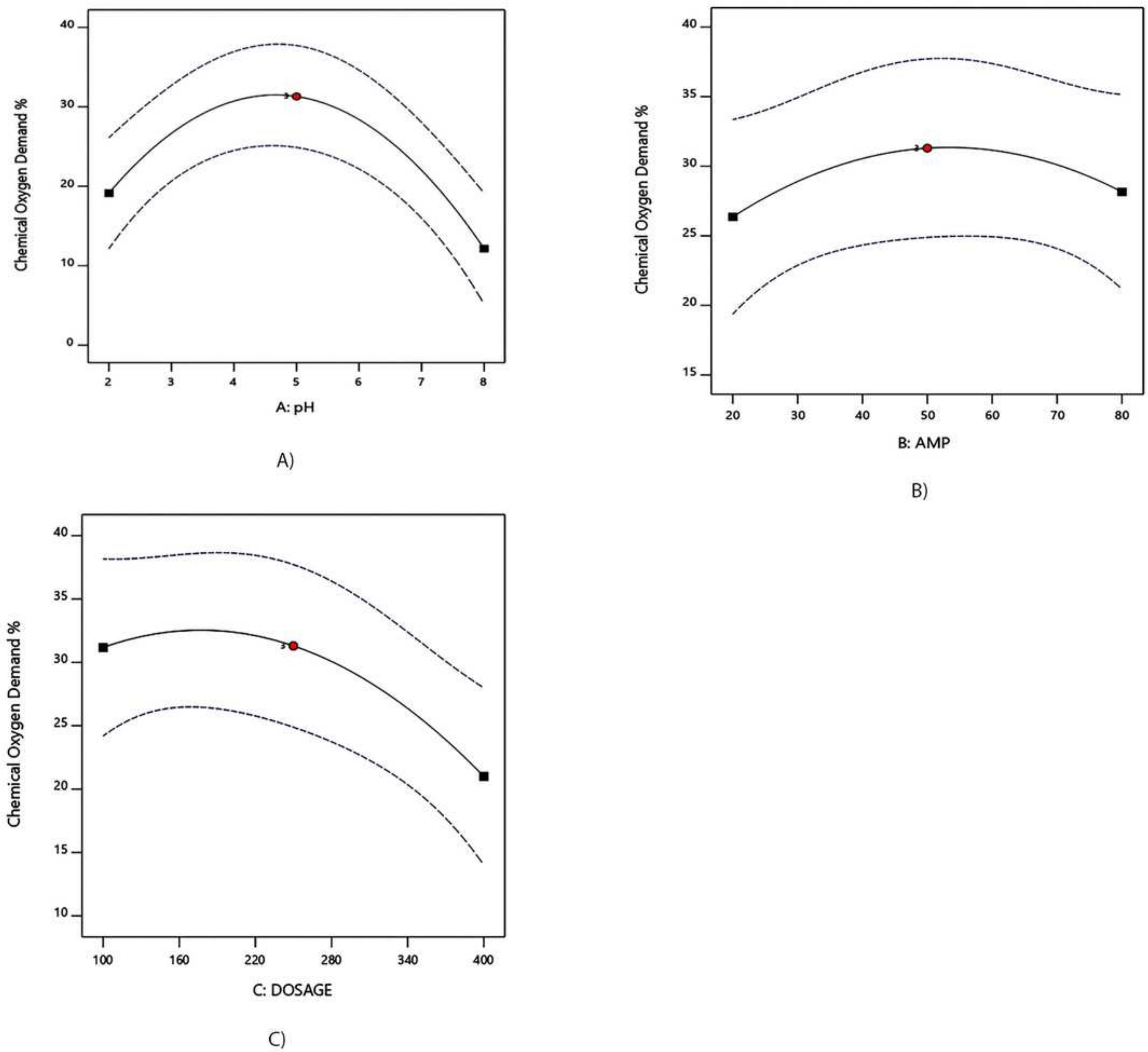


Figure 3

(a)Profile of Individual Parameter Plot with two reference curves based on ANOVA for Process Parameter pH from 2 to 8, with fix parameter amplitude of 50%, and Persulfate Dosage of 250 mg/l on Removal of COD with 95% of confidence interval band. (b)Profile of Individual Parameter Plot two reference curve based on ANOVA for Process Parameter Amplitude from 20%(18W) to 80%(78W) with fix parameter pH of 5, and Persulfate Dosage of 250 mg/l at mid-level on Removal of COD (mg/l) with 95% of confidence interval band. (c)Profile of Individual Parameter Plot two reference curve based on ANOVA for Process Parameter Persulfate Dosage 100 to 400 (mg/l) with fix parameter of pH 5 and amplitude of 50% on Removal of COD with 95% of confidence interval band.

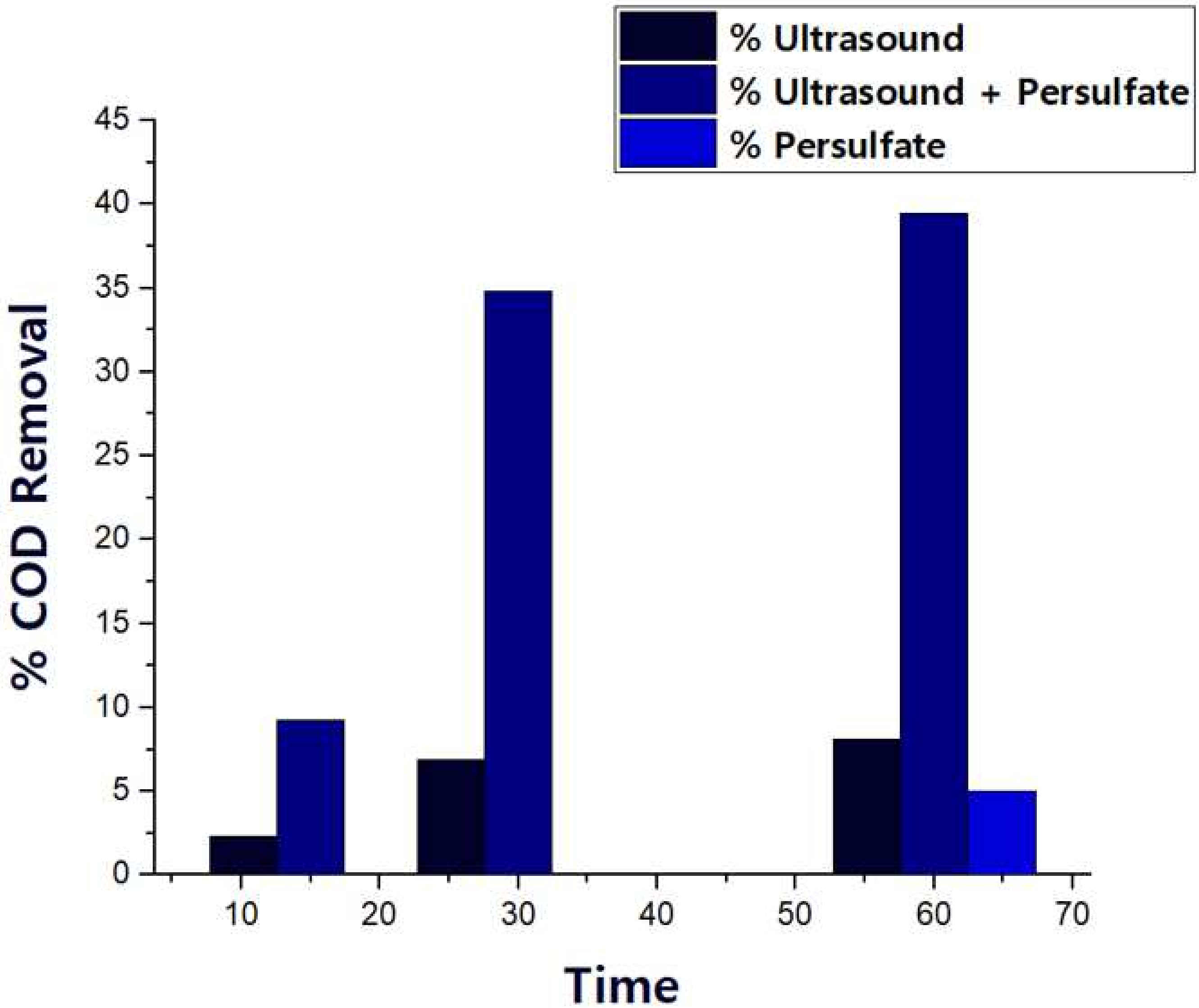


Figure 4

Profile of percentage COD removal with Individual treatment; ultrasound at pH 5, amplitude 20%; Persulfate of 100 mg/l; Combine Effect of ultrasound with persulfate at pH 5 & Persulfate Dosage of 100 mg/l, Amplitude of 20%within 60 min reaction time.

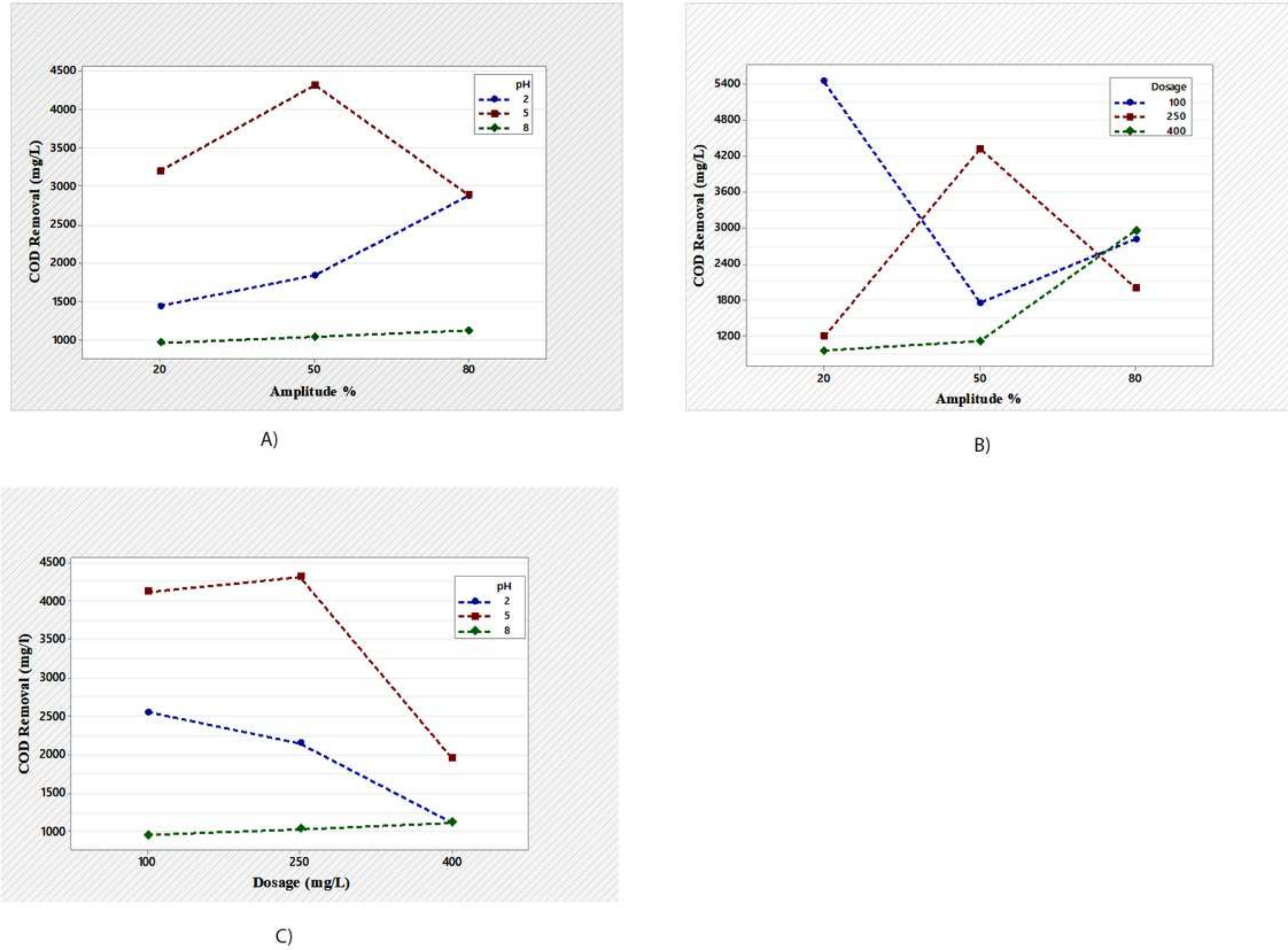


Figure 5

(a) Profile of Interaction effect plot for process parameter pH 2-8 to Amplitude20%-80% (AB) maintaining Persulfate Dosage (mg/l) at middle level (b)Profile of Interaction effect plot for Amplitude 20%-80% to Persulfate Dosage 100-400 (mg/l) (BC) maintaining pH at middle level (c)Profile of Interaction effect plot for pH 2-8 and Persulfate Dosage 100-400 (mg/l) (AC) maintaining Amplitude % at middle level