



Removal of TCOD and phosphate from slaughterhouse wastewater using Fenton as a post-treatment of an UASB reactor

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Abstract

A pilot was designed to study the removal efficiencies of total chemical oxygen demand (TCOD) and phosphate by a combined biological and chemical method. Two stages of Up-flow anaerobic sludge blanket (UASB) reactor and advanced oxidation processes was operated in batch mode. The UASB reactor was operated with hydraulic retention time of 26 h. UASB removal efficiency of TCOD and phosphate were 62.2 and 36.5%, respectively. Fenton process was used as a post-treatment so as to remove organic matter and nutrients. At this stage, the removal efficiencies of TCOD and phosphate were investigated considering the effect of parameters such as pH, hydrogen peroxide and Fe (II) dose based on Taguchi experimental design. Accordingly, under optimum conditions, pH = 3, 1000 mg/l of H₂O₂ and 400 mg/l of Fe (II) the removal efficiencies of TCOD and phosphate reached 95.41 and 85.29%, respectively. The combined method removed TCOD and phosphate up to 98.6 and 90.5%, respectively.

Keywords Slaughterhouse wastewater · Biological treatment · UASB reactor · Advanced oxidation processes · Fenton

Introduction

Treatment of industrial wastewater is of cardinal importance because of the harmful effects of wastewater on the environment [1]. Meat processing industries have the highest freshwater consumption among the beverage and food industries [2]. Among the total freshwaters used for agriculture in the world, 29% of them were used for meat processing industry [3].

Slaughterhouse wastewater is specified by high concentrations of suspended solids, organic matter, oil and grease, nitrogen and phosphorus. The primary sources of organic matter and nutrients are blood, feces and fat [4]. The nitrogen content

generates from blood, urine and feces significantly as organic nitrogen. Residual blood, manure detergents together with disinfectants are primary sources of phosphorus, having appeared as organic and inorganic phosphates [5]. Typically, slaughterhouse wastewaters are treated in an anaerobic condition because of high organic and nutrients concentrations. Nevertheless, anaerobic treatment methods have disadvantages such as the need for post-treatment because of the harmful effluent [6].

Up-flow Anaerobic Sludge Blanket (UASB) reactor represents a proven viable method of treatment for a wide variety of industrial wastewater [7]. Low capital investment and maintenance cost, less energy and land requirements, low sludge production and biogas production made the UASB reactor be widely used [8, 9]. Granules and sludge aggregates play an essential role in the performance of the UASB reactor [10]. Under anaerobic condition, organic material were converted into methane, carbon dioxide, and biomass while purifying the wastewater [11]. The profitable byproduct of UASB reactor (i.e., methane) can be recovered (from 28% to 75%) and converted into energy [12]. V. Del Nery, et al. evaluates the performance of combined of screens, an equalization tank, a dissolved-air flotation (DAF) and two up-flow anaerobic sludge blanket (UASB) reactors, indicating that for both UASB reactors, the TCOD and SCOD removal efficiencies

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were 67 and 85%, respectively [13]. Removal efficiencies of total nitrogen and ammonia in UASB reactor by recycling of nitrified ABF effluent were 74 and 96%, respectively. TP removal efficiency of UASB reactor was 90% with alum dose at Al/P mole ratio of 2.6 [14]. The performance of a laboratory scale UASB reactor at mesophilic temperature (35 °C) indicates that at an optimum OLR of 7 g/L d⁻¹, the system could remove COD and SCOD up to 73% and 85%, respectively [15]. Hybrid up-flow anaerobic sludge blanket reactor consisting polypropylene media applied to treat slaughterhouse wastewater. The results indicate that at 10 h HRT, the maximum TOC, TN, TSS removal efficiency were 96%, 78% and 98%, respectively with an influent TOC of 1680 mg/L [16]. UASB reactor has the low capacity nitrogen and phosphorus removal, so in order to remove the remaining part, a post-treatment is required [17].

Despite all advantages, anaerobic reactors effluents may scarcely fulfill the discharge standards of environmental agencies. Accordingly, the effluents of anaerobic reactors usually need a post-treatment step in order to reach the treated effluent to the standards of the environmental legislation [18]. In order to produce water for disposal and reuse standards, post-treatment of UASB effluent is of utmost importance to attain the effluent disposal guidelines [9]. There are several methods as post-treatment via which the effluent reaches standard values. Advanced oxidation processes is an alternative for post-treatment, frequently used in many wastewater treatment plants.

The AOPs involve the generation of hydroxyl radicals which convert the organic molecules to non-toxic forms such as carbon dioxide or water by either breaking a hydrogen atom or by adding to double bonds [8]. Among the different types of advanced oxidation processes, Fenton process is used broadly due to high performance, simplicity, short reaction time and its non-toxicity [19, 20]. In the Fenton process, H₂O₂ reacts with Fe²⁺ to generate hydroxyl radicals. The generated hydroxyl radicals oxidized the organic matters [21]. The Fenton process takes less time than aerobic reactor due to high oxidation capability which increases the popularity of this method.

The investigations into the treatment of the slaughterhouse wastewater using a combined approach of the anaerobic process and AOPs are limited. Bustillo-Lecompte et al. investigated that combined anaerobic baffled bioreactor (ABR) and an aerobic activated sludge and UV/H₂O₂ processes enhanced the biodegradability of the total organic carbon (TOC), total nitrogen (TN), and carbonaceous biochemical oxygen demand (CBOD₅) present in the synthetic slaughterhouse wastewater [22]. Jorge Vidal et al. studied the treatment of slaughterhouse wastewater by a combination of anaerobic digestion and solar photoelectro-Fenton (SPEF). The combined processes produced a high quality effluent, with a COD removal greater than the separate processes [23]. The combination of a

laboratory scale anaerobic baffled reactor (ABR) and UV/H₂O₂ for treating synthetic slaughterhouse wastewater exhibits high treatment efficiency [6].

In this research, Taguchi experimental design was used which simplifies and standardizes the design of experiment and also reduces the number of test, required time and experimental cost. The contribution of each factor, the optimal condition and the response can be determined by this method [24, 25].

In the present study, a novel method, combination of UASB and Fenton process, were used to evaluate the performance of the combined method for real slaughterhouse wastewater treatment, which has not been done yet. The authors aimed to find the treatment efficiency of UASB reactor, process condition and also the applicability of Fenton as a post-treatment of anaerobic treatment which could decrease the time consumption. Taguchi method was applied in order to investigate the effect of parameters and experiments. The key parameters, such as H₂O₂ dose, pH and Fe (II) dose, play an essential role in the process.

Material and method

Slaughterhouse wastewater characteristics

The wastewater used in this research was prepared from a local slaughterhouse plant in Guilan, Iran. The company's wastewater comes from diverse operations such as scalding, de-feathering, packing, and plant cleaning. In slaughterhouses, the amount of produced wastewater is estimated to be about 10 to 15 l per head of chicken. The samples were taken from the equalization tank after passing the screen. The average BOD₅ was about 1490 mg/L. Analyses of slaughterhouse wastewater accomplished several times, is the average of which presented in Table 1.

Table 1 Characteristics of slaughterhouse wastewater

Parameters	N	Mean values
TCOD (mg/L)	12	3360±279.86
SCOD (mg/L)	12	2930±323
N – NH ₃ (mg/L)	8	629.2±136.9
P – PO ₄ ³⁻ (mg/L)	8	15.9±0.8
pH	12	7.44±0.11
TU (NTU)	12	180±18
TSS (mg/L)	10	290±28.7
TDS (g/L)	14	2.82±0.14
Temperature (°C)	25	24±2.8
Conductivity (mS/cm)	14	5.46±0.3

TCOD: Total COD; SCOD: Soluble COD; TU: turbidity; TSS: Total suspended solids; TDS: Total dissolved solids. N: number of tests

Experimental set-up

Figure 1 shows the schematic diagram of the pilot-scale, made of plexiglass. Influent of UASB reactor was taken from the feed tank to an up-flow anaerobic sludge blanket reactor by a pump (Soft water TYP-2500). The UASB has the working volume of 26 L. To evaluate the characteristics of sludge, five points along the reactor were tested. The reactor was equipped with a gas separation system. A sedimentation tank was used after UASB reactor in order to settle the sludge and prevent solids coming out from the effluent. The circulation system was used in order to provide optimal up-flow velocity. Under optimum condition, H₂O₂ and Fe (II) were added to the UASB effluent. A mixer with speed controller was utilized in order to control the speed of mixer. A glass electrode pH meter was applied to monitor the pH in the reactor.

Start-up of the UASB reactor

Aerobic sludge was prepared from a local slaughterhouse wastewater treatment plant and converted to anaerobic sludge in a bioreactor in approximately two months. During the period of converting to anaerobic sludge, the microorganisms fed every day in order to provide proper F/M ratio for optimum growth. The UASB reactor was inoculated with the anaerobic sludge of 1 L that has been grown in a bioreactor. Afterward, the process of sludge growth has occurred in about four months. The reactor operated with HRT of 26 h during 25 days with average organic loads 2.67–3.66 Kg COD/m³/d.

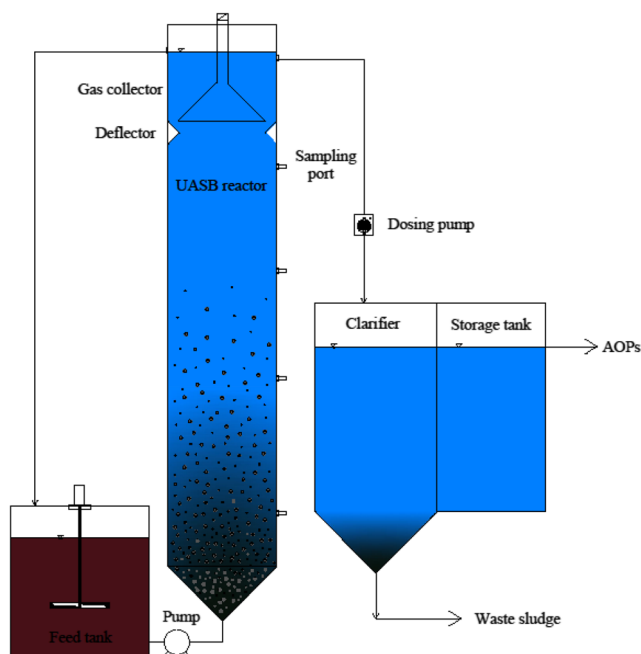


Fig. 1 Schematic diagram of pilot system

AOPs procedure

Sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were used in order to adjust the specific pH. Then the optimum concentration of Fe (II) was added to the reactor. After several minutes, a certain amount of H₂O₂ was added to the solution. The optimum reaction time of one hour is given at a speed of 120 rpm. In the end, NaOH was used in order to increase the pH up to 8 and terminating the reaction.

Chemical materials

All chemicals of this research, including hydrogen peroxide (H₂O₂) and iron (II) sulfate heptahydrate (FeSO₄ · 7H₂O) were purchased from Merck, Germany. In order to set the pH, the solutions of sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄) were prepared from Merck, Germany [26].

Analytical method

The sample analysis for measuring soluble COD, Total COD, total suspended solids, ammonia, and phosphate were determined according to the APHA standard methods [26]. TCOD was determined by thermo-reactor (AL125-AQUALYTIC). Phosphate concentration analyzed with a spectrophotometer (UNICO 2100 Vis), and ammonia concentration was determined using photometer (AL450-AQUALYTIC). pH was measured by a glass electrode pH meter (AL15-Aqua Lytic-Germany) and turbidity with a turbidity meter (TU-2016-Lutron). TDS and EC were determined by CLEAN instrument CON 500.

Design of experiments

Design of AOPs experiments was done based on the Taguchi method, established by Dr. Genichi Taguchi [27]. The efficiency of AOPs heavily depends on variables such as pH, H₂O₂ dosage and catalyst dosage because of their remarkable effect on the oxidation capacity of the Fenton reagent [28]. The effects of parameters on AOPs were studied at four levels presented in Table 2. In this study, the design of experiments was done with Minitab 17.1.0 Statistical Software, as presented in Table 3. According to the type of optimization, the “larger-the-better” criteria were chosen for S/N ratio [29]. The S/N

Table 2 The studied levels of parameters’ effect

Parameters	Levels			
	1	2	3	4
pH	3	4	5	6
H ₂ O ₂	400	600	800	1000
Fe (II)	100	200	300	400

Table 3 Experimental layout using L16

Experimental Number	pH	Fe(II)	H ₂ O ₂
1	3	100	400
2	3	200	600
3	3	300	800
4	3	400	1000
5	4	100	600
6	4	200	400
7	4	300	1000
8	4	400	800
9	5	100	800
10	5	200	1000
11	5	300	400
12	5	400	600
13	6	100	1000
14	6	200	800
15	6	300	600
16	6	400	400

ratios were calculated for TCOD and phosphate removal by the following equation:

$$S/N \text{ (dB)} = -10 \log \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{Y_i^2} \right) \text{ (Larger-the-better)} \quad (1)$$

Y_i is the performance value of i^{th} experiment and n is the number of experiments [30]. The optimization of the factors, which are effective on the AOPs, is of huge importance, since using traditional techniques such as full factorial design, is not cost effective and is time consuming. The Taguchi method helps to reduce the number of experiments [31].

Analysis of variance (ANOVA)

After designing experiments based on the Taguchi method, ANOVA analyses were used to evaluate the variance of errors and to determine the relative importance of different factors. The ANOVA indicates whether the observed changes in the response are due to a change in level adjustment or experimental errors. The ANOVA method is used to calculate the sum of squares (SS), mean square (variance), the degree of freedom and associated F-test of significance (F) [32].

Results and discussion

UASB reactor performance

Despite the fluctuation of influent concentrations, the UASB reactor behaved robustly to the alterations. The UASB reactor was operated for 120 days for biomass growth. Thirty days

later the system had reached the steady state regime. The pilot was performed at 24°C for 25 days. The average mixed liquor suspended solid for UASB reactor was of 10,995 mg/l. The mean values of the parameters were presented in Table 4. The Average removal efficiencies of TCOD and phosphate were 62.2 and 36.5% for the average influent TCOD and phosphate of 3360 and 15.9 mg./L, respectively with HRT of 26 h. The minimum and maximum concentrations of effluent TCOD were 890 and 2454 mg/L and they were as 8.1 and 12.1 mg/L, respectively for phosphate. In particular, the process could remove TU and TSS, as presented in Table 4.

TCOD removal efficiency

The UASB reactor operated for 25 days in order to investigate the pattern of TCOD alteration in the reactor. Figure 2 presents the TCOD removal of UASB reactor, with average organic loads 2.67–3.66 kg COD/ m^3 /day. The average TCOD removal efficiency was 62.2% with HRT of 26 h. In constant HRT, the increase in MLSS improves TCOD removal. Poultry slaughterhouse wastewater with the organic loading rate of 1.6 ± 0.4 kg COD/ m^3 /day applied to the UASB reactors resulted in TCOD and SCOD removal efficiencies of 67 and 85%, respectively [13]. Under mesophilic condition, with HRT of 1.02 days, the circular UASB reactor could remove COD up to 77–88% with influent COD of 2000 mg/L [33]. Using UASB reactor in a wastewater treatment plant (consisting DAF, UASB, aerated-facultative pond (AFP) and chemical-DAF) indicate that UASB reactor could bring COD from 2485 ± 385 to 745 mg/L, with HRT of 1 day [34]. The study of a lab-scale UASB under mesophilic temperature reveals that at OLR pf 0.4 g/L d^{-1} the COD removal was about 90%, but by increasing the OLR to 15 g/L d^{-1} , the removal efficiency dropped below 50% [15].

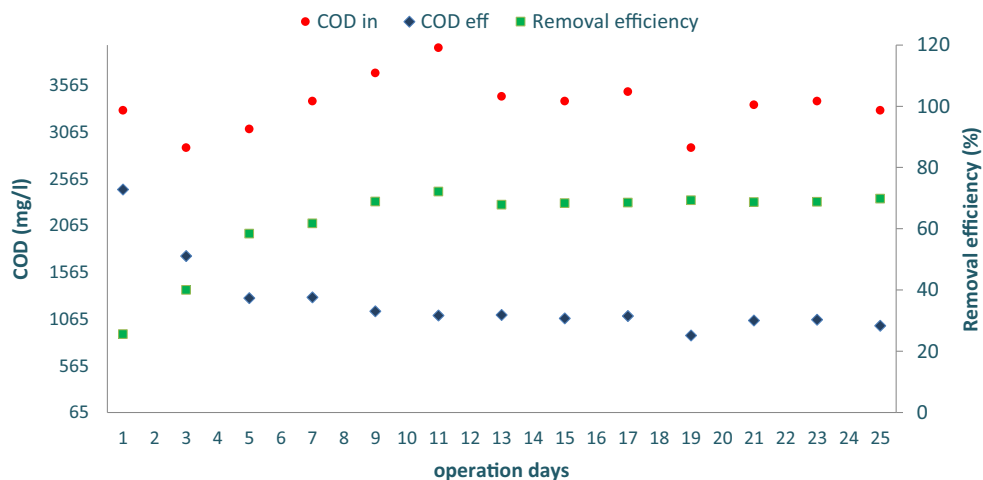
Phosphate removal efficiency

Studies indicate that anaerobic system has little nutrient removal of treating domestic wastewater [17, 35, 36]. Figure 3

Table 4 Characteristic of UASB reactor's effluent

Parameters	UASB reactor effluent	
	Average effluent	Removal efficiency
TCOD (mg/L)	1255.3	62.2
SCOD (mg/L)	1015	64.4
P-PO ₄ ³⁻ (mg/L)	10.2	36.5
TU (NTU)	105	41.6
TSS (mg/L)	140	51.7
pH	8.1	–

Fig. 2 TCOD removal pattern in UASB reactor



shows phosphate removal in UASB reactor. The average phosphate removal efficiency was 36.5%. The sludge concentration in the system plays an essential role in removing phosphate. In this study, the release of phosphate was observed at the beginning; afterwards, the phosphate removal, observed as the sludge concentration, subsequently increased. The UASB reactor was operated at 3 runs, at first run the UASB reactor could remove TP about 21% with HRT of 4 h and average OLR of 2.33 kg COD/m³/d. At second and third runs with HRT of 3 h and OLR of 2.93 kg COD/m³/d, the UASB reactor could remove TP in the range of 21–24% [35].

AOPs process performance

In order to measure the mean value (signal, the desirable effect) and the standard deviation (noise, the undesirable effect) simultaneously, the S/N ratio was used [37]. The S/N ratios and removal efficiency of TCOD and phosphate are shown in Table 5. In this research, the removal efficiency of parameters

are considered as the response functions of S/N by using Equation 8. Since the purpose of this study was to achieve maximum removal efficiency, “larger-the-better” criteria were chosen for S/N ratio, while the operational conditions of experiment were presented in Table 3. According to Table 5, the number four experiment has the highest S/N ratio, which indicates the highest removal efficiency of the design with pH = 3, 400 mg/L of Fe (II) and 1000 mg/L of H₂O₂. The TCOD and phosphate removal efficiency at optimum condition were 95.41% and 85.29%, respectively. Treating real textile wastewater by Fenton indicates that at operating condition of T = 25 °C, pH = 3, 1650 mg/L of H₂O₂ and 216 mg/L of Fe (II), the COD and TOC removal efficiency were 70% and 64% with influent COD and TOC of 2100 and 465 mg/L, respectively [38]. Using Fenton process for treating industrial wastewater revealed that, at operation condition of T = 50 °C, pH = 3.5, FeSO₄=6 g/L and 222 g/L, the COD removal efficiency was about 95% with influent COD of 2700–4000 mg/L [39]. Evaluation of landfill leachate by Fenton at optimum

Fig. 3 Phosphate removal pattern in UASB reactor

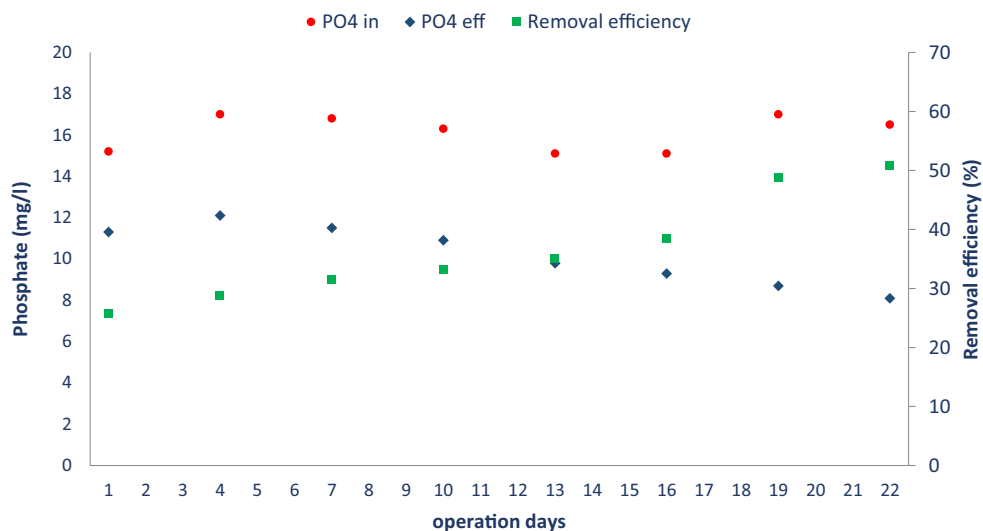


Table 5 The studied parameters removal efficiencies

Exp. no.	TCOD removal		Phosphate removal	
	Percentage (%)	S/N(db)	Percentage (%)	S/N(db)
1	81.77	38.25	65.69	36.64
2	85.89	38.68	77.45	37.94
3	91.98	39.27	81.86	38.38
4	95.41	39.59	85.29	38.71
5	77.96	37.84	72.55	37.42
6	80.92	38.16	69.80	37.12
7	86.93	38.78	81.37	38.34
8	88.85	38.97	82.55	38.45
9	75.90	37.60	68.63	36.98
10	82.98	38.38	76.37	37.83
11	79.37	37.99	67.65	36.87
12	83.96	38.48	72.55	37.42
13	76.92	37.72	60.78	36.03
14	82.49	38.33	67.45	36.84
15	78.92	37.94	65.69	36.64
16	75.49	37.56	64.22	36.46

condition of 1.7 g H₂O₂/g COD raw leachate; FeSO₄.7H₂O: H₂O₂ = 1:5.3; pH = 3.8 and reaction conditions = 115 rpm/28 min, reduced COD and TP up to 63% and 52% with influent COD and TP of 2863 and 13.5 mg/L, respectively [40].

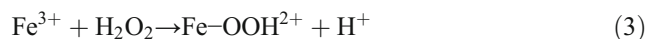
The effect of pH

pH is considered one of the most critical factors influencing the operation of the Fenton process [41]. In order to achieve the maximum amount of radical hydroxyl produced in the Fenton process, it is necessary to provide an acidic environment. Therefore, this factor plays a crucial role in controlling the catalytic activity of iron species and H₂O₂ sustainability [42]. Typically, pH of 2.8–3 is known as the ideal pH for Fenton reaction [43, 44]. In the pH less than 3, iron complexes, such as [(H₂O)₆]²⁺, [Fe(H₂O)₆]³⁺ and [Fe(H₂O)₅OH]²⁺, are formed, reacting slowly with hydrogen peroxide, and it reduces the Fenton reaction rate and the number of hydroxyl radicals produced [45, 46]. Furthermore, in the presence of high concentrations of H⁺, hydrogen peroxide dissolves and becomes a stable form of oxonium ion [H₃O₂]⁺ (Equation (2)) [44]. The reactivity of the oxonium ion with iron ion is much less than that of hydrogen peroxide; as a result, this reduces the reaction time of the Fenton [47].



Also, since the radical hydroxyl was trapped by H⁺, based on Equation (2), the removal efficiency is reduced in very high

acidic environments. Therefore, generally, in pH = 3, or above, the optimum pH of the Fenton process is selected [47]. So, the pH = 3 was selected as the first choice for the Fenton process. In pH = 3 (acidic environment), Fe(OH)⁺ complex species are formed, which are more active than non-iron species in Fenton oxidation process. As can be seen in Fig. 4, in pH above 3, the removal efficiency is linearly declined to pH = 4. The decrease in efficiency is due to the reduction of the free catalyst content in the solution, resulting from the replacement of hydroxyl complexes such as Fe(OH)₃ instead of iron ions [48, 49]. Also, in the presence of Fe(OH)₃, hydrogen peroxide decomposes into oxygen and water and; therefore. Its oxidation power decreases [50]. Furthermore, at pH greater than 5, the compounds of Fe(II) such as [Fe(II)(H₂O)₆]²⁺ reacting more slowly with H₂O₂ than [Fe(II)(OH)(H₂O)₅]²⁺ caused lower production of hydroxyl radicals. But, at low pH, excess hydrogen ions led to increase of Fe (III) concentration (Equation 3) Which in turn it decrease the Fe(II) available for hydroxyl radicals production [51].



The effect of Fe (II)

Catalyst concentration has a high effect on the removal efficiency [52]. According to reaction 1, the increase in Fe (II) concentration results into further hydroxyl radical generation

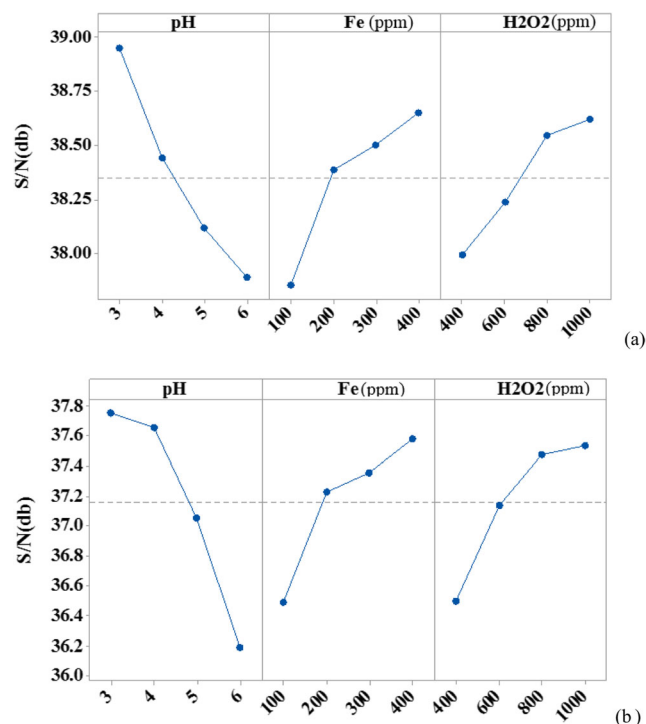


Fig. 4 S/N ratios of different levels of related factors on TCOD and phosphate removal. **a** TCOD removal and **b** Phosphate removal

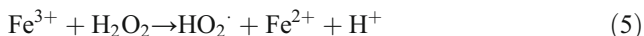
Table 6 ANOVA analyze results

Factor	DOF		Sum of squares		Variance		F ratio	
	TCOD removal	Phosphate removal	TCOD removal	Phosphate removal	TCOD removal	Phosphate removal	TCOD removal	Phosphate removal
pH	3	3	2.54	6.21	0.84	2.07	18.00	43.75
H ₂ O ₂	3	3	1.00	2.74	0.33	0.91	7.13	19.32
Fe (II)	3	3	1.44	2.65	0.48	0.88	10.19	18.73
Error	6	6	0.28	0.28	0.04	0.04	–	–
Total	15	15	5.27	11.9	–	–	–	–

[53]. However, as shown in Fig. 4, the removal efficiency increases with increasing dose of Fe (II) from 100 to 400 ppm but after dose of 200 ppm, the slope of graph decreases. With an excessive increase in the concentration of iron, the number of iron salts present in the solution will increase. In addition to increasing the amount of soluble solids, it leads to the reaction of hydroxyl radicals with the remaining iron ions, which, consequently reduces the number of free radicals available and thus reduces the efficiency of the Fenton process (Equation (4)) [54, 55].



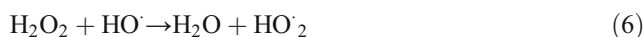
The Fe³⁺ can generate Fe²⁺ and hydroperoxyl radicals by reacting to H₂O₂. The oxidation capacity of HO₂[·] is less than OH[·] which reduces the removal efficiency [39]. So the optimum dose of Fe(II) should be chosen in order to reach the maximum removal efficiency.



The effect of H₂O₂ on removal efficiencies

Increasing the amount of H₂O₂ leads to high removal efficiency as a result of increasing of hydroxyl radicals [53]. This may be due that H₂O₂ reacts to high FeSO₄ and generates more hydroxyl radicals inducing more waste degradation. Also, it could be the generation of Iron(III) sulfate (Ferric sulfate) which works

like coagulant and improves removal efficiency [39]. According to the Figure 4b, increasing H₂O₂ concentration up to 600 ppm, the removal efficiency slope is high. However, with increasing H₂O₂ concentration, the slope is declining. In this case, H₂O₂ acts at high concentrations as the radical scavenger. Based on Equation (6), hydroxyl radical will react with H₂O₂, producing a hydroperoxyl radical (HO₂[·]) that has low oxidation properties [56]. Besides, according to Equation (7), hydroperoxyl radical reacts with hydroxide radical, which will reduce the removal efficiency of the Fenton process [57].



Statistical analyzes

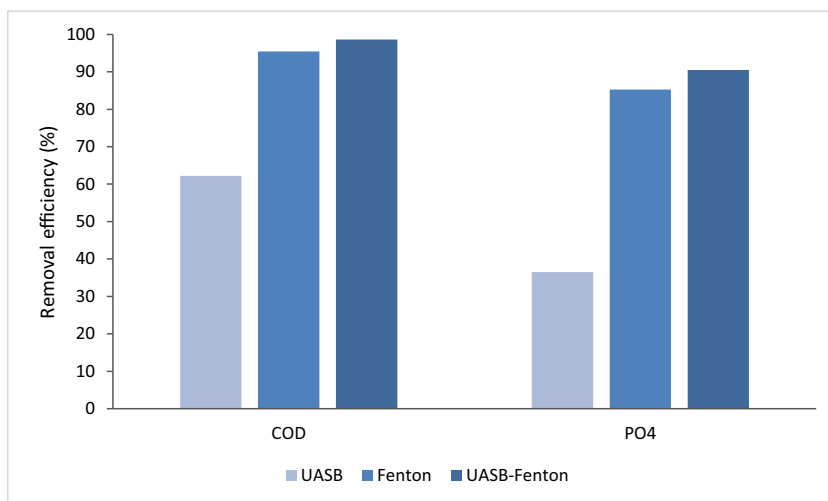
In order to determine the effects of factors on mean response and signal-to-noise ratio, analysis of variance (ANOVA) was applied. The F-value of each parameter shows which parameter has the significant effect on removal efficiency. The larger F-value has more effect on removal efficiency. Sum of squares (S), mean square (variance), F (variance ratio) and DOF (degree of freedom) based on S/N data are shown in Tables 6 for TCOD and phosphate. According to these results, pH has the most significant effect on removal efficiency [58].

The F ratio was applied to examine the influence probability of the surveyed factor on the response. The critical F (F_{cr}) was obtained 4.76 with the confidence level of 95%. This value was obtained from the F distribution curves [59].

Table 7 Verifying the results

Responses	Operating parameters			Removal efficiency (%)	Predicted removal efficiency (%)	Error (%)
	pH	H ₂ O ₂ (mM)	Fe(II) (mM)			
TCOD	3	1000	400	95.41	94.53	0.92
Phosphate	3	1000	400	85.29	84.69	0.7

Fig. 5 Removal efficiency of UASB, Fenton and UASB-Fenton



If the calculated F is more than the F_{cr} with confidence interval of α (in this case $\alpha = 0.05$), the factor will be statistically significant on the response [58]. The effect of factors in a particular order as $pH > H_2O_2 > Fe(II)$ has the largest influence on phosphate removal. Also for TCOD removal follows the order of $pH > Fe > H_2O_2$.

Verifying the results

The last step in Taguchi approach is confirmation experiment. After determining the optimum condition, the confirmation experiment was conducted through combining the optimal levels in order to compare the results with estimated performance [60]. The obtained results from confirmation tests shall be confined with the optimum performance predicted through analysis. In the case the average of obtained results of confirmation experiment falls in confidence range, thus the optimum conditions are confirmed; otherwise further analysis and experimentation will be required [61].

Table 7 indicates the comparison among experimental and predicted results in the optimum condition. As shown in Table 7, the error percentage of all responses is in the acceptable range. Based on the S/N graphs, the optimum point of pH , H_2O_2 and $Fe(II)$ was obtained for each parameter, and $pH = 3$, 1000 ppm of H_2O_2 and 400 ppm of $Fe(II)$ was identified as the optimal condition with maximum removal efficiency. According to Table 7, at the optimum condition the TCOD and phosphate removal efficiency were 94.53% and 84.69%, and predicted values were 94.53 and 84.69, respectively. The results indicate a suitable match between predicted and observed values.

Combined method

According to the results, the UASB reactor performed efficiently in removing easily degradable organic matter and

nutrients. The removal of TCOD and phosphate of the UASB reactor is shown in Fig. 5. The Fenton process was used for further removal. Fenton, a powerful oxidation process, is a viable method to remove hard non-biodegradable organic matter and nutrient. According to the results, in the optimum condition of $pH = 3$, 1000 mg/l of H_2O_2 and 400 mg/l of $Fe(II)$ the removal efficiency of TCOD and phosphate reaches 95.41 and 85.29%, respectively. By comparing the results of the UASB reactor and the UASB-Fenton process, it can be inferred that the use of the Fenton as a post-treatment will be an appropriate UASB complementary process. Also, the removal efficiency of TCOD and phosphate for the combined method was 98.6 and 90.5%, respectively.

The research on treatment of poultry manure wastewater by UASB reactor and Fenton process revealed that the UASB reactor could remove COD up to 90.7% with influent TOCD of 12,100(± 910) mg/L at mesophilic conditions during HRT of 8 days. Fenton process as a post treatment, at operating condition of $pH = 3$, 400 mg/L of Fe^{2+} and 200 mg/L of H_2O_2 , COD and color removal efficiency were 88.7% and 80.9%, respectively. By increasing H_2O_2 to 1200 mg/L and decreasing the Fe^{2+} to 100 mg/L, Fenton process could remove COD and color up to 95% and 95.7%, respectively. The overall process (UASB-Fenton) could remove about 99.3% of COD [62]. Combined anaerobic fluidized bed reactor (AFBR) and Fenton process were studied to treat landfill leachate. The AFBR could remove COD in the range of 80–90% with OLR of 2–15 kg COD/ m^3/d . Fenton process at optimum condition of $pH = 2.5$ and H_2O_2 of 1200 mg/L could remove 85% COD at OLR of 2 kg COD/ m^3/d [63].

Conclusion

The performance of the combined UASB-Fenton process was studied which indicate high removal efficiency of TCOD and

phosphate. The following results can be conferred from the research:

- Up-flow anaerobic sludge blanket reactor could remove TCOD considerably which indicate a great performance of UASB reactor, but it indicates low performance in removing phosphate.
- The effects of pH, oxidant, and catalyst concentration were studied for each parameter, which the results indicate that the effect of factors in a particular order as $\text{pH} > \text{H}_2\text{O}_2 > \text{Fe (II)}$ has the most influence on phosphate removal. Also, for TCOD removal follow the order of $\text{pH} > \text{Fe} > \text{H}_2\text{O}_2$.
- Fenton process indicates an appropriate performance in removing TCOD and phosphate. And also in the terms of turbidity removal, it could remove turbidity up to 99.3%.
- The combined UASB-Fenton process remove TCOD and PO_4^{3-} up to 98.6 and 90.5%, respectively.

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Compliance with ethical standards

Competing interests The authors declare that they have no competing interests.

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