Fenton's treatment of actual agriculture runoff water containing herbicides

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ABSTRACT

This research was to study the efficiency of the Fenton's treatment process for the removal of three herbicides, namely 2,4-dichlorophenoxy acetic acid (2,4-D), ametryn and dicamba from the sugarcane field runoff water. The treatment process was designed with the Taguchi approach by varying the four factors such as H_2O_2/COD (1–3.5), H_2O_2/Fe^{2+} (5–50), pH (2–5) and reaction time (30–240 min) as independent variables. Influence of these parameters on chemical oxygen demand (COD), ametryn, dicamba and 2,4-D removal efficiencies (dependent variables) were investigated by performing signal to noise ratio and other statistical analysis. The optimum conditions were found to be H_2O_2/COD: 2.125, H_2O_2/Fe^{2+}: 27.5, pH: 3.5 and reaction time of 135 min for removal efficiencies of 100% for ametryn, 95.42% for dicamba, 88.2% for 2,4-D and with 75% of overall COD removal efficiencies. However, the percentage contribution of H_2O_2/COD ratio was observed to be significant among all four independent variables and were 44.16%, 67.57%, 51.85% and 50.66% for %COD, ametryn, dicamba and 2,4-D removal efficiencies, respectively. The maximum removal of herbicides was observed with the H_2O_2 dosage of 5.44 mM and Fe^{2+} dosage of 0.12 mM at pH 3.5.

Key words | 2,4-D, agricultural runoff, ametryn, dicamba, herbicides, Taguchi design

INTRODUCTION

Herbicides are mainly used to kill unwanted plants (weed) from farm lands, industrial sites and forestry. During rainfall, immediately after application of herbicides leads to agricultural runoff and it moves towards downstream along with pollutants (natural and man-made) and thereby contributing the pollutant load on surface water body (Conte *et al.* 2016). The major source of water pollution includes overdose, improper application, air spraying, container washing and unintentional leakage from containers.
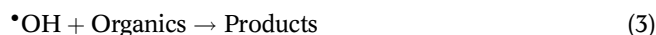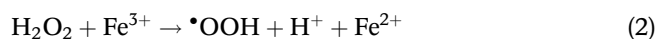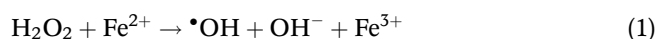
2,4-Dichlorophenoxy acetic acid (2,4-D) and dicamba are most commonly used herbicides around the world. These are inexpensive type of herbicides, used to control the Plantain plantago and White clover broad leaf types of weeds present in the field. It is a known fact that more than 1,500 pesticides contain 2,4-D as the main ingredient (Chu *et al.* 2004). When these herbicides are released to the water and soil environment, they undergo different biochemical processes and thereby form a variety of transformation products (2,4-dichloroaniline), which have a higher toxicity than the 2,4-D and dicamba (Farran & Ruiz 2004). Due to low soil sorption (k_{OC}) and high water solubility (890 ppm for 2,4-D

and 4,500 ppm for dicamba), the traces of these herbicides are detected in surface water body (Gouin *et al.* 2008). The 2,4-D and dicamba are well-known endocrine disrupting chemicals and exposure to these chemicals affects eyes, thyroid, liver, kidneys and nervous system of human beings (USEPA 2005). Also, these herbicides are having a significant effect on birds, beneficial species in soil and aquatic life. Therefore, the 2,4-D concentration in drinking water is recommended as 29 μg L^{-1} as its maximum permissible limit (WHO 2003). Ametryn is a triazine class herbicide used to control the Moneywort type of broad leaf weeds. Ametryn is also highly toxic to human beings and an extremely phytotoxic PSII type of herbicide (Jones & Kerswell 2003), low affinity towards soil (water solubility of 185 ppm) and high leachability, thereby creating a threat to the aquatic environment.

Nowaday's mixture of 2,4-D and dicamba, 2,4-D and ametryn, dicamba and ametryn formulations are more popular due to their synergic effect (Cserhati & Forgacs 1998) on variety of broad leaf weeds that are present in the field and these are economical, save time and destroy the 30–50% of

other gross types of weeds (sedges) also. However, these herbicides do not ensure that they are safe for non-targeted plants, animals and useful microorganisms in soil. Therefore, the knowledge about residual concentration, degradation mechanism and the interaction between these herbicides with insecticides, fungicides and fertilizers in the farmland is more important than the ultimate receiving water body (Heppell & Chapman 2006).

Advanced oxidation processes have a special interest due to their high oxidation potential for the removal of toxic compounds present in water and wastewater. The Fenton's process is the popular treatment method in advanced oxidation processes (AOPs), which is the combination of H_2O_2 and Fe^{2+} (II) and releases highly reactive hydroxyl radicals ($^\bullet OH$) shown in Equations (1) and (2). These $^\bullet OH$ radicals are having high standard oxidation capacity (E_0) of 2.8 V, reacts with organic contaminants and forms the final products like CO_2, H_2O and inorganic ions shown in Equation (3) and also this process works in ambient conditions such as room temperature, atmospheric pressure, etc. (Pignatello et al. 2006; Bigda 1995).

$$H_2O_2 + Fe^{2+} \rightarrow {}^\bullet OH + OH^- + Fe^{3+} \qquad (1)$$

$$H_2O_2 + Fe^{3+} \rightarrow {}^\bullet OOH + H^+ + Fe^{2+} \qquad (2)$$

$${}^\bullet OH + \text{Organics} \rightarrow \text{Products} \qquad (3)$$

The biodegradation studies were reported for the mixture herbicides such as 2,4-D, mecoprop and dicamba (Ghoshdastidar & Tong 2013), 2,4-D and ametryn (Sandoval-Carrasco et al. 2013), but herbicides containing stable carbon halogen bonds in their structures have been described to be much more resistant to microbial degradation. Therefore, many researchers successfully applied AOPs for the degradation of 2,4-D with photo-Fenton, (Conte et al. 2016), mixture of 2,4-D and dicamba with Zno-Fe_2O_3 catalyst (Maya-Treviño et al. 2014) and ametryn with UV/H_2O_2 (Gao et al. 2009). According to the best of the authors' knowledge, no research work has been reported on Fenton's treatment of mixture of 2,4-D, dicamba and ametryn in real agriculture runoff water. Therefore, in this research work, the Fenton's treatment was performed and the parameters were optimized with proper Design of Experiments (DOEs) tool.

In traditional optimization technique, changing one factor at a time and keeping other factors constant is impracticable and it does not give any interaction between different variables with responses. To overcome these limitations the different types of DOEs are proposed such as factorial design, response surface design, mixture of designs and Taguchi design. The Taguchi method involves the systematic way of designing the experiments and analysis of variance (ANOVA) is a tool for analysis of the results. The Taguchi design is cost effective, flexible, provides the high quality of the information at each point, and reduces the experiments than central composite design (CCD) (Ali et al. 2004), save the time and provides a global knowledge with help of standard statistical analysis (signal to noise, S/N ratio). In the present study, the objective is to treat the actual agricultural runoff water by Fenton's reagent and to optimize the variables involved in the process with the Taguchi method. This work also investigates the interactions between the independent factors (H_2O_2/COD (A), H_2O_2/ Fe^{2+} (B), pH (C) and reaction time (D)) and dependent factors (2,4-D, ametryn, dicamba and chemical oxygen demand (COD) removal).

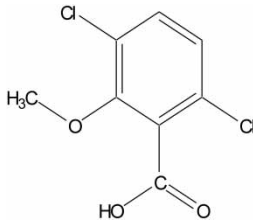## MATERIALS AND METHODS
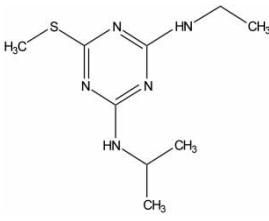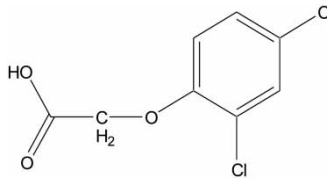
Chemicals

The 2,4-D, ametryn and dicamba were purchased from Sigma Aldrich. The physical and chemical properties of all these three herbicides are listed in Table 1. The reagents hydrogen peroxide (H_2O_2, 50%w/w), hydrochloric acid (HCl, 35%), sulfuric acid (H_2SO_4, 98%), iron (II) sulfate heptahydrate (FeSO$_4$·7H$_2$O), sodium hydroxide (NaOH, 98%), potassium iodide (KI), mercuric sulfate (HgSO$_4$), potassium dichromate, silver sulfate (Ag$_2$SO$_4$), ferrous ammonium sulfate, ferroin indicator, starch, sodium thiosulfate (Na$_2$S$_2$O$_3$) and ultra pure water were procured from Merck, manufactured in India.

Actual agricultural runoff water sampling

The agriculture runoff water was collected from Veerapur village, Belgaum district, Karnataka state, India (Latitude: 15°41′27.64″N; Longitude: 74°39′9.11″E). This district, produces more than 82 lakh tons per year of sugarcane in 2,000 ha area (80% of the total district) and the farmers are using the three herbicides 2,4-D, ametryn and dicamba with different formulations based on the type of weeds (broad leaf weeds) and the quantity of weeds that are present in the field. The usage of these herbicides increased 10 times from last four years and the farmers were spraying six to nine times in a year. Near that sampling site there is Malaprabha river (Latitude: 15°40′32.73″N; Longitude: 74°38′33.43″E) flowing and there are likely chances that

Table 1 | Physical and chemical properties of dicamba, ametryn and 2,4-D

Properties	Dicamba	Ametryn	2,4 -D
Structure			
Synonym	3,6-dichloro-2-methoxybenzoic acid	(2-ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine	2,4-dichlorophenyloxy acetic acid
Appearance	white crystalline solid	white crystalline solid	white to yellow powder
M. W	221 g/mol	227.35 g/mol	221 g/mol
Chemical formula	$C_6H_2 Cl_2(OCH_3)CO_2H$	$C_9H_{17}N_5S$	$C_8H_6Cl_2O_3$
Water solubility (mg/L)	4,500 at 25 °C	209 at 25 °C	890 at 20 °C
M. P and B P	115 °C and 200 °C	84–85 °C and 337 °C	140.5 °C and 160 °C
Density (g/cc)	1.57	1.18	1.416

the runoff water may reach the river and contaminate it. The runoff water was collected from 0.5 acres of land and water was preserved below 4 °C according to *Standard Methods* (APHA 2005) for further analysis.

Experimental methodology

The 1 mM of stock solution and the standard solutions of 0.13, 0.26, 0.39, 0.52, 0.65 mM were prepared in ultra pure water for all three compounds. The high performance liquid chromatography (HPLC) calibration curves were prepared by applying proper conditions listed in Table 2. Then, the runoff water was filtered with 0.2 μ filter paper and the herbicide concentrations were quantified with help of HPLC and they are 25.5 mg/L, 93.7 mg/L and 3.4 mg/L of 2,4-D, dicamba and ametryn, respectively.

The batch experiments were performed for 250 mL of actual samples in 500 mL capacity Erlenmeyer conical flasks at room temperatures (29–31 °C) and atmospheric pressure in a magnetic stirrer at a speed of 200 rpm. The pH of the actual sample was maintained between 2–5 with 0.1 N H_2SO_4. Each experimental run was conducted in triplicate by adding the suitable amount dosages of H_2O_2 (5.45mM–17.71 mM) and Fe^{2+} (0.11–3.54 mM) with a reaction time of 30–240 min and average or concordant values were finally considered. After each set of experiment the samples were filtered with 0.2 μ Sartorius filter paper and the final concentrations of all three herbicides were quantified with HPLC and results were analyzed with the help of Minitab software version 17.

Analytical methods

The λ_{max} values were obtained with ultra violet (UV) double beam spectrophotometer (Systronics, AU-2701 model). The initial and final concentration of herbicide were monitored by HPLC (Agilent, 1260) equipped with UV and diode array detector. The pH, conductivity and turbidity were measured with Systronics pH meter, conductivity meter and turbidity meter. *Standard Methods* (APHA, 2005) were used to determine the nitrates, sulfates and chlorides in runoff water. The COD of the sample was measured with closed reflux titration method and the COD removal efficiency was calculated according the Equation (4). The residual hydrogen peroxide was measured with iodometric titration and the interferences due H_2O_2 in COD determination is corrected according to the method given in the literature (Wu & Englehardt 2012). The residual iron as

Table 2 | HPLC conditions of dicamba, ametryn, and 2,4-D

Parameter	Dicamba	Ametryn	2,4-D
Ratio of mobile phases	50: 50	58: 42	80: 20
Temperature of the column	35 °C	25 °C	30 °C
Retention time (min)	1.382	8.882	1.7
Wavelength λ_{max}	274 nm	223 nm	230 nm
Flow rate	0.75 mL/min	1 mL/min	0.5 mL/min

Sample volume = 20 μL; total run time = 20 min; column name and size = RP-C18, 100*4.6 mm, 3.5 μ pore size; mobile phase = methanol: water.

Table 3 | Initial characteristics of agricultural runoff water

Parameter	Value	Unit
Nitrate nitrogen as NO_3-N	57 ± 3	mg/L
pH	5.9 ± 1	–
Chlorides as Cl^-	88 ± 2	mg/L
Conductivity	0.8 ± 0.01	mS/cm
Turbidity	52 ± 2	NTU
Iron as Fe^{3+}	1.6 ± 0.01	mg/L
COD	185 ± 4	mg/L
Ametryn	3.4	mg/L
2,4-D	25.5	mg/L
Dicamba	93.7	mg/L
Sulfates as SO_4^{2-}	78 ± 2	mg/L

Fe^{3+} was measured with potassium thiocyanate method in visible-spectrophotometer (Lovibond). All physico-chemical parameters are listed in Table 3.

$$\text{COD removal efficiency} = \frac{(COD_i - COD_f)}{COD_i} \qquad (4)$$

where COD_i is the initial COD (mg/L) of all three herbicides and COD_f (mg/L) is its final COD after reaction time.

Taguchi experimental design

In Taguchi method, the output of the design is transformed to S/N ratio instead of results itself. The S/N ratio is the mean value of standard deviation, which tells about the deviation from the desired value of the each response with actual experimental values. There are mainly three types of S/N ratios in Taguchi design depending upon the type of process: smaller-the-better, larger-the-best, and nominal-the-better. In Fenton's process, the larger S/N ratio was selected to optimize the variables involved and it was calculated for each factor level combination according to the Equation (5). In the present study, four independent variables (H_2O_2/COD (A), H_2O_2/Fe^{2+} (B), pH (C) and reaction time (D)) and four responses (%COD, % ametryn, % dicamba and % 2,4-D removal) were considered.

$$\frac{S}{N} = -10 \log \left(\frac{\sum (1/Y^2)}{n} \right) \qquad (5)$$

where Y = responses at the given factor level and n = number of responses at the factory level.

In Fenton's process, the selection of H_2O_2 dose is very important and there should have some basis like COD or total organic carbon value of herbicides. Therefore, in this research work, the initial COD value of herbicide was taken as reference. The ratio of H_2O_2/COD was selected as 2.125 (center value), which is the theoretical relation between the COD and H_2O_2, in which the maximum number of ˙OH radicals are produced (Kim et al. 1997). The minimum and maximum values were selected as 1 and 3.25, respectively, and these values were near to 2.15–2.4 (Kavitha & Palanivelu 2004). The selection of H_2O_2/Fe^{2+} ratio is typical and in many literature sources it was reported as 9.5 (Torrades et al. 2011), 50 (Martins et al. 2010) and 165 (Manu & Mahamood 2011). It was also said that this ratio was case specific and depends on the type of the compounds (Mater et al. 2007). Therefore, with extensive literature survey the ratios of H_2O_2/Fe^{2+} are selected as 5, 27.5 and 50. Here, the ratio of H_2O_2/ Fe^{2+} is based on mass (molar basis) and it was reported by many of the researchers (Bach et al. 2010; Hasan et al. 2012). In the Fenton's process, the pH has been considered an important factor than other treatment technologies, because it was reported that the process works in the acidic range from 2–5 (KiriMart et al. 2010). Based on this, the pH values were selected as 2, 3.5 and 5. The range of reaction times was selected from the evidence given by the literature, such as 30–240 min (Hasan et al. 2012), 60–240 min (Martins et al. 2010) and 120–360 min (Li et al. 2010). Therefore, the reaction time was selected as 30, 135 and 240 min. All the four factors with three levels are listed in Table 4 and the Fenton's dosage along with four responses are shown in Table 5.

RESULTS AND DISCUSSION

Interactions between independent factors (A, B, C and D) and % COD removal

The experimental results generated by performing experiments with the help of the Taguchi orthogonal array and

Table 4 | Factors and levels of orthogonal array

Parameter	Level 1	Level 2	Level 3
A (H_2O_2/COD)	1	2.125	3.25
B (H_2O_2/Fe^{2+})	5	27.5	50
C (pH)	2	3.5	5
D (reaction time in min)	30	130	240

Table 5 | Taguchi design matrix

	Independent variables				Dosage of H_2O_2 and Fe^{2+} (mM)		Dependent variables (%)				S/N ratio			
Run no.	A	B	C	D	H_2O_2	Fe^{2+}	COD R	AR	D R	2,4-D R	COD R	AR	D R	2,4-D R
1	1	5	2	30	5.44	0.67	37	85	45.35	64.94	31.36	38.59	33.13	36.25
2	1	27.5	3.5	135	5.44	0.12	75	100	95.42	88.02	37.50	40.00	39.59	38.89
3	1	50	5	240	5.44	0.07	50	75	81.19	68.09	33.98	37.50	38.19	36.66
4	2.125	5	3.5	240	11.56	1.42	58	80	83.47	77.81	35.27	38.06	38.43	37.82
5	2.125	27.5	5	30	11.56	0.26	71.3	95.93	86.27	82.4	37.06	39.64	38.72	38.32
6	2.125	50	2	135	11.56	0.14	64	95.43	78.49	80.19	36.12	39.59	37.90	38.08
7	3.25	5	5	135	17.68	2.16	45	62	53.71	61.74	33.06	35.85	34.60	35.81
8	3.25	27.5	2	240	17.68	0.39	47.6	65	58.31	60.93	33.55	36.26	35.31	35.70
9	3.25	50	3.5	30	17.68	0.22	46	70	47	70	33.25	36.90	33.44	36.90

S/N ratios are almost close to each other and these values are listed in Tables 5 and 6. It is seen that the delta value of A is higher than the other three parameters and the values were 3.74, 2.81, 1.02 and 2.54 for A, B, C and D, respectively. Therefore, the A, B, C and D, parameters were ranked as 1, 2, 4 and 3, respectively and it can be concluded that the parameter A has more influence on the COD removal. Furthermore, the ANOVA analysis was carried out in Table 7 to confirm the results obtained in Table 6. The

Table 6 | Taguchi analysis of % COD removal (%COD R) versus A, B, C and D as S/N ratio

Level	A (H_2O_2/COD)	B (H_2O_2/Fe^{2+})	C (pH)	D (reaction time)
1	34.28	33.23	33.68	33.02
2	36.15	36.04	34.47	35.56
3	32.42	33.58	34.70	34.27
Delta	3.74	2.81	1.02	2.54
Rank	1	2	4	3

Table 7 | ANOVA analysis of % COD removal (% COD R) versus A, B, C and D

Source	DF[a]	Adj SS[b]	Adj MS[c]	F-value[d]	PC[e]
A	2	742.4	371.2	2.37	44.16
B	2	564.0	282.0	1.51	33.54
C	2	72.48	36.24	0.14	4.31
D	2	302.5	151.2	0.66	17.99

[a]DF = degrees of freedom.
[b]Adj SS = adjacent sum square.
[c]Adj MS = adjacent mean square.
[d]F-value.
[e]PC = percent contribution.

Fisher's test (F-test) value were 2.37, 1.51, 0.14 and 66 with percentage contribution (PC) of 44.16, 33.54, 4.31 and 17.99 for A, B, C and D, respectively, with 95% (P-value) confidence interval level. Therefore, it can be seen that the higher the F-value, the higher contribution for the response. The main effects plot for S/N ratios for % COD removal is shown in Figure 1 and it was observed that the optimum values were found to be 2.125, 27.5, 3.5 and 135 min for A, B, C and D, respectively.

The dosage of H_2O_2 was varied from 5.44–17.68 mM and these values were calculated from H_2O_2/COD (A) and H_2O_2/Fe^{2+} (B). Usually, by increasing the H_2O_2 concentration, increases the COD removal by producing the more ˙OH radicals (Pignatello 1992). However, from Table 5, it is seen that the dosage of (17.68 mM) H_2O_2 was able to yield lesser % COD removal (34–45%). This is due to the fact that by adding the excess amount of H_2O_2, the Fenton's process was inhibited by decreasing the ˙OH radical production
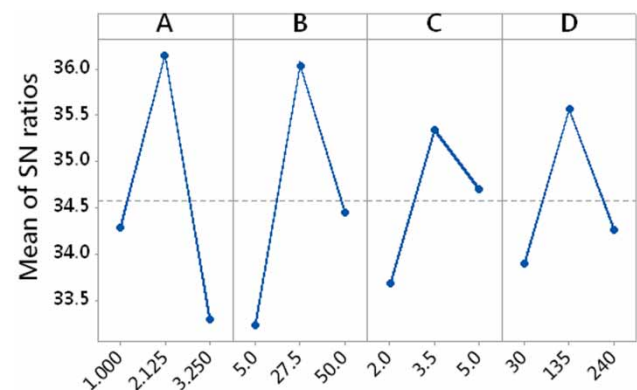
Figure 1 | Main effects plot for SN ratios for % COD removal.

and increasing the O_2 production (Masomboon *et al.* 2009). When the dosage of H_2O_2 was decreased from 17.68–11.5 mM, 71.3% COD removal was achieved. Decreasing the H_2O_2 dosage from 11.5–5.44 mM, maximum removal of 75% was achieved with 0.12 mM of Fe^{2+} in 135 min. The removal was faster at 30 min and then it was slowly increased from 71.3–75% irrespective of pH 5 (Run 5). After that, no COD removal was observed. Hence, the pH has less contribution in the Fenton's process. This is probably due to the fact that, initially, there was a reaction between ferrous ion (Fe^{2+}) and H_2O_2, after that there is a reaction between ferric (Fe^{3+}) and H_2O_2 (Masomboon *et al.* 2009). Therefore, the ratio of H_2O_2/Fe^{2+} helps in higher COD removal efficiency.

The role of ferrous iron is very important and it was varied from 0.07–2.16 mM, which promotes the hydrogen peroxide to produce more ˙OH radicals by increasing the rate of reaction. However, when the iron dosage was at 2.16 mM, only 45% COD removal was achieved and this may be due to, the excess iron reacts with ˙OH radicals and stops further production of radicals shown in Equation (6) (Pignatello 1992). Therefore, the optimum values of H_2O_2, Fe^{2+} were taken as 5.44 and 0.12 mM with a reaction time of 135 minutes at pH 3.5. The residual H_2O_2 of 0.35 mM (93.57% consumption) and residual iron of 0.02 mM (97% iron as Fe^{3+}) were observed at optimum conditions. The yield of Fe^{3+} (residual iron) was almost similar to the research work (Colombo *et al.* 2013).

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \tag{6}$$

Interactions between independent factors (A, B, C and D) and % ametryn removal (%AR)

Table 5 shows that 100% removal was achieved at 5.44 mM of H_2O_2 and 0.12 mM of Fe^{2+} with reaction time of 135 min at pH 3.5. However, Table 8 shows the values of the Taguchi analysis of % ametryn removal (%AR) versus A, B, C and D.

Table 8 | Taguchi analysis of % ametryn removal (%AR) versus A, B, C and D as S/N ratio

Level	A (H_2O_2/COD)	B (H_2O_2/Fe^{2+})	C (pH)	D (reaction time)
1	38.70	37.50	38.15	38.38
2	39.10	38.63	38.32	38.48
3	36.34	38.00	37.66	37.27
Delta	2.76	1.13	0.66	1.21
Rank	1	3	4	2

The delta values are 2.76, 1.13, 0.66 and 1.21 and they are ranked as 1, 3, 4 and 2 for A, B, C and D, respectively. Therefore, it can be concluded that the parameter A has more influence on the ametryn removal efficiency and factor D (reaction time) has second priority than B (H_2O_2/Fe^{2+}). Furthermore, the ANOVA for % ametryn removal versus A, B, C and D were carried out in Table 9 to confirm the results obtained in Table 8. The F-test values were 6.25, 0.42, 0.10 and 0.61 with PC of 67.57, 12.30, 3.29 and 16.84 for A, B, C and D, respectively. The main effects plot for S/N ratios for % ametryn removal is shown in Figure 2 and the optimum values were found to be 2.125, 27.5, 3.5 and 135 min for A, B, C and D, respectively.

As presented in Tables 6 and 8, it was observed that pH is having a fourth influencing parameter in both responses (% ametryn and COD removal) and also it was found that the ametryn removal was decreased when the pH was lesser than 3.5 and more than 3.5 (Table 5). In case of higher pH (>3.5), the decomposition of H_2O_2 was observed by losing its oxidation potential and also there might be deactivation of Fe^{2+} observed by forming ferric hydroxide complexes and thereby reducing the ˙OH radical production (Lucas & Peres 2006; Wang 2008). Hence, ametryn removal efficiency was reduced. At lower pH (<3.5), the scavenging effect of ˙OH radicals by H^+ ions was observed, which leads

Table 9 | ANOVA analysis of % ametryn removal versus A, B, C and D

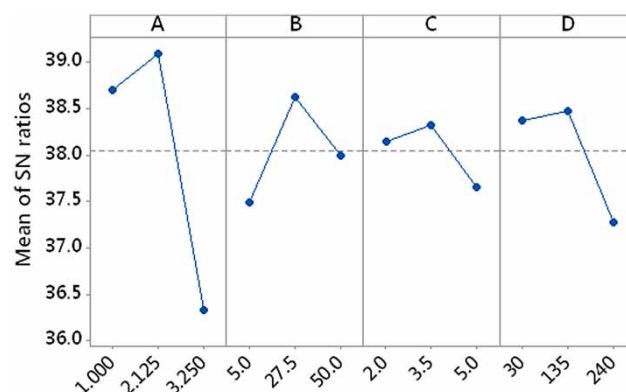| Source	DF	Adj SS	Adj MS	F-value	PC
A	2	1,069.7	534.86	6.25	67.57
B	2	194.7	97.33	0.42	12.30
C	2	52.06	26.03	0.10	3.29
D	2	266.7	133.3	0.61	16.84

Figure 2 | Main effects plot for S/N ratios for % ametryn removal.

to the lesser degradation of ametryn (Equation (7)) (Martins *et al.* 2010). Therefore, the optimum pH was selected as 3.5. This acidic pH (3.5) can be overcome by the use of hetero-geneous catalyst (FeOOH) (Yaping & Jiangyong 2008), in which the % removal efficiency of the pollutant was rela-tively better at pH at 7.47 (86.4%) compared to pH 3.07 (98.2%).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \tag{7}$$

From Table 8, it is seen that the reaction time (D) is also showing significant effect on ametryn removal efficiency along with H_2O_2/COD (A). Based on the experimental results presented in Table 5 it was observed that, at 30 min (run 5), the reaction was faster and 95.9% of ametryn removal was achieved, after that 100% removal efficiency was achieved at 135 min (Run 2). It clearly says that within 30 min, a large number of hydroxyl radicals are pro-duced (Equation (1)) and after 30 min the hydroperoxyl radicals ($HO_2^{\bullet}$) were produced (Equations (8) and (9)), which are having lesser oxidation capacity than $\cdot$OH radical.

$$H_2O_2 + Fe^{3+} \rightarrow H^+ + FeOOH^{2+} \tag{8}$$

$$FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \tag{9}$$
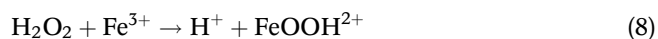
Interactions between independent factors (A, B, C and D) and % dicamba removal

It can be seen from Figure 3 that the optimum values of A, B, C and D were found to be 2.125, 27.5, 3.5 and 135 min, respectively. The same trend was observed in COD and ame-tryn removal efficiencies. From Table 5, the maximum
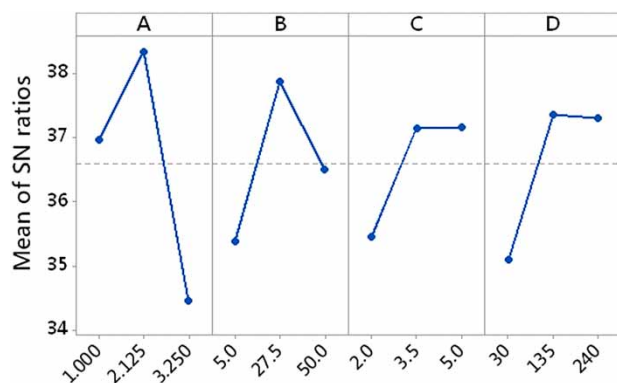

Figure 3 | Main effects plot for S/N ratios for % dicamba removal.

Table 10 | Taguchi analysis of % dicamba removal (% D R) versus A, B, C and D as S/N ratio

Level	A (H_2O_2/COD)	B (H_2O_2/Fe^{2+})	C (pH)	D (reaction time)
1	36.97	35.39	35.45	34.56
2	38.35	37.87	36.61	37.36
3	33.91	35.97	37.17	37.31
Delta	4.44	2.49	1.72	2.81
Rank	1	3	4	2

dicamba removal efficiency was observed to be 95.42% with 5.44 mM and 0.12 mM of H_2O_2 and Fe^{2+}, respectively. From Table 10, the delta values are 4.44, 2.49, 1.72 and 2.81 and they are ranked as 1, 3, 4 and 2 for A, B, C and D respectively. The ANOVA analysis was performed in Table 11 and the PC values were achieved as 51.85, 18.01, 9.60 and 20.54 for A, B, C and D respectively. The same trend followed in both % ametryn removal and dicamba removal, however the variation in the PC was observed. The F-test value are 3.23, 0.66, 0.32, and 0.78 for A, B, C and D, respectively. Comparing with PC values of B and D, only 2% difference was observed and it clearly says that, these two parameters contributing equally in degra-dation process.

The results indicate that increasing initial concentration of H_2O_2 to 17.68 mM could degrade only 60–70% (Runs 7, 8, 9) of dicamba. Decreasing the H_2O_2 values from 17.68–11.56 mM enhanced the dicamba removal from 70–86%. However, 95% of removal was achieved at 5.44 mM of H_2O_2. It clearly says that by an increase in the H_2O_2 concen-tration, the oxidation process might be inhabited by deactivating the produced $\cdot$OH radical and formed the $\cdot$OOH radical according to the Equation (10) (Duesterberg & Waite 2006).

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + OOH^{\bullet} \tag{10}$$

The dicamba removal was increased from 81–95% by increasing the Fe^{2+} dosage of 0.07–0.26 mM (Runs 2, 3).

Table 11 | ANOVA analysis of % dicamba removal versus A, B, C and D

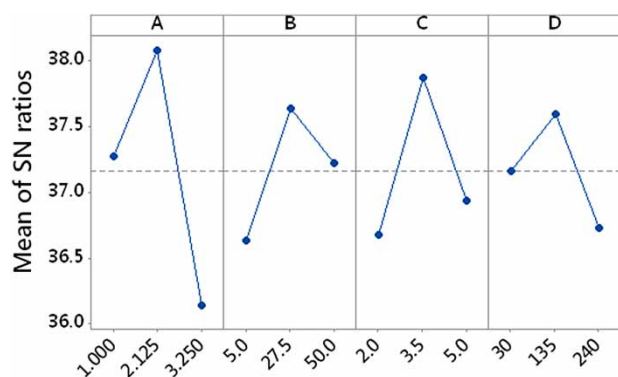| Source	DF	Adj SS	Adj MS	F-value	PC
A	2	1,686	843.1	3.23	51.85
B	2	585.7	292.9	0.66	18.01
C	2	312.2	156.1	0.32	9.60
D	2	668.1	334.1	0.78	20.54

Figure 4 | Main effects plot for S/N ratios for % 2,4-D removal.

However, the removal efficiency was decreased at iron concentration >0.26 mM. Perhaps, at higher concentration of iron the Fe^{2+} enhances self-scavenging of •OH radicals given in Equation (11) (Hameed & Lee 2009).

$$Fe^{2+} + {}^{•}OH \rightarrow Fe^{3+} + OH^{-} \tag{11}$$

Interactions between independent factors (A, B, C and D) and % 2,4-D removal

Figure 4 displays the main effects plot of % 2,4-D removal versus A, B, C and D. The optimum values were achieved to be 2.125, 27.5, 3.5 and 135 min for A, B, C and D, respectively. From Table 12 the delta values are observed as 1.94, 1.01, 1.20 and 0.87 and they are ranked as 1, 3, 2 and 4 for A, B, C and D respectively. The ANOVA results shows that, the PC values were 50.66, 15.86, 21.70 and 11.78 with F-values of 3.08, 0.57,0.83 and 0.40 for A, B, C and D respectively, which are listed in Table 13. It was also observed that the factor A (H_2O_2/COD) is contributing more in all the responses. This is mainly due to the fact

Table 12 | Taguchi analysis of % 2,4-D removal (% 2,4-D R) versus A, B, C and D as S/N ratio

Level	A (H_2O_2/COD)	B (H_2O_2/Fe^{2+})	C (pH)	D (reaction time)
1	37.27	36.63	36.68	37.16
2	38.07	37.64	37.87	37.60
3	36.14	37.22	36.93	36.73
Delta	1.94	1.01	1.20	0.87
Rank	1	3	2	4

Table 13 | ANOVA analysis of % 2,4-D removal versus A, B, C and D

Source	DF	Adj SS	Adj MS	F-value	PC
A	2	384.2	192.11	3.08	50.66
B	2	120.3	60.14	0.57	15.86
C	2	164.6	82.29	0.83	21.70
D	2	89.33	44.67	0.40	11.78

that, the H_2O_2 is directly taking part in the removal of COD and also the optimum value 2.125(A) is following the standard relation (1 g of COD = 2.125 g of H_2O_2). Since, the pH variable was ranked as 2, which has a significant effect on the 2,4-D removal efficiency than reaction time (D) and H_2O_2/Fe^{2+} (B). At pH 2, the 2,4-D degradation efficiency of 60–80% (Runs 1, 6, 8) and at pH 5, 61.74–68.09% removal was observed (Runs 3 and 7). However, in case run 5, the removal efficiency was observed to be 82.4%. This increase in 2,4-D removal is due to the proper selection H_2O_2/Fe^{2+} ratio (27.5). The highest removal efficiency of 88% was found to be at pH 3.5. At pH values below 3, perhaps the oxidation process was inhibited by the production of oxonium ions and makes the H_2O_2 less reactive towards ferrous ion and thus decreasing the •OH radical production (Oliveira et al. 2006).

It was also said that at a low pH of 2, the less soluble species of Fe^{3+} are available to enhance the •OH radical production and at higher pH(>3.5) the formation of iron hydroxides were observed, which helps in suppressing the Fe^{2+} species regeneration and thereby reducing efficiency of treatment process (Wang 2008). In this Fenton's process with similar optimum conditions of 5.44 mM (H_2O_2), 0.12 mM (Fe^{2+}) and 3.5 (pH), 40–50% of sulfates, nitrates and chlorides were removed along with dicamba, ametryn and 2,4-D. Therefore, finally the optimum values of A, B, C and D were selected as 2.125, 27.5, 3.5 and 135 min, respectively.

Finally, to confirm the accuracy of the experimental results, the normal probability distribution plots versus residuals were performed in Figure 5(a)–5(d). These plots were linear in nature and all the points were distributed along the straight line and it was confirmed that obtained results were in good agreement with model values.

To know the distribution pattern of the residuals, the graphs were plotted for all nine set of experiments in Figure 6(a)–6(d). From these figures, it was concluded that the points were randomly distributed along the both sides of the center line (0-line) and it is a good trend for all four responses.
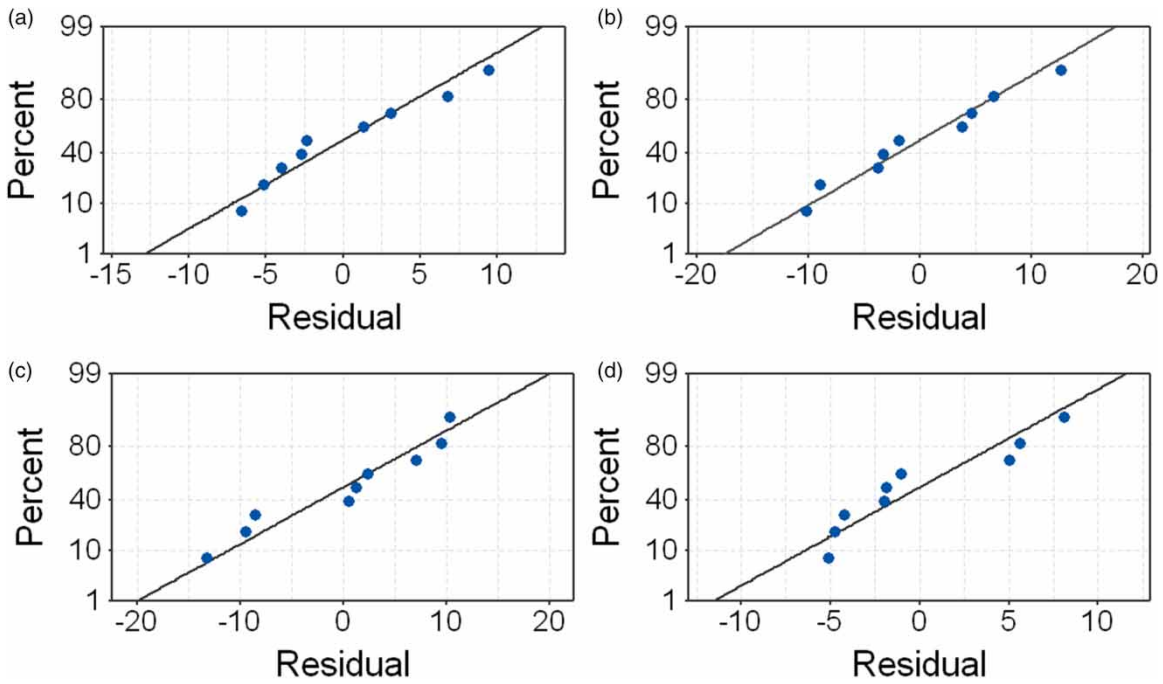
Figure 5 | Normal plot of residuals: (a) % COD R, (b) % AR, (c) % D R, (d) % 2,4-D R.
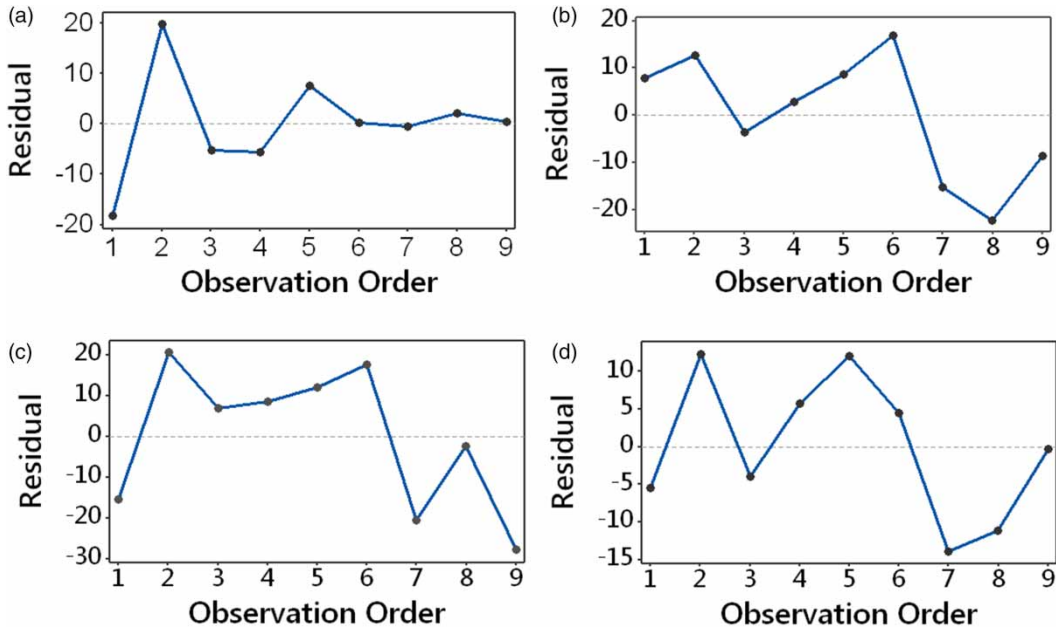

Figure 6 | Residuals vs. observation order: (a) % COD R, (b) % AR, (c) % D R, (d) % 2,4-D R.

CONCLUSIONS

Agricultural runoff water containing three herbicides (ametryn, dicamba and 2,4-D) was successfully treated with Fenton's reagent and Taguchi method was applied to study the interactive effects between the variables involved in the treatment process. The obtained results are summarized as follows:

- The optimum values were found to be 2.125, 27.5, 3.5 and 135 min for A, B, C and D, respectively, for all four responses.
- From the ANOVA results, it was found that higher F-value was observed for H_2O_2/COD ratio, which indicates that percent contribution is (PC) more in all four responses and they are 44.16%, 67.57%, 51.85% and 50.66% for %COD, ametryn, dicamba and 2,4-D removal efficiencies, respectively.
- In addition, H_2O_2/Fe^{2+}, reaction time and pH are ranked as 2 for all four responses. The optimal COD, ametryn, dicamba and 2,4-D removal was observed at reaction time of 135 min and they are 75%, 100%, 95% and 88%, respectively.
- The maximum removal efficiency was achieved with H_2O_2 dosage of 5.44 mM and Fe^{2+} dosage of 0.12 mM at pH 3.5 for all three herbicides. Therefore, with these results, Taguchi approach can help to identify the most influencing factor in Fenton's treatment process for the removal herbicides from actual agricultural runoff water.

ACKNOWLEDGEMENTS

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