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Research Article

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Taguchi experimental design used for Nano photo catalytic degradation of the pharmaceutical agent Aspirin

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ABSTRACT

Acetyl salicylic acid (A.S.A.) is a drug which can be used as a pain soother, anti-inflammatory and antipyretic property. Photo catalytic degradation of ASA was carried out in an aqueous suspension of TiO_2 irradiated by ultraviolet light. A multivariable center composite design was applied for factors including pH, TiO_2 loading and Temperature. A Taguchi experimental design is used to obtain optimal parameters .The optimal condition would be obtained as followed: PH = 5.5, $[TiO_2] = 50\ {}^{mg}/_{l}$ and T = 40 ℃. After 60 min irradiation about 73% of aspirin is decomposed.

Keywords: Acetyl salicylic acid,TiO_2, experimental design, photo catalytic degradation

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INTRODUCTION

In recent decades, the presence of pharmaceuticals and personal care products (PPCPs) in the environment is emerging as a new environmental concern of the scientists as well as the public, which has low concentration in the environment and usually does not show acute toxicity. After digestion and metabolism of this compounds in body, residual parts with their metabolites are excreted in human urine and manure, which are the main inlets of them to enter the environment [1, 2]. There are still some residual parts of them getting into the surface and ground water during and after the sewage treatment [3-5].

Acetyl salicylic acid (ASA) (known Aspirin commercially) is a non steroid anti-inflammatory drug that is usually used to ease pain and reduce fever. Today, aspirin is one of the most widely used medicines in the world, with an estimated 40000 tones of it being consumed each year. In addition it is also used as an anti-inflammatory medicine, as well as showing ulcer effects and blood clots preventions. However, aspirin today is mainly used to prevent heart disease 37.6%, arthritis 23.3%, Headache 13.8%, body aches 12.2% and other pains 14.1% [6].

Several different analytical methods have been proposed for the determination of this ingredient, including solid phase spectra photometry (SPS) with flow injection analysis (FIA) [7], gas chromatography- mass spectrometry [8] and spectrofluorimetry [9-11] methods. In the last few years, new technologies for the decomposition of organic micro-pollutants in the aqueous environment have been developed. Photo catalytic an example of advanced oxidation processes (AOPs) capable of achieving a complete oxidation of organic and inorganic species, including pharmaceutical substances as well [12-15]. It takes advantage of some semiconductor solids, which can be used as photo catalysts suspended in the water effluent to be treated. Among them TiO_2 is widely used because it is non-toxic, inexpensive photocatalyst, as well as biologically and chemically inert. The electron/hole pair (e^-/h^+)

generated under light illumination of energy greater than 3.2ev reacts with the molecules object of degradation, or water molecules oxidized by the photo holes (h^{+}) and increases hydroxyl radicals, needed to accomplish decomposition of the chemical substances [16].

Operating parameters such ac catalyst dosage, pH, time and temperature have significant influence on the degradation rate. To achieve an effective performance, optimization of operating parameters is necessary for aspirin degradation. To establish better conditions by relating all the factors considered, numerous experiments have to be carried out with all the possible parameter combinations, which is not practical. Conventional experimental procedures, involve altering one factor at a time keeping all other factors constant, resulting in assessing the impact of those particular factors, which are time consuming and require more experimental sets. Design of Experiments (DOE) is one approach, which helps to gain information about the optimized levels, by taking large number of variables.

DOE methodology by Taguchi orthogonal array (OA) is a factorial based approach which merges statistical and engineering techniques. Taguchi method utilizes OAs to study a large number of variables with a small number of experiments, which significantly reduces the number of experimental configurations to be studied.

Analysis of experimental data using ANOVA (analysis of variance) and factor effects provide information about statistically significant factors and result in finding optimum levels of factors to design parameters. The Taguchi method not only helps considerably in saving of time and cost, but also leads to a fully developed process and provides systematic, simple and efficient approach for the optimization of the near optimum design parameters. Taguchi method was successfully applied to improve material processing technology, medical instrumentation, environmental applications, biotechnological process and experimental chemistry [17].

The main objectives of this research were to assess the photo catalytic treatment of aspirin (see Figure 1). To optimize the variables simultaneously, Taguchi experiment was used. All factors were investigated such as Temperature, TiO_2 concentration, pH and time.

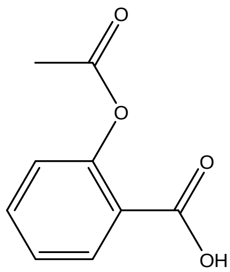

Figure 1. Aspirin of structure

EXPERIMENTAL SECTION

Material

Aspirin was purchased from Hakim pharmaceutical Co. Nano titanium dioxide (15-20 nm, Annataz form) was purchased High Technology Nano Co. Ltd. HCL and NaOH (Merck) aqueous solution were used to adjust pH. The reaction solutions were prepared in Ethanol 98%.

Photo catalytic degradation experiment

In all cases 100 ml of the aspirin solution in 5 mg/l concentration containing appropriate quantity of the photo catalyst suspensions were used. At regular time intervals, 5 ml of the sample were withdrawn and centrifuged at 2500 rpm for 20 min to separate the catalyst. The absorbance of the solution samples were measured by a UV-Vis Spectra photometer (Unicoi 4802 UV/Vis double beam). To explore the pH effect, the pH of all solutions were initially adjusted by adding 0.1 N HCL or 0.1N NaOH and controlled by a pH meter (Horiba F12).

The percentage of degradation was calculated by using the equation given below:

$$\text{Degradation (\%)} = \frac{C_0 - c}{C_0} \times 100 \qquad (1)$$

In which is the initial ASA concentration and C is the ASA concentration after the irradiation.

Multivariate experimental design
The central composite design (CCD) was applied to investigate the effect of pH, concentration, time and temperature in the photo catalytic degradation technique. For this experiment, 9 experiments (L_9) by three onus reptile were performed, at which variables were codified in three levels.

The response surface was built by using Taguchi software, based on the experimental data obtained for aspirin degradation (%) after 60 min of irradiation during the photo catalytic treatment method.

RESULTS AND DISCUSSION

Control experiment
Aqueous solutions of ASA were irradiated by using a 40 W Phillips lamp. The effect of nano and lamp were shown in Figure 2. The variability and changing in aspirin concentration in the absence of during the 60 min of irradiation were not noticeable. This was because ASA had weak absorption in the range from 200 to 400nm, which means only few amounts of ASA have been directed photolysis when a Phillips lamp was used as the irradiation source. However, had showed its importance in the photocatalytic degradation of ASA in the UV/ . After 60 min irradiation, almost 63% of ASA disappeared in solution. This shows that the decomposition of ASA could be attributed to photo catalytic reaction. Also, no new bands in the UV-Vis region due to the reaction intermediates formed during the degradation process.

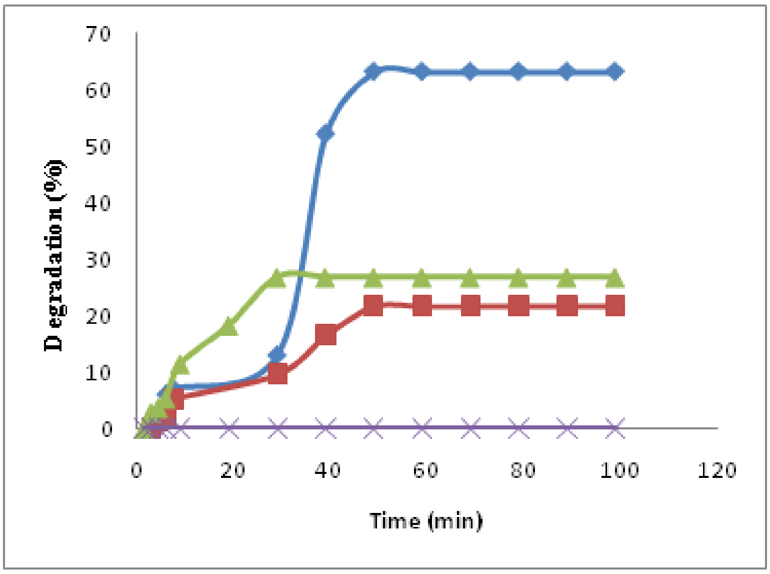

Figure 2. Control of photo catalytic degradation. (◆) nano+A.S.A+ UV , (■) nano + A.S.A , (▲) A.S.A + UV , (×) A.S.A.

Kinetics of disappearance
Several experimental results indicated the degradation rates of various organic contaminants over illuminated fitted the Langmuir- Hinshelwood kinetic model:

— —— (2)

Where r is the oxidation rate of the treatment, c the concentration of the reactant, t the illumination time, k the reaction rate constant and K is the adsorption coefficient of the reactant [18]. When the chemical concentration c_0 is a mill molar solution (c_0 small) the equation can be simplified to an apparent first-order equation [19]:

— or (3)

A plot of — versus time represents a straight line, the slop of which upon linear regression equals the apparent first order rate constant k_{app} .

Figure 3 shows the process profile of aspirin photo catalysis by during irradiation. According to the figure, our data consistent with the Langmuir- Hinshelwood model as by plotting — versus time, a straight line is obtained.

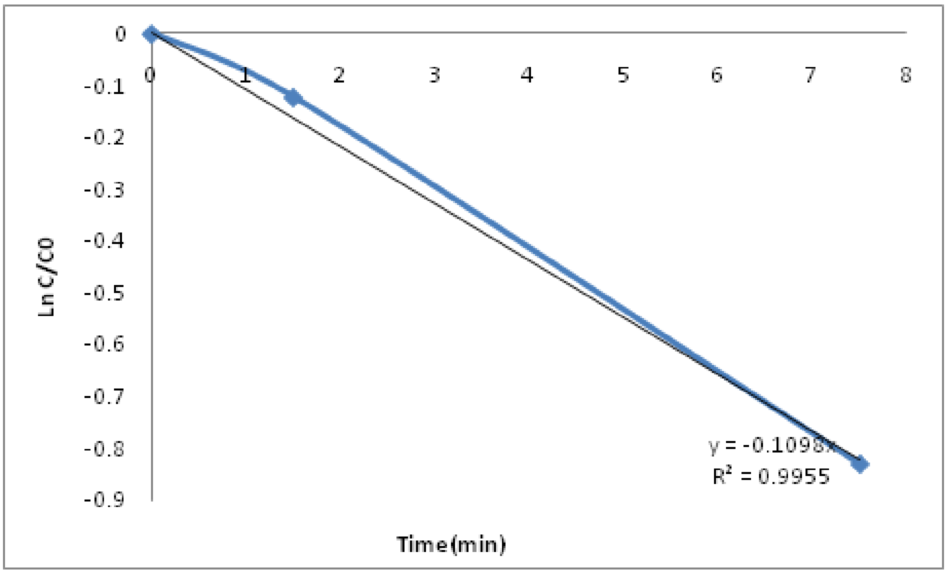

Figure 3. Kinetic of aspirin photo catalysis: , , .

Experimental design
It has to be mentioned that the properties and initial concentration of pollutant, catalyst dosage, temperature, UV light intensity, pH and time for aqueous phase photoreactions are the main parameters pathetic ting the removal rate. However, it is quite difficult to carry out an experimental design including all these factors due to the large number of experiments and complex data analysis required. Therefore, the most important factors were chosen. It was found that the four factors, concentration, pH, temperature and time, have the most significant effect on aspirin photocatalysis rate. This means that all the experiments were carried out at a constant UV light intensity and initial aspirin concentration of 50 mgL^{-1} in the central composite design.

Central composite design
A central composite design (CCD) was applied in order to optimize the ASA degradation. Four factors were considered: dosage, temperature, pH and time. Table 1 condenses the level for each factor involved in the design strategies. These levels were chosen according to preliminary experiments carried out.

Table1 Range of the parameter variation used in the central composite design

parameter	Low level(-1)	Center level(0)	High level(+1)
	40	50	60
PH	3.5	5.5	6.5
T	30	40	50
time	20	30	50

Taguchi method
Using Taguchi software, and considering the data in table 1 we drawn table L_9 (Table 2). According to this table each run was repeated three times and the percentage of aspirin was obtained. Average effect of each factor on

response surface data is shown in Figure 4. It can be seen in the figure the average maximum is located for dosage, pH and temperature in the center and time at the highest level.

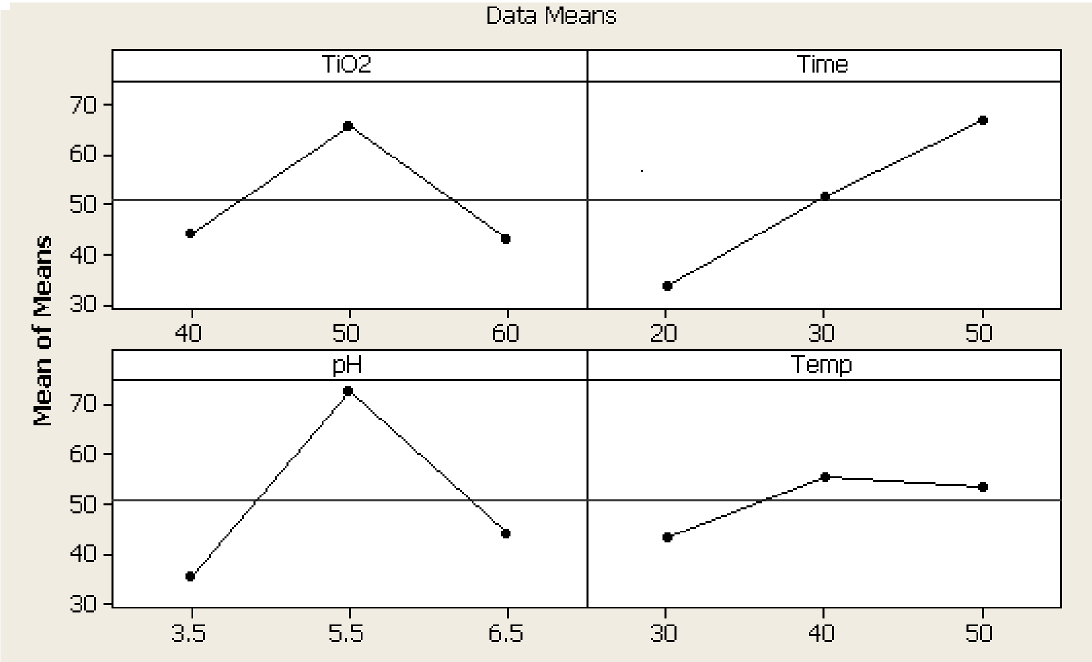

Figure 4. Main effects plot for means

Table2 Experimental data in central composite design

Run		Temp.	Time	pH	Degradation (%)	S/N
1	40	30	20	3.5	4.35	12.77
2	40	40	30	5.5	71.45	37.08
3	40	50	50	6.5	56.40	35.02
4	50	50	20	5.5	73.03	37.27
5	50	30	30	6.5	52.20	34.35
6	50	40	50	3.5	71.20	37.05
7	60	40	20	6.5	23.70	27.50
8	60	50	30	3.5	31.50	29.97
9	60	30	50	5.5	73.00	37.26

Table 3 shows the amount of sum square calculated and mean of square factors. According to these results, it is clear that pH and time have the greatest effects; concentration and temperature have the minimum effects on the degradation rate.

Table3 Amount of sum square, variance and share of each factor

Factor	DOF	SS	Mean Sq	F	P (%)
	2	977	489	0.71	19.06
Time	2	1655	827	1.43	32.28
pH	2	2232	1116	2.31	43.53
Temp.	2	263	132	0.16	5.13

Also, we calculated the amount of variance ratio and the percentage contributed to each factor by ANOVA software, which is listed in Table 3. From the table it is clear that the F values for all factors are less than F values derived from statistical table. In the level of confidence of 95% is F = 5.14. So the H_0 Hypothesis cannot be refuted, significantly is this factor full active. The following table is showed the P values, in order to pure SS to total SS ratio share of each factor to be explained. Considering the contribution of each factor it is resulted that time and pH has the greatest effect.

The S/N ratio

We examined the effect of various factors on S/N ratio, which is shown in figure 5 and data are summarized in Table 2. It can be seen in the table related to the maximum S/N of 4 tests, which are time and temperature in high level, whereas pH and dosage in central level. According to Figure 5 maximum S/N is achieved when , , pH=5.5 , t=50 min and the percentage of ASA with these conditions is 73%.

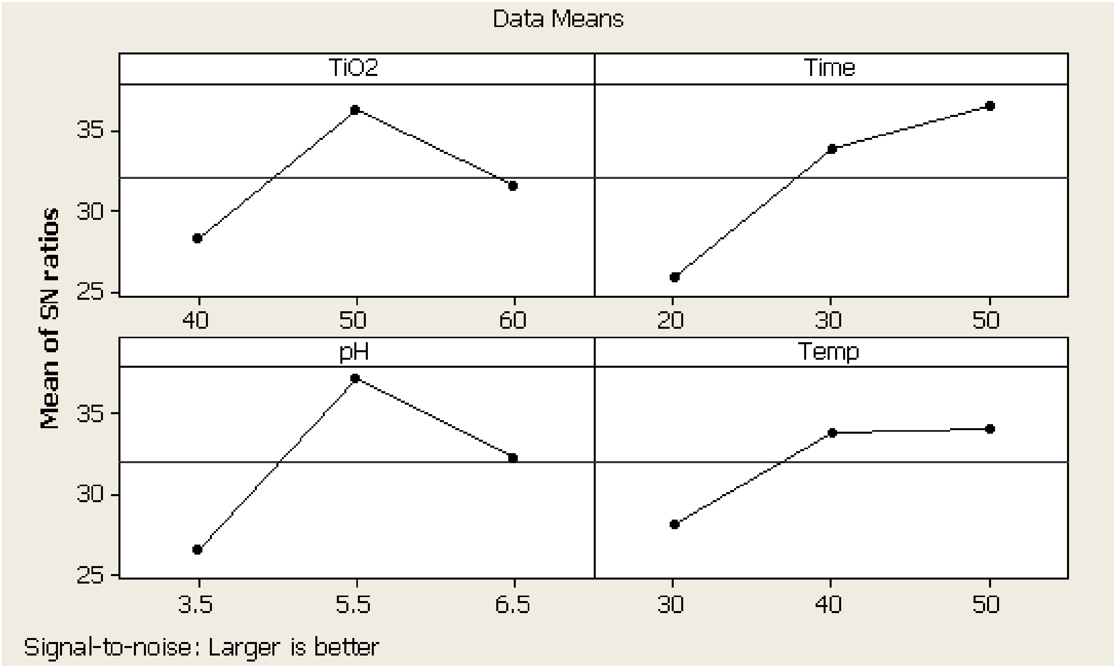

Figure 5. Main effects plot for S/N ratios

Screening of effects

Concentration effect

In this work, the photo degradation efficiency of ASA developed when the concentration of was increased to 50 mgL^{-1}. When dosage goes above 50 mgL^{-1} the reaction time decreases. Concerning the influence of catalyst ( ) concentration, the scattering phenomena occur when the amount of catalyst was higher than the optimal which hinders the increase of the reaction rate [20].

The optimum amount of should be added in order to avoid superfluous catalyst and also to ensure total absorption of radiation photons for efficient photo degradation [21, 22]. When we increased the dose of the catalyst, of course, it increases the adsorption amount of the reaction target resulting in a faster degraded rate [23].

Initial pH effect

Photo catalytic degradation efficiency of ASA became higher when the pH value increased to 5.5, when the solution became more alkaline, the degradation efficiency was much lower than acidic solutions.

In reality, the interpretation of pH effects the efficiency of ASA photo degradation process which is a very difficult task since three possible reaction mechanisms can contribute to ASA degradation, namely, hydroxyl radical attack (1), direct oxidation by the positive hole (2) and direct reduction by the electron in the conducting band (3) [24]. It appears that the effect of pH on degradation of pollutants is variable and controversial since the positive holes are considered to be the major oxidation species at low pH where as hydroxyl radicals are considered as the predominant species at neutral or high pH levels [25].

$$ASA + OH^{\cdot} \rightarrow degradation\ product \quad (1)$$
$$ASA + h_{VB}^{+} \rightarrow oxidation\ product \quad (2)$$
$$ASA + e_{CB}^{-} \rightarrow reduction\ product \quad (3)$$

Regarding to the reported papers [26, 27], the pH of the solution significantly affects TiO_2 activity, including the charge on the particles, the size of the aggregates it forms and the positions of the conductance and valance bands. The point of zero charge (PZc) of the TiO_2 is widely reported at PH = 6 and the TiO_2 surface will remain positively charged in acidic medium $(pH < 6.25)$ and negatively charged in alkaline medium $(pH > 6.25)$, since the photo catalyst can be protonated and deprotonated under acidic and alkaline conditions respectively, as it is shown in the following equations:

$$TiOH + H^{+} \rightarrow TiOH_2^{+} \quad (4)$$
$$TiOH + OH^{-} \rightarrow TiO^{-} + H_2O \quad (5)$$

pH changes can thus influence the adsorption of ASA on TiO_2 surface, an important step for photo oxidation to occur. Thus, at PH = 5.5, a strong adsorption of ASA on the TiO_2 particles is observed as a result of the electrostatic attraction of the positively charged TiO_2 with ASA.

Effect of temperature
At higher or lower temperature, the degradation rate of the contaminant load decays. The photo degradation efficiency of ASA increased when the temperature increased at 40 ℃. According to results, the temperature played a less important role in the photo catalytic reaction system, although the changes in the temperature variable between $30 - 50$ ℃ .

CONCLUSION

In this research, photo catalytic degradation of aspirin was investigated by the nano particles of TiO_2 . The observation clearly demonstrates the importance of choosing the optimum degradation parameters to obtain a high degradation rate.

The chemo metric approach used in this study has been shown to be a valuable tool for the identification and interpretation of the photo catalytic reaction parameter. Temperature, TiO_2 dosage, pH and time have been systematically evaluated via the center composite design based on response surface methodology.

The optimum amount are obtained for aspirin were$[TiO_2] = 50\ mgL^{-1}$, PH = 5.5, $T = 50$ ℃ and t = 50 min. According to this condition, about 73% of ASA decomposed.

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