Photocatalytic degradation of Malachite Green by $Sr_3M_xAl_2O_{6+\delta}$ (M=None, Sm^{3+}, Eu^{3+}, Ho^{3+} and Yb^{3+}) nanomaterials as an excellent and recyclable photocatalyst

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ABSTRACT

As reported in our previous work, $Sr_3Al_2O_6$ nano powders were synthesized by a one-step solid state reaction using $Al(NO_3)_3.6H_2O$, $Sr(C_2H_3O_2)_2$ and $Sr(NO_3)_2$ at 800 and 900 ℃ for 8 h. For the synthesis of $Sr_3M_xAl_2O_{6+\delta}$ (M= Sm^{3+}, Eu^{3+}, Ho^{3+} and Yb^{3+}) nano powders, $Al(NO_3)_3.6H_2O$, $Sr(NO_3)_2$, Eu_2O_3, Ho_2O_3 and Yb_2O_3 were used at 800℃ for 8 h. In the present work, the photocatalytic performance of $Sr_3M_xAl_2O_{6+\delta}$ (M=None, Sm^{3+}, Eu^{3+}, Ho^{3+} and Yb^{3+}) nanomaterials were investigated for the degradation of Malachite Green (MG) water pollutant in aqueous solution under direct white visible light irradiation with the light power 40 W. The optimum conditions were obtained by design expert software for (5%) Al_2O_3 - (95%) $Sr_3Al_2O_6$ (S_1). It was found that the optimum conditions were 0.2 mL of H_2O_2, 20 mg of catalyst, and 40 min. The initial volume and concentration of MG solution were 150 mL and 100 ppm, respectively. It was found that $Sr_3Al_2O_6$ had excellent efficiency under the optimized conditions at the presence of direct visible light irradiation. The degradation yield in the optimized conditions was 100 %.

1-Introduction

Strontium based aluminates are efficient luminescence materials. They are an important class of phosphors for their high efficiency in the visible region, and provide durable properties under ultraviolet light irradiation [1]. In $SrO-Al_2O_3$ system, there are four stable double oxides, namely $Sr_3Al_2O_6$, $SrAl_2O_4$, $SrAl_4O_7$ and $SrAl_{12}O_{19}$, and other strontium aluminate phases, such as $Sr_4Al_2O_7$, $Sr_4Al_{14}O_{25}$, $Sr_{12}Al_{14}O_{33}$ and $Sr_{10}Al_6O_{19}$ [2]. $Sr_3Al_2O_6$ has a cubic crystal unit with the space group Pa-3 containing a packed six-membered AlO_4 tetrahedral ring [3]. Strontium-based aluminate ($Sr_3Al_2O_6$) is one of the most well-known host material and is the most covalent and alkaline phosphor among all aluminates [4]. It has been reported that $Sr_3Al_2O_6$ nanomaterial has been used as catalyst for biodiesel production [5].

MG is a triarylamine dye and used in pigment industry. MG is used in leather, paper, silk, cotton, and jute dyeing processes. It is also used as an antifungal and anti-protozoan agent in fisheries and aquaculture industry [6,7]. It is a non-biodegradable dye pollutant and is a highly controversial compound. Furthermore, MG and its metabolites are known to cause mutagenic, carcinogenic, and teratogenic effects to living organisms [8]. It should not be used for beverages, food, medicines. Its inhalation may cause irritation to the respiratory tract, and in large quantities causes tissue damage and inflammation of kidneys [9,10]. Several metal oxides and sulfides have been used for the

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degradation of MG under different conditions summarized in refs. [11-13].

The present work reports a photocatalytic application of the pure and doped $Sr_3Al_2O_6$ nanomaterials for the degradation of MG under visible light condition. The experimental design method is used to optimize the factors affecting the degradation process. The parameters are the amount of the nanocatalyst amount, H_2O_2 volume and the reaction time. The data show that the synthesized $Sr_3Al_2O_6$ nanocatalyst has very good efficiency at aqueous solution under the optimized conditions.

2- Experimental

2-1- General remarks

The pore diameter size of the as-synthesized nanomaterials was calculated using the Brunauer-Emmett-Teller (BET) equation. BET surface areas were acquired on a Beckman Coulter SA3100 surface area analyzer. The concentration of MG is determined at 606 nm using a Shimadzu UV-visible1650 PC spectrophotometer. A BEL PHS-3BW pH-meter with a combined glass-Ag/AgCl electrode is used for adjustment of the solution pH.

2-2- Photocatalytic activity

The photocatalytic activity of the previously reported synthesized samples [14] was investigated for the degradation of MG in the presence of H_2O_2 (30%, w/w) under direct visible light irradiation. Table 1 present the purity, counts and elemental composition of the as prepared samples. The elemental compositions for S_1 to S_4 are based on the XRPD rietveld analysis data. Figure 1 presents the pore diameter size histograms of the synthesized nanomaterials obtained by BET method. The data reveals the high homogeneity of the pore diameter size distribution. To prepare a 70 ppm MG dye solution, 0.07 g of MG powder was dissolved in 1000 mL of deionized water. The pH value of the obtained solution was 4. The sample 1 (S_1) was used to find the optimum conditions using design expert software for the degradation of MG. Then, the photoactivity of the other synthesized materials was studied at the optimized condition. To obtain the optimum condition in a typical photocatalytic process, a certain amount (g) of S_1 was added into 60 mL of the as-prepared MG solution and sonicated for 10 min in a dark room to establish an adsorption/desorption equilibrium between MG molecules and the surface of the photocatalyst. Afterwards, certain volume (mL) of H_2O_2 was added into the solution followed by further magnetic stirring (250 rpm) under direct visible light irradiation. When the designed time (min) was elapsed, the solution was drawn out and the photocatalyst was separated by centrifugation in order to measure the absorption spectra of MG and calculate the MG concentration using UV-Vis spectrophotometry. The photodegradation yield (%) of MG was calculated by the following formula:

$$\left(\frac{A_0\text{-}A_t}{A_0}\right) \times 100$$

where, A_0 and A_t represent the initial absorbance of MG at 612 nm and the absorbance at time t, respectively.

Table 1. Counts, purity and elemental composition of the obtained nanomaterials.

Sample	Counts	Purity (%)	Elemental Composition
S_1	777	95	Al_2O_3-$Sr_3Al_2O_7$
S_2	1049	92	Al_2O_3-$Sr_3Al_2O_7$
S_3	3270	93	(5%)Al_2O_3-(2%)$SrCO_3$-$Sr_3Al_2O_7$
S_4	1211	65	(21%)Al_2O_3-(6%)$SrCO_3$-(8%)$SrAl_2O_4$-$Sr_3Al_2O_7$
S_5	2525	100	$Sr_3Sm_{0.04}Al_2O_{6+\delta}$
S_6	1824	100	$Sr_3Eu_{0.06}Al_2O_{6+\delta}$
S_7	2063	100	$Sr_3Ho_{0.037}Al_2O_{6+\delta}$
S_8	1293	97	Al_2O_3-$Sr_3Yb_{0.06}Al_2O_{6+\delta}$

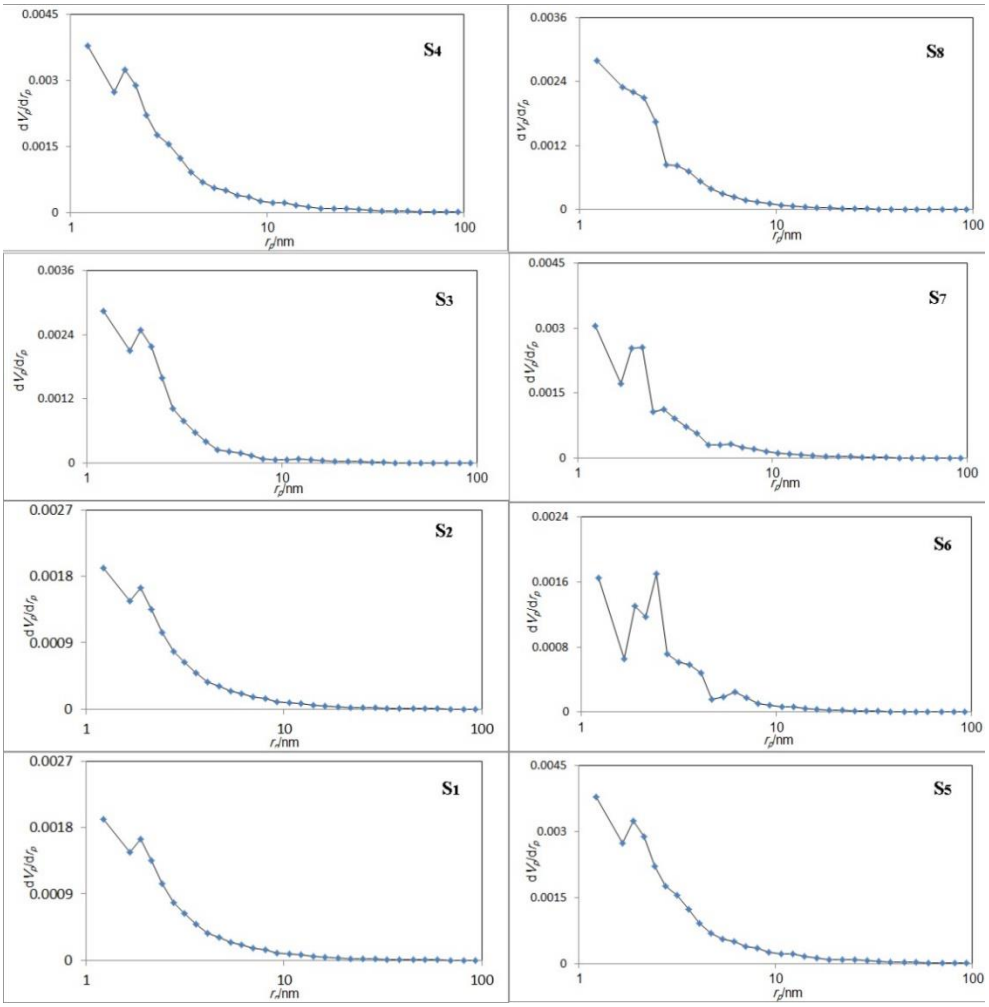

Fig. 1. Pore diameter size distribution profiles of the synthesized nanomaterials.

3-3-Experimental design for achieving optimal conditions in MG degradation process

In the present study, we determine the optimum values of nanocatalyst, time and H_2O_2 needed for the degradation of MG. The response is the degradation yield (R%). Different possible combinations of the three factors are designed which are reported in table 2. All the experiments are performed at two days with random order. The central composite design (CCD) is chosen for modelling the proposed procedure. A three-level CCD with three factors (catalyst (A), H_2O_2 (B), and time (C)) is used to investigate the effects of the factors. The conditions of the 20 experiments accompanied to dye degradation percentage are given in table 2.

The observed data of the design were fitted to a polynomial response model. The below equation shows the relation between the factors and the reaction yield, R%, based on the first order model:

$$R_1=+18.32+4.61\times A+20.10\times B+17.98\times C-9.75\times A\times B+13.50\times A\times C+9.75\times B\times C+1.60\times A2+14.33\times B2+9.02\times C2$$

The experimental range and levels of the variables are shown in table 3. The independent variables (catalyst amount (A), H_2O_2 volume (B) and stirring time (C)) are given in the coded form (-α, -1, 0, +1, +α).

Evaluation of the model to find the optimum conditions for the photocatalytic degradation of MG was performed by the analysis of variance (ANOVA) technique (Table 4). The analysis compares the differences between group means with the variability within the groups around the corresponding mean values. This ratio is called F-distribution (F-value). In order to obtain the significant and reliable model at the 95% confidence level, p-value for the fitted model and its corresponding terms should be smaller than 0.05.

Table 2. Experimental results of the applied model for photo-catalytic malachite green degradation over $Sr_3Al_2O_6$.

H_2O_2	Catalyst	Time	Yield
0.2	0.01	40	63
0.1	0.01	40	7
0.15	0.0175	30	21
0.1	0.01	20	17
0.2	0.025	20	17
0.2	0.01	20	18
0.15	0.0175	30	19
0.1	0.025	40	84
0.15	0.0175	30	20
0.1	0.025	20	54
0.15	0.0175	30	17
0.2	0.025	40	100
0.07	0.0175	30	13
0.15	0.030	30	94
0.23	0.0175	30	29
0.15	0.005	30	20
0.15	0.0175	30	19
0.15	0.0175	13	13

Table 3. Ranges of operational parameters for experimental design in CCD.

Factor	Name	Low Actual	High Actual	Low Coded	High Coded
A	H_2O_2	0.1	0.2	-1	1
B	Catalyst	0.01	0.025	-1	1
C	Time	20	40	-1	1

The p-value of the present regression is smaller than 0.05 showing that the model is significant at a high confidence level (95%).A further assessment of the fitted model can be carried out using the lack-of-fit test. At 95% confidence level, the p-values for the lack-of-fits are greater than 0.05, which is not significant. As shown in table 4, the outcomes of ANOVA are completely in agreement with the above statements.

Also, the coefficient of determination (the R-square, adjusted–R-square) was used to express the quality of fit of polynomial model equation. In this case, R^2 of variation fitting for R% = 97 indicated a high degree of correlation between the response and the independent factors (R^2 = 0.99). The high value of adjusted regression coefficient (R^2-adj = 0.98) indicated high significance of the proposed model. This means that the difference between the experimental and the predicted responses is negligible. Also the predicted R-squared value (0.97) was reasonable.

Figures 2 represents plots of the dispersal residuals and predicted versus the experimental degradation efficiency, and figure 3 shows the plots of the residual for each parameter and ramp. This figure shows a good agreement between the predicted and experimental degradation efficiency (R^2 = 0.99) and represents the adequacy and significance of the model. Figure 2 shows the normal plots of the residual versus the studentized residuals. As it is evident in this figure, the data points appear on a straight trend line, demonstrating that there is no considerable dispersal. Figure 3 shows that the optimum conditions obtained by design expert software were 0.2 mL of H_2O_2, 20 mg of catalyst, and 40 min. The volume and concentration of the as prepared MG solution for obtaining the optimum conditions were 150 mL and 100 ppm, respectively.

Table 4. ANOVA analysis results for the degradation of malachite green by the photocatalytic process.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Block	17.63333	1	17.63333			
Model	16996.02	9	1888.447	298.728	< 0.0001	significant
A-H_2O_2	289.7814	1	289.7814	45.83969	< 0.0001	
B-Catalyst	5515.492	1	5515.492	872.4798	< 0.0001	
C-Time	4414.768	1	4414.768	698.3596	< 0.0001	
AB	760.5	1	760.5	120.3013	< 0.0001	
AC	1458	1	1458	230.6368	< 0.0001	
BC	760.5	1	760.5	120.3013	< 0.0001	
A^2	36.74579	1	36.74579	5.812712	0.0392	
B^2	2955.107	1	2955.107	467.46	< 0.0001	
C^2	1172.123	1	1172.123	185.4148	< 0.0001	
Residual	56.89464	9	6.321627			
Lack of Fit	46.14464	5	9.228928	3.43402	0.1278	not significant
Pure Error	10.75	4	2.6875			
Cor Total	17070.55	19				

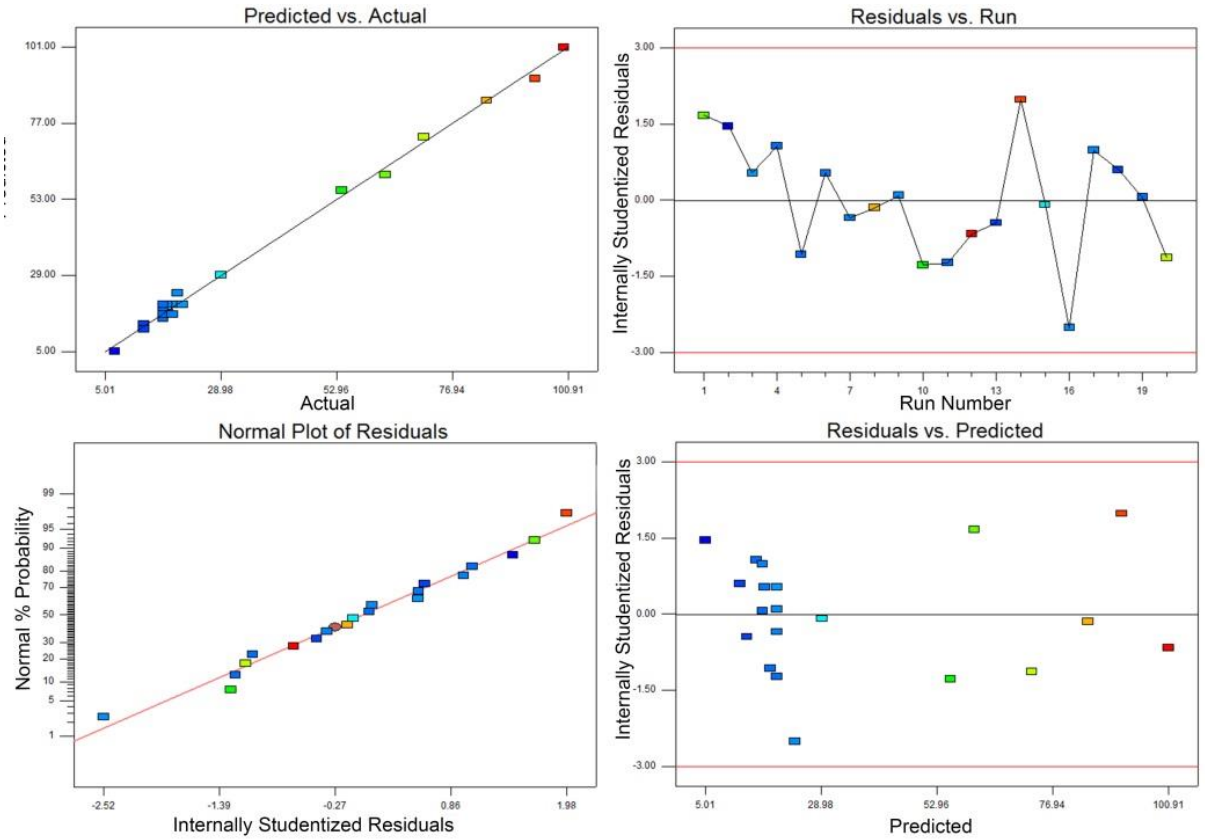

Fig. 2. Plots of dispersal and normalized residuals for the degradation process.

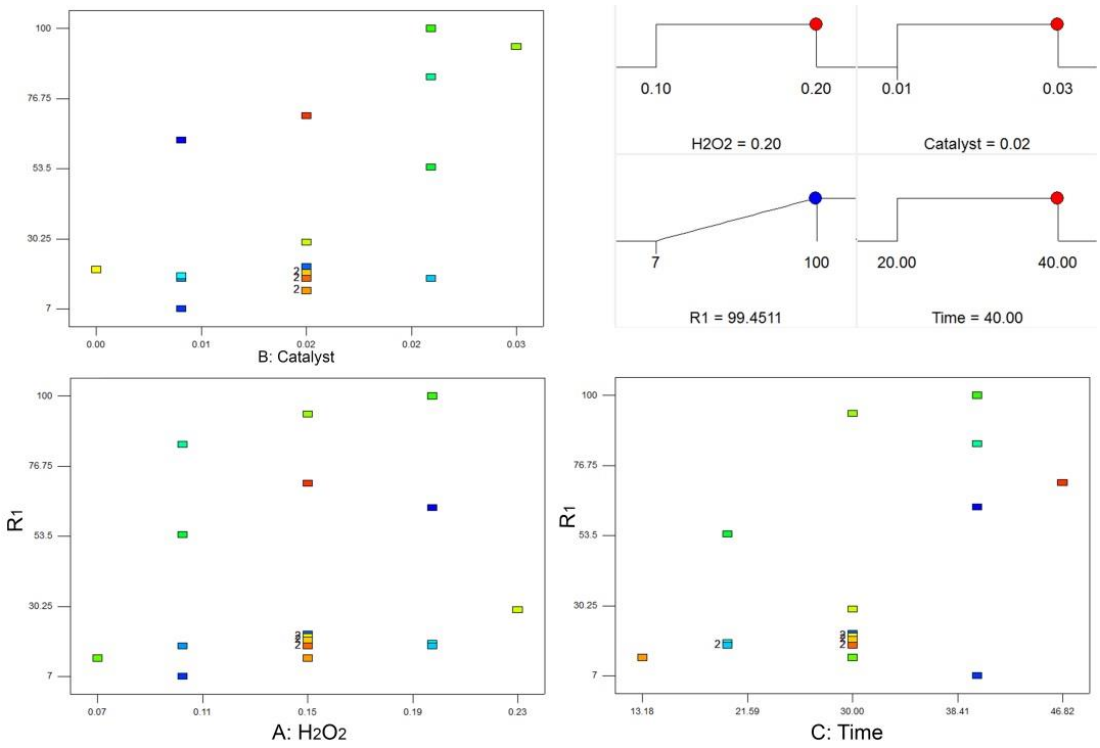

Fig. 3. Plots of ramp, and Yield (R_1) versus each of the parameters.

To investigate the interactive effects of three influential factors on the proposed process, the response surface methodology (RSM) was used. The two and three–dimensional response surface plots are shown in figure 4 to illustrate the effects of the parameters on the R value in the above model. Figure 4 represents the 3D and counter plots related to the interaction of AB, AC and BC. The semi-curvatures of these plots indicate the interaction between the variables.

In other words, by increasing the catalyst amount and reaction time at a constant volume of H_2O_2, high amount surface area of adsorbent is available for the dye molecules leads to enhance the dye removal percentage. Also, at a constant amount of catalyst, when H_2O_2 and reaction time are increased, dye removal percentage is improved. This means that the mass transfer of dye molecules enhances more and the dye adsorption process on the catalyst reaches equilibrium state quickly.

3-3- Effect of different parameters on the photocatalytic degradation of MG

Figure 5 shows the dye degradation graphs for the obtained materials at the optimum conditions. Figure 5a shows the effect of dye concentration on the degradation yield. It is clear that the dye degradation percent is high when the dye concentration is in the range of 100 to 120 ppm. However, when the dye concentration is increased more up to 120 ppm, the degradation is decreased, considerably. It seems that when the dye concentration is high, light wavelength cannot be penetrated into the dye solution (light screening effect) and/or the available active catalyst sites for MG molecules for adsorption and reaction is reduced. Figure 5 b shows the dye volume effect on the degradation yield. It is found that when the dye volume is up to 170 mL, the degradation yield is high; when the volume is increased to 180 mL, the degradation is decreased. It can be due to the decreasing the adsorption of dye on the catalyst making the process rate slower than the diluter solution. Figure 5 c shows the influence of irradiation time on the photocatalytic performance of the as-synthesized samples. It is clear that the efficiency is high when the irradiation time is increased to 40 min. Figure 5 d shows the reusability of the samples. It indicates that the synthesized catalyst shows reusability performance for the process until run 4.

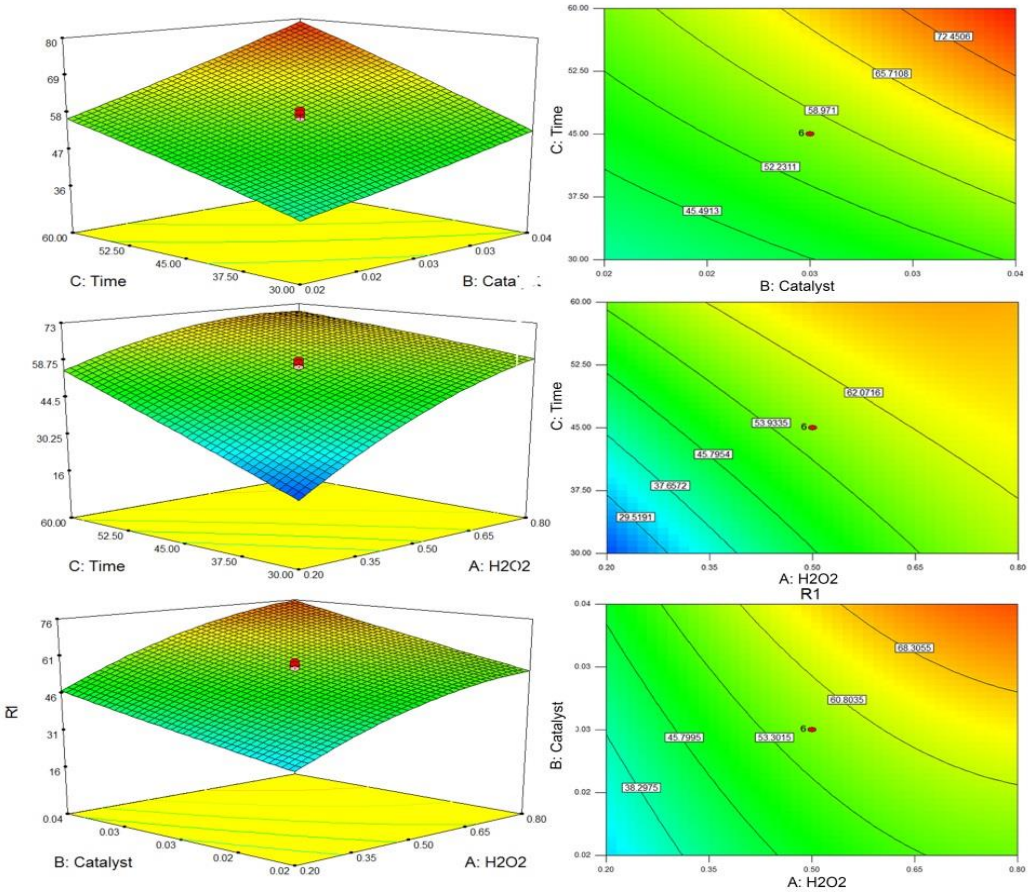

Fig. 4. 2 and 3D surface plots of removal of MG dye.

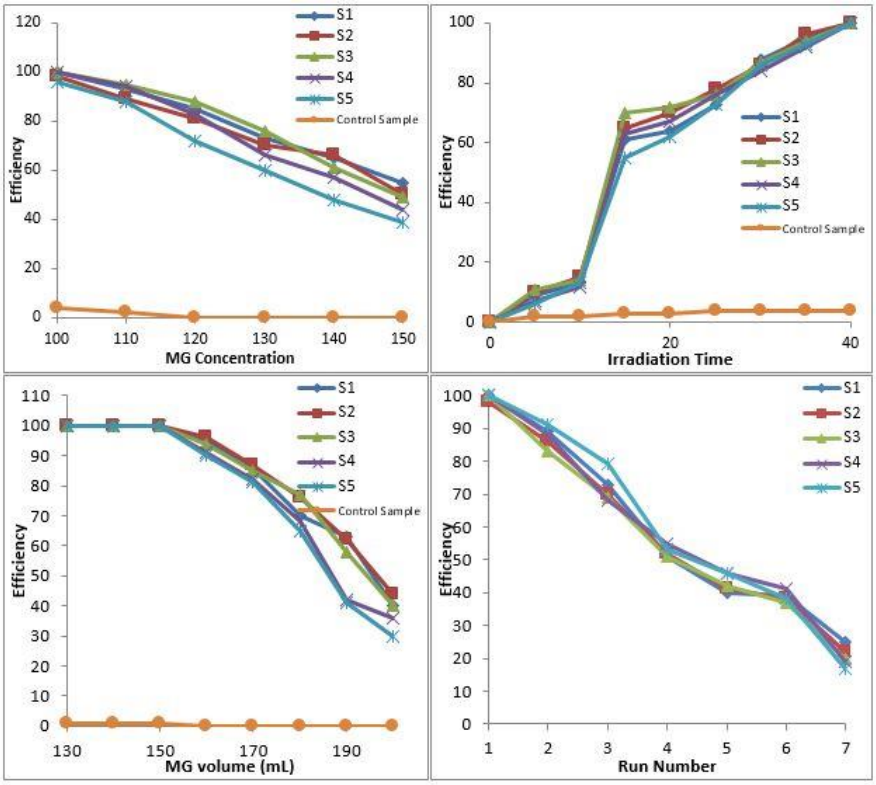

Fig. 5. MG degradation (%) at different (a) dye volume, (b) dye concentration, (c) irradiation Time; and (d) reusability.

Table 5. Comparison study for the degradation efficiency [14].

Catalyst	Condition	Yield (%)
$Sr_3Al_2O_6$(Present work)	H_2O_2, 20 mg catalyst, 40 min, visible ligth, 150 mL and 100 ppm MG	100
Carbon/TiO_2	25 ppm MG, 30 min, pH=8	82-100
MoS_2/TiO_2	40 min, sunlight irradiation, 0.1 g catalyst, 10 ppm MG	97
$PbCrO_4$	365 ppm MG, 0.1 g catalyst, 4 h, pH=7.5, visible light, 60 min	90
$Ni_{1-x}Co_xFe_2O_4$	Sunlight, 50 mL solution, 25 ppm catalyst, 1 μM MG, H_2O_2, 15 h	100
Mg-doped TiO_2	Vis light, pH=9, 100 ppm MG	89
ZnO	4h time, 60 ppm MG, pH=7.5, solar radiation	98
$FeSO_4$ -7H_2O	10 mM Fe2+, 40 °C, 25.5mM H_2O_2, 10 ppm MG	94
$Sr_2As_2O_7$	H_2O_2, 20 mg catalyst, 33 min, 70 mL of 100 ppm MG, solar light	97

The photocatalytic performance of the as-synthesized nanomaterials was compared to some other previously reported works (table 5). The data reveal the high performance of the as-synthesized nanomaterials for the degradation of MG in the present photocatalytic conditions.

4-Conclusion

The photocatalytic degradation of MG was studied under direct visible light irradiation. It was found that the optimum condition was 0.2 mL H_2O_2, 20 mg catalyst, and 40 min time. The volume and concentration of the as prepared MG solution were 150 mL and 100 ppm, respectively. Several tests were performed for investigating the effect of different parameters on the degradation yield. It was found that the catalytic performance was excellent when the pH value was in the basic range, the dye concentration was up to 120 ppm and the dye volume was up to 170 mL. The considerable reusability value of the photocatalyst suggested the commercial using the catalyst in the industry to remove water pollutant dyes.

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