PHOTOCATALYTIC TREATMENT OF WASTEWATER OF FRUIT JUICE INDUSTRY USING NANO PARTICLES OF FE3O4/SIO2/TIO2

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Abstract - The aim of this study is to reduce the COD (Chemical Oxygen Demand) of diluted wastewater of Iranian fruit juice industry. The experiments were carried out in a laboratory-scale using a Plexiglas slurry reactor of a capacity of 2 liters under 450 rpm stirring at room temperature and UV irradiation. $Fe_3O_4/SiO_2/TiO_2$ nano particles with a well-defined core-shell structure was prepared by sol-gel method and used as photocatalyst. The effect of important photocatalytic reaction parameters including pH, dose of catalyst, irradiation power and time of reaction were examined. Response surface methodology (Box-Behnken Design) was applied to optimize the conditions for the reduction of COD in wastewater. At the optimum conditions pH=5, with 275 mg of photocatalyst under 14.5 W of irradiation and 97 min COD removal of 75.16% was achieved.

Index Terms - $Fe_3O_4/SiO_2/TiO_2$, wastewater of fruit juice industry, photocatalytic treatment, COD reduction.

I. INTRODUCTION

Most fruit juice and soft drink industries in developing countries are moving towards wastewater reuse or recycling. Water and wastewater reutilization, costs of treatment and disposal guidelines, remain the most critical factors for the development of sustainable water use for fruit juice and soft drink industries. Wastewater reuse or recycle has potential in these industries, depending on the wastewater characteristics such as concentration and volume. Concentrated fruit juice industries use a wide volume of water for washing and fruit processing, generating a large volume of wastewater [1]-[3].

The Water Quality Management Methodology to be applied to assess the production process and relevant discharges in order to achieve conservation of water, raw material and energy, elimination of pollutants and to obtain reusable water and energy flows. By this approach, it was specifically aimed to achieve a bridge between production and environmental concerns [4]-[6]. In recent years many different methods for food wastewater treatment were investigated. For example some of these methods are as: Anaerobic digestion (AD) and MBR technologies, adsorption by solid natural and synthesis sorbents, advanced oxidation processes (AOP) like using a heterogeneous photocatalytic reaction, Fenton and photo Fenton Processes, membrane filtration (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis), using UV irradiation in nano photocatalytic reactions. In this research the ability of COD reducing in diluted wastewater of a fruit juice industry under moderate conditions and acting as economical and more importantly environmentally friendly particles was investigated. Firstly, core-shell photocatalyst nanoparticles synthesized with sol gel method [6]. Secondly, these particles were used in the batch experiments to find the optimum conditions in which the highest COD reduction can be achieved.

II. MATERIALS AND METHODS

A. Materials

Tetraethyl ortosilicate (TEOS), ammonia solution (25%), ethanol were purchased from Merck. Tetraethyl orto titanate and Magnetic Fe_3O_4 nanoparticles (MPS ≈ 20 nm) were purchased from sigma Aldrich. All the chemicals were analytical grade. Preparation of samples consists of two steps. In the first step the magnetic Fe_3O_4 nanoparticles are covered with a SiO_2 layer and in the next step the TiO_2 layer is covered as the photoactive layer as shown in Fig. 1.

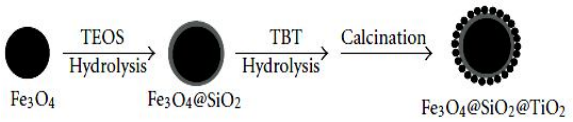

Fig.1: Layers of SiO_2 and TiO_2 on magnetic Fe_3O_4

B. Synthesis of Fe_3O_4/SiO_2

0.5 gram of Fe_3O_4 nanoparticles was dispersed in 30 cm^3 deionized water and 100 cm^3 ethanol and ultrasonicated for 30 minutes. Then a certain amount of ammonia solution was added to the solution until the pH reached 12. 0.55 cm^3 of TEOS solution was added drop wise under vigorous mechanical stirring. The solution was stirred at room temperature at 600 rpm for 6 hours and aged for 2 hours afterwards. The obtained Fe_3O_4/SiO_2 nanoparticles were separated by a magnet and washed with water and ethanol for 5 times.

C. Synthesis of $Fe_3O_4/SiO_2/TiO_2$

The prepared Fe_3O_4/SiO_2 nanoparticles were dispersed in 30 cm^3 deionized water and 30 cc ethanol and

ultrasonicated for 30 minutes. Then the mixture of 2 cm^3 TBOT and 25 cm^3 ethanol was added drop wise to the solution under vigorous mechanical stirring. The process was followed by stirring for 4 hours at 600 rpm and aging for 1 hour. The resulted $Fe_3O_4/SiO_2/TiO_2$ nanoparticles were separated with a magnet and washed 5 times with water and acetone, Fig. (1). The particles was calcinated for 6 hrs at 450 ^oC after driying. To characterization of synthesized nano phototocatalyst the FTIR, XRD and FE-SEM examines were done [6]. These tests proved the successful coating of SiO_2 on magnetite and formation of Si-O bonds. According to the obtained results, the size of the magnetic core was 69.39 nm and the size of the prepared $Fe_3O_4/SiO_2/TiO_2$ nanoparticles was approximately 100 nm and Si to Fe_3O_4 ratio was 13.94% and Ti to Fe_3O_4 ratio was 56.24%.

D. Photocatalytic performance

Photocatalytic batch tests were carried out in a 2 L Plexiglas slurry reactor under 450 rpm stirring at room temperature and UV irradiation. $Fe_3O_4/SiO_2/TiO_2$ nano particles with defined dose and diluted wastewater (COD = 140 mg/l) under irradiation of UV lamps (6 W each) were put on reactor. The reactor was then placed in a cube which its internal surface was made from mirror. Using of mirror surfaces could utilize the reflection of the UV rays and enhance the efficiency of COD removal. In the end of experiments nonoparticles were separated using a magnet and COD examine were done on the solution to measure COD and COD reduction was calculated as below:

$$COD\ Reduction\% = (Initial\ COD - Final\ COD) \times 100 / Initial\ COD$$

In previous work this photocatalyst showed the excellent performance in the methylen blue from aqueous solution [6].

III. EXPERIMENTAL DESIGN

Response surface methodology (Box-Behnken Design) was applied to optimize the conditions for the reduction of COD in wastewater [7]-[10]. This study considered 4 variable factors in 3 levels (Table 1).

Factor	Description	Level 1	Level 2	Level 3
A	Time (min)	30	60	120
B	UV Power (W)	6	12	18
C	pH	5	7	9
D	Photocatalyst (ppm)	100	200	300

Table 1: Variable factors

The experimental conditions based on RMS design are presented in Table 2.

IV. RESULTS AND DISCUSSION

Results of experiments are shown in table 3. After elimination of less effective terms, the regression equation after the analysis of variances (ANOVA) gave the percentage of COD reduction as a function of the pH, dosage of photocatalyst, UV power and time as below:

$$COD\ Reduction\% =$$

$$235.66 - 63.90 \times pH + 0.0645 \times Photocatalyst\ conc. + 0.4325 \times time +$$

$$2.839 \times power - 0.346 \times pH \times power + 4.149 \times pH^2 - 2.136 \times 10^{-3} \times time^2$$

Actual percent of COD reduction and the predicted by the above equation are presented in table 3. Good agreement between the actual and predicted values of reduction of COD shows the suitability of model to predict the results, Fig. 2 [4]. The effect of time and pH on COD removal is presented in Fig. 3 based on the model. It can be seen that pH is a very effective factor on COD removal. COD reduction will increase with decrease in pH.

Optimum conditions were obtained from the model are 275 mg of nano photocatalyst at pH = 5 with 14.5 W of UV irradiation at 98 min which remove 75.16% of COD. An experiment was done at conditions near optimal values using 275 mg of nano photocatalyst at pH=5 with 18 W UV irradiation at 98 min. 78.62% reduction in COD was obtained which has 1.04% error from the result of model.

No.	pH	Photocatalyst (ppm)	Time (min)	Power (W)
1	7	100	60	18
2	7	200	30	18
3	5	100	60	12
4	7	300	60	6
5	9	200	60	6
6	7	200	60	12
7	7	300	60	18
8	5	200	60	6
9	7	300	30	12
10	7	200	120	6
11	9	300	60	12
12	9	200	30	12
13	9	100	60	12
14	7	200	60	12
15	9	200	120	12
16	7	100	120	12
17	7	100	30	12
18	9	200	60	18
19	7	200	60	12
20	5	200	30	12
21	7	300	120	12
22	5	200	120	12

23	5	200	60	18
24	7	200	30	6
25	7	100	60	6
26	7	200	120	18
27	5	300	60	12

Table 2: Design of experiments

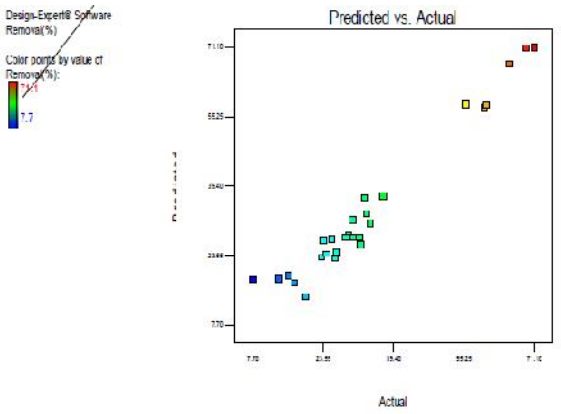

Fig. 2: Actual verses predicted of percent of COD reduction

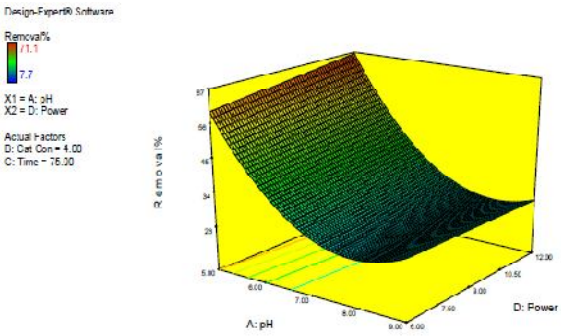

Fig. 3: Effect of time and pH on COD removal

No.	1	2	3	4	5	6	7	8	9
Actual	24.3	23.2	55.7	30.2	31.9	28.6	32.8	60.2	23.5
Predict	23.86	23.11	57.89	31.75	26.14	27.88	36.77	57.68	27.05
No.	10	11	12	13	14	15	16	17	18
Actual	29.3	34.1	17.1	7.7	31.7	25.5	26.5	19.6	26.2
Predict	28.17	30.92	17.26	18.02	28.8	27.34	24.23	14.15	22.83
No.	19	20	21	22	23	24	25	26	27
Actual	30.3	59.9	37.1	65.5	71.1	13.5	15.8	33.4	69.3
Predict	27.81	57.13	37.13	67.21	70.99	18.09	18.85	33.19	70.79

Table 3: Actual and predicted of COD reduction

V. CONCLUSION

$Fe_3O_4/SiO_2/TiO_2$ nanoparticles were prepared by sol-gel method. Response surface methodology with Box-Behnken approach was used to determine the optimum conditions to achieve highest efficiency in removal of COD from wastewater of fruit juice industry. Optimal conditions obtained were 275 mg of nano photocatalyst at pH = 5 with 14.5 W of UV irradiation at 98 min which remove 75.16% of COD. Higher percent of COD removal can be achieved using more dosage of nano photocatalyst or applied higher power of UV irradiation.

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