Discoloration of Soy Sauce Using Photo-Fenton Process Utilizing Rust and Nano TiO_2

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Abstract:- The availability of Wastewater treatment for soy sauce is confine to several treatments such as nano filtration, adsorption and advance oxidation process. This work utilize the photo-fenton process, one method in advance oxidation process that utilize the radicals for pollutant degradation in treating the stubborn color from soy sauce. The results reveals a color removal efficiency of 100 percent for 1000 ppm and 6000 ppm for 6 hours sun's exposure and 80 % removal for 10000 ppm sample concentration. The amount of rust-TiO_2 catalyst is 2 g reacted with a 20 % H_2O_2 solutions. TiO_2 use is in nanoparticles form while rust was obtained from an oxidized metal.

Keywords: *Nano particles, advance oxidation process, Photo-Fenton Process, radical species.*

1. Introduction

Soy Sauce is consider as one of the most important condiments being used worldwide like in China, Japan, Thailand and Korea.It contains a lot of Biological and Chemical Oxygen Demand as well as color due to one of its ingredients called caramel pigments. This waste come from the production line via the, materials used and via washing of equipment as well. In China alone, 8 tons of soy sauce produce an annual of 6 -9 m^3 of soy sauce wastewater (Wang et. al, 2021). To be able to address this issues,different water treatment methods were employed such as nitrification ,biological treatment , nano filtration and advance oxidation process to treat soy sauce from wastewater discharge(Jang et al., 2018)).Advance oxidation process uses metallic oxide catalyst like TiO_2, CuO, ZnO and FeO. This catalyst helps in the production of radicals such as ·OH and ·O that degrades or attack the contaminants and converted it into CO_2 (Haeyong, 2024) Different types of Advance Oxidation Process are currently being use in many studies. This includes chemical electrochemical, sonochemical and photochemical (Kumari&Kumar, 2023). Under the photochemical process, the most common is the photo fenton process that is typically given by the following reactions:

$Fe^{3+} + H_2O_2 + hv \rightarrow OH^- + OH^·$ (1)

$OH· + \text{soy sauce} \rightarrow \text{Oxidize soy sauce} + H_2O$ (2)

Competing reactions is shown as follows:

$OH· + Fe^{2+} \rightarrow Fe^{3+} + OH·$ (3)

$OH· + H_2O_2 + HO·$ (4) (Wakrim, et al., 2018)

Since photo fenton proess involves ions of Fe in the form of $Fe^{3+}$and Fe^{2+}, this study decided then to tap the compound that is a by product of oxidation of metals due to reaction with air and water known as rust. It contains same ions that is being use in the fenton process and thus can act as an alternative sustainable solution to the commercial.

Fe_2SO_4 commonly used in the photo-fenton process. The use of rust which contains ions of Fe is very much advantageous in terms of cost of production and operation since FeO or rust maintains a narrow band gap (Pylarinou et.al, 2021) that makes it suitable to harvest visible light coming from the sun instead of pure UV rays which is quite expensive to operate.

To enhance the speed and efficiency of oxidation process, a support system was utilized in this studies. This support system is TiO_2 which provides additional production of radicals (Bullo et al,.2021) and it works synergistically with FeO through doping effect in which the metal oxides provides a confinement for electrons in order to prevent the recombination of electron-hole pair which will reduce the efficiency of dye degradation (Anucha,2022). TiO_2 has a high band gap which make it suitable only under UV-region. (Amarasinge et al., 2019). to facilitates it photocatalytic effect on the pollutant. Since sum contains some UV rays, TiO_2 in nano form will partially contribute to the degradation of soy sauce.

The reaction that involved radical production from TiO_2 are shown as follows:

$$TiO_2 \xrightarrow{hv} TiO_2\ (e_{CB}^- + h_{VB}^+)$$

h_{VB}^+ = is an electron hole where radical are form and oxidation occur

e_{CB}^-= electrons ejected fro surface ot TiO_2

hv = UV rays

$h_{VB}^+ + H_2O \rightarrow HO\cdot + H^+$

$h_{VB}^+ + OH^- \rightarrow HO\cdot$

HO· = radicals responsible for soy sauce discoloration (Fernandes et al.,2020)

Currently there is a little studies being conducted on the use of Rust with TiO_2 and the utilization of ultrasonicator to modify the physical and chemical structures of the solid catalyst. To address this gap, the researcher decided to implement this innovative process in removing color from soy sauce

2. Method

Materials

The stock of Nano TiO_2 powder was obtained from Dalkem supplier under Titanium Dioxide Anatase. Rust under the chemical name of hydrated iron oxide was obtained from rusted metals. It was washed with D.I. water, dry in an oven at 110^0 C for 1 hour and kept in a clean container. Soy sauce was bought from a supermarket under the tradename Silver Swan.H_2O_2 used is supplied by Daikem trading with a 35% solution by volume.Methylene blue that served as a standard was purchased from an online store under the tradename methylene blue.

Equipment used are Photocolorimeter (vis range 340 nm-1100 nm) equip with a filter of blue, yellow and red. Digital balance with a precision of 0.01g, mini open furnace, porcelain crucible and ultra sonicator.

Photocatalyst Preparation

10 g of TiO_2 was mixed with 1 g of rust. The mixture were turn into slurry by addition of 20 mL of H_2O_2. It was then subjected to sonication for 1 hour for surface modification via deagglomeration and to maintain homogeneity of the structures. It was then subjected to a temperature of 110^0C to vaporize all the liquid for 1 hour. The final treatment is calcination under 500^0 C for 10 hours in an open furnace to infuse the rust in the TiO_2.

Sample Preparations

In a two 250 mL beaker and 500 mL Erlenmeyer flask, 3 types of concentration of soy sauce were prepared. Soy sauce was added to each container followed by the dilution of hydrogen peroxide until each container reached the target concentration of 1000 ppm, 6000 ppm and 10, 000 ppm soy sauce concentration. While a standard solution of methylene blue was prepared with a concentration of 100 ppm. Each initial concentration was determined using photo colorimeter using the following equation:

$$C_x = \frac{A_x}{A_s} C_s$$

Where: C_x = concentration of sample

C_s = Standard concentration

A_x = Absorbance of sample

A_s = Absorbance of standard

The absorbance was determined base on the reading given by the photocolorimeter.

Batch Sample Test

In each container, a 100 mL of sample was added. Then each was added with 2 grams of catalyst and mixed for 5 minutes using manual stirring. The open containers were exposed to sunlight from 12 pm to 3 pm for two consecutive days Each sample was filtered after treatment and then subjected to absorbance determination using photocolorimeter to calculate the final concentration.

3. Results and Discussion

Results

The table below shows the results of the photo-fenton process for the three samples after 2 days (6 hours) treatment

Table 1. Initial and Final Concentrations data

C_i	1000 ppm	6000 ppm	10000 ppm
C_f(3h)	600 ppm	4000 ppm	7000 ppm
C_f(6h)	0 ppm	0 ppm	2000 ppm

The percent removal is computed as follows:

$$\% \text{ removal} = \frac{C_i - C_f}{C_i} x\ 100$$

Table 2. Percentage Removal

Day	1000 ppm	6000ppm	10000ppm
1 (3h)	40 %	33 %	30 %
2 (6h)	100 %	100 %	80 %

Statistical analysis using anova shows that there is a significant difference in the percentage removal among the three different concentrations from table 2. A result of 31.37 for F using manual calculation and compared it to 5.39 from a table of F for anova shows that computed values is greater than the table for F which confirms the rejection of Null Hypothesis stating that there is no significant difference among the values for percentage removal for 2 days treatment period.

Table 1 and table 2 shows that among the three, the highest percentage removal is 1000 ppm, the lowest among the three initial concentration for 1 day or equivalent to 3 hours sun exposure from 12 pm to 3 pm. This was followed by 6000 ppm and 10 000 ppm with a percentage removal of 40%, 33 % and 30 % respectively. The difference in the data lies on the concentration of hydrogen peroxide in which optimal concentration must be maintain to achieve high removal efficiency (Raja et.al, 2022).

The second day of treatment showed a 100 % removal of color for 1000 ppm and 6000 ppm initial concentration after 3 hours period, but in the case of 10000 ppm, 80% removal was only achieved due to very high initial concentration that affect the optimum Fe ions and hydroxyl radicals in the solution (Munter, 2001).

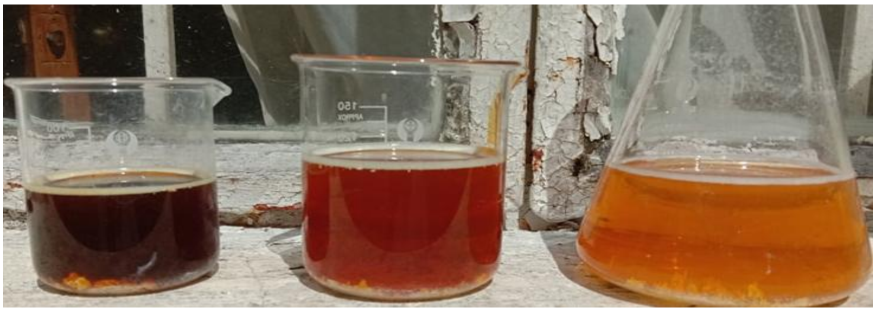

Figure 5. Initial Concentrations

Figure 6. Treatment for 3 hours

Figure 7. Treatment for 6 hours

The figures above showed the actual photos of the soy sauce before and after treatment. The cloudy white formation is due to the catalyst that was mixed with the treated water. Further nano filtration must be conducted to clear the solution from additional impurities.

4. Conclusion

The effectiveness of Photo-Fenton process in decolorizing soy sauce is evident in the results of this study. The amount of 11 g of photocatalyst in the form of FeO and nano TiO_2 produced a 100 % color removal of soy sauce for 1000 ppm and 6000 ppm after 3 hours treatment for 2 consecutive days from 12 pm to 3 pm sun's exposure. An 80 % removal was observed on the other hand for 10000 ppm initial concentration due to optimization issue on the amount of hydrogen peroxide use as well as to the amount of catalyst use. Statistical analysis revealed that there is a significant difference on the percent removal for the three prepared sample concentrations which strongly suggest that Fenton process with nano-TiO_2 degrade soy sauce color under visible light region,

5. Thank -You Note

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