www.directivepublications.org

Journal of
Environmental And Sciences

ISSN 2836-2551

DIRECTIVE PUBLICATIONS

Research Article

Modification Of Mineral Vermiculite With Fe (II) To Remove Sunset Yellow Food Coloring From Water By Absorption And Oxidation Method: Optimization, Mechanism, Degradation Intermediates And Toxicity.

Esmail Mohseni[1], Habib Abbasi[2,3]*, Zeinab Habibi[3].

[1] *Food Chemistry Lab, Ewaz School of Health, Larestan University of Medical Sciences, Larestan, Iran.* ***Email:*** *mohseniesmail210@gmail.com*

[2*] *Department of Chemical Engineering, Jundi-Shapur University of Technology, Dezful, Iran.*

[3*] *Department of Nutrition Sciences, Ewaz School of Health, Larestan University of Medical Sciences, Larestan, Iran.*

Abstract

This study investigates the degradation and removal of Sunset Yellow from simulated wastewater using oxidation and adsorption methods. A composite of vermiculite/iron oxide was synthesized via the co-precipitation method and utilized to activate peroxymonosulfate (PMO) for the degradation and removal of Sunset Yellow. The response surface method (RSM), based on the central composite design (CCD), was employed to optimize the effects of independent factors and their interactions on Sunset Yellow color removal. The maximum removal efficiency, exceeding 78.69%, was achieved at a pH of 4, Sunset Yellow concentration of 30 mg/L, persulfate oxidant dose of 75 mM, vermiculite/iron oxide composite dose of 3 g/L, and a reaction time of 20 minutes. The removal process of Sunset Yellow was enhanced with increasing temperature. The presence of chloride, nitrate, and carbonate reduced the degradation efficiency of Sunset Yellow by reacting with the main radicals. The proposed PMO activation mechanism indicated that SO4•- plays a pivotal role in the degradation removal. Toxicity tests conducted with Daphnia pulex revealed that the treated effluent necessitated further catalytic treatment and improved stabilization due to the presence of Fe ions and intermediates.

Keywords : Sunset Yellow, Vermiculite/iron oxide, Byproducts, Toxicity, Peroxymonosulfate, Oxidation, Adsorption.

INTRODUCTION

Numerous industrial processes employ various chemical dyes for diverse applications (Dezhampanah, Mousazadeh and Mousazadeh 2014). Wastewater originating from food factories is a significant source of environmental pollution. The impact on flowing water and the unpleasant odor emitted by this wastewater serves as examples of the problems (Khazri, Ghorbel-Abid et al. 2017). The majority of dyes employed in these industries are synthetic, and due to their toxicity and slow decomposition, they have the potential to cause irreparable damage to the environment if released without proper treatment (Kong, Liu et al. 2017). Among the highly useful dyes, sunset yellow dye is utilized as an additive in pharmaceutical tablets and capsules, as well as in confectionery items, beverages and various other segments of the food industry (Sharma and Kaur 2011). Sunset Yellow is a hydroxyl mono-azo disulfone dye with conjugated aromatic rings and an azo functional group. azo dyes could cause mild to severe side effects, such as persistent headaches, hyperactivity in children, asthma, allergic reactions, urticarial, liver and kidney disorders, cancer, and interference with human serum albumin and hemoglobin (Moghadasi, et al. 2019). Its maximum allowed level in alcoholic and non-alcoholic beverages is 200 and 50 mg L−1, respectively (Shokri, et al. 2024). Because of its carcinogenic and mutagenic properties, sunset yellow may elevate the risk of cancer and various other diseases (Mitter and Corso 2012). Consequently, it is essential to treat such waste using appropriate methods before its discharge into

***Corresponding Author:** Habib Abbasi , Department of Nutrition Sciences, Ewaz School of Health, Larestan University of Medical Sciences, Larestan, Iran, **Postal code:** 64616-18674, **Email:** habbasi@larums.ac.ir, habbasi@jsu.ac.ir ; **ORCID ID:** https://orcid.org/0000-0001-7722-6794.
Received: 25-Jan-2025, Manuscript No. JOES - 4474 ; **Editor Assigned:** 29-Jan-2025 ; **Reviewed:** 27-Feb-2025, QC No. JOES - 4474 ; **Published:** 3-March-2025, **DOI:** 10.52338/Joes.2025.4474
Citation: Habib Abbasi. Modification of mineral vermiculite with Fe (II) to remove sunset yellow food coloring from water by absorption and oxidation method: Optimization, mechanism, degradation intermediates and toxicity. Journal of Environmental And Sciences. 2025 January; 9(1). doi: 10.52338/Joes.2025.4474.

the environment. Various methods have been employed to date for the removal of color from wastewater including physical methods (precipitation, membrane processes), chemical methods (coagulation, advanced oxidation, chlorine, hydrogen peroxide, photocatalyst) and biological purification (aerobic purification, anaerobic purification, combination of aerobic and anaerobic purification methods (El-Ashtoukhy and Amin 2010, Gupta, Gupta et al. 2011, Tayyab et al. 2023). In Ho et al. reported the removal of basic dye from aqueous solution using tree fern as a biosorbent (Zhang, Zhou and Ou 2012). Zhang et al. studied the adsorption of methyl orange by chitosan/alumina interface. They found that as the concentration of methyl orange increased from 20 mg/L to 400 mg/L, the percentage of dye removal, which was initially 99.53%, decreased to 83.55% (Ho, Chiang and Hsueh 2005). Some of these methods only transfer pollutants from one state to another and do not perform any analysis on it and increase the pollutant load in the environment. Therefore, it is crucial to select a method that is environmentally optimal, does not generate additional pollution, and is cost-effective. Advanced oxidation processes have received a lot of attention in the research and treatment of wastewater in recent years (Bagal and Gogate 2013). In these methods, the objective is to produce radicals with high oxidizing ability such as OH, O, and SO4 in order to remove compounds that resistant to biological degradation (Fernández, Suárez-Ojeda et al. 2013). Persulfate radicals are able to oxidize toxic and resistant organic compounds. At room temperature, persulfate exhibits limited capability to decompose organic substances. In fact, the rate of decomposition remains low under such conditions. Therefore, to expedite the oxidation process with persulfate, an activation procedure is required (Liu, Yu et al. 2011). Activation of persulfate is done by different methods such as heat, Me2+ intermediate metals and UV light (Tan, Gao et al. 2015). Among divalent iron transition metals, Fe2+ is the most used for sulfate activation (Zhang, Chen et al. 2015). During the activation process, the O-O bonds within the persulfate structure are broken, resulting in the production of sulfate radicals with an oxidizing power equal to E=2.67 (Ghauch, Tuqan and Kibbi 2015). Another pollutant removal process is the absorption process (Ansari, Seyghali et al. 2012). In most cases, due to the weak van der Waals bond between the adsorbent and the adsorbed, the adsorption process is reversible. The phenomenon of absorption is of interest due to its low cost, design flexibility, and the absence of harmful substance production after the removal of the desired compounds for color removal (Sadaf and Bhatti 2014). Various adsorbents have been used to remove colors, with the most common ones being zeolite, alumina, activated carbon, and silica gel (Walker and Weatherley 2000). In 2013, Desha et al. reported the effect of pH on the removal of sunset yellow dye using zeolite adsorbent modified with calcium and aluminum metal. The results demonstrated the highest removal of sunset yellow color occurred at pH 10, achieving an 88% removal rate (de Sá, Cunha and Nunes 2013). Natural absorbents have gained widespread attention due to their availability and cost-effectiveness in preparation (Ramakrishna and Viraraghavan 1996). Vermiculite is a natural 2:1 layered clay mineral that is relatively cheap and easily available (Mathialagan and Viraraghavan 2003). Vermiculite possesses permanent negative charge, a large surface area, deep reactive surface sites, and a high capacity for cation absorption and exchange (Liu, Xiao and Li 2007). Such unique properties enable vermiculite to be a promising adsorbent for the absorption of pollutants (Liu, Xiao and Guo 2006). In 2014, Yu et al investigated vermiculite modified with divalent iron to remove chromium pollutant, and the percentage of chromium pollutant removal was reported as 99% (Liu, Li et al. 2010). In 2020, Şenol et al. investigated the removal of food colors from an aqueous solution with chitosan-vermiculite beads, and the removal efficiency was reported to be 93% (Şenol, Gürsoy et al. 2020).

The current research is conducted in light of the growing concern over water source contamination by food colorings and the imperative need to eliminate these substances from water sources. It also anticipates the high efficiency of the oxidation and absorption system in eliminating these pollutants. In this method, mineral vermiculite, persulfate salt, and iron salt are used as raw materials for preparing the oxidation and absorption system. Design-Expert software was employed to determine the optimal conditions, considering the impact of various parameters, including pH, catalyst dosage, Potassium peroxymonosulfate (PMO) dosage, and the duration of contact between the absorbent and the sample. To suggest the mechanism of sunset yellow removal by oxidation and adsorption method, GC-MS analysis was performed on the treated solution. The toxicity of treated samples was determined by Daphnia pulex.

XPERIMENTAL

Chemicals and reagents

Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$, 97%), sodium hydroxide (NaOH, ≥98%), hydrochloric acid (HCl, 36%), Potassium peroxymonosulfate ($KHSO_5.0.5KHSO_4.0.5K_2SO_4$) were purchased from Sigma–Aldrich company, Spain. The intended vermiculite was provided by Australian mines (The Mud Tank Vermiculite Mine, located 150 km northeast of Alice Springs). All other chemicals were of analytical grade, commercially available and used without further purification.

Preparation of vermiculite particles

The raw vermiculite is initially sieved through a 60-mesh sieve. Afterward, to eliminate contaminants, the vermiculite particles undergo multiple washes with hydrochloric acid. Subsequently, the vermiculite particles are rinsed with distilled water to remove any remaining acid and neutralize the pH. Finally, the particles are dried at 90°C for a duration of 6 hours.

Preparation of vermiculite- iron oxide particles

First, in the reaction cell, dissolve 15 gr of iron (III) chloride in 50 ml of water, then add 7 gr of prepared vermiculite particles to the solution, and put the reaction container under reflux for 18 hours. The dried solid was separated by centrifugal apparatus and washed twice with distilled water to remove excess chemicals. Subsequently, it was dried at 90°C for a duration of 6 hours and screened through a 60-micron mesh sieve.

Adsorption experiments

This is an experimental study for investigating the capacity of vermiculite/iron oxide composite to remove sunset yellow dye from solution. A certain amount of vermiculite/iron oxide composite (30–150 mg) was added to the solution containing sunset yellow dye with a certain concentration (50 mg/L). To completes the absorption and oxidation process for the color target, the solution was stirred at certain times on the stirrer with constant speed of 200 rpm. The pH of the solution was adjusted with 0.1 M HCl and NaOH at a given pH. After the completion of the removal process at specified intervals (ranging from 10 to 60 minutes), a 10 ml sample was extracted for analysis via High-Performance Liquid Chromatography (HPLC) to determine the adsorption capacity of the adsorbents for sunset yellow dye.

Characterization

The concentration of Sunset Yellow color in the samples was measured using a high performance chromatography (HPLC, Alliance e2695 Model), the C18 column (250 × 4.6 mm, 5 m) with the mobile phase of Acetonitrile-C_2H_5O (40:60, v/v). The flow rate was 1 mL/min and the detection wavelength were 323 and 230. Energy-dispersive X-ray spectroscopy (EDX) test will be used to confirm the fixation of iron particles on the vermiculite adsorbent. Field-scattering scanning electron microscopy (FE-SEM, Mira 3) was used to analyze the morphology of the adsorbent structure. MAP analysis was used to distribute the abundance of iron on the adsorbent. The structure adsorbents were investigated by recording XRD patterns with a SIEMENS D5000 X-Ray Diffractometer using Cu-Kα radiation (λ = 1.54059 Å) over the range of $10° < 2\theta < 90°$. Differential scanning calorimetry (DSC) model METTLER FP90 has been used to study the properties of compounds. At the end, GC-Mass analysis will be used to calculate the removal percentage and identify side products. The GC column was operated in a temperature program as follows: the initial temperature was maintained at 80°C for 4 min, then the temperature was raised to 300°C with a ramp of 15°C/min, and finally, the temperature was maintained for 5 min. The sample was analyzed in full scan mode in the range of 50-1000 m/z, and the peaks were interpreted by NIST and Wiley library.

Experiment design

Response surface method based on central composite design (CCD) was used to investigate the effect of independent factors and their interaction on sunset yellow color removal. Four factors in 5 levels were selected to evaluate the effect of operating parameters including pH, reaction time, potassium peroxymonosulfate dosage (PMO) and catalyst dosage (**Table. 1**). The experiments were conducted randomly, employing a Central Composite Design (CCD) with 8 replications at the central point. The experimental data were analyzed using a second-order multiple regression technique, as illustrated in the equation below.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_{ii}^2 \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j + e_i \qquad (1)$$

where Y is the response variable, β0 is a constant, βi is the linear coefficient, βii is the second order coefficient, βij is the interaction coefficient, Xi and Xj represent the coded independent variable, K is the number of parameters and ei is an error.

Table 1. The ranges and levels of the independent variables.

Variables	Symbol	-2	-1	0	+1	+2
Catalyst dosage (mg/L)	A	0	1	2	3	4
PMO dosage (mM)	B	0	25	50	75	100
reaction time (min)	C	5	10	15	20	25
pH	D	2	4	6	8	10

Toxicity test

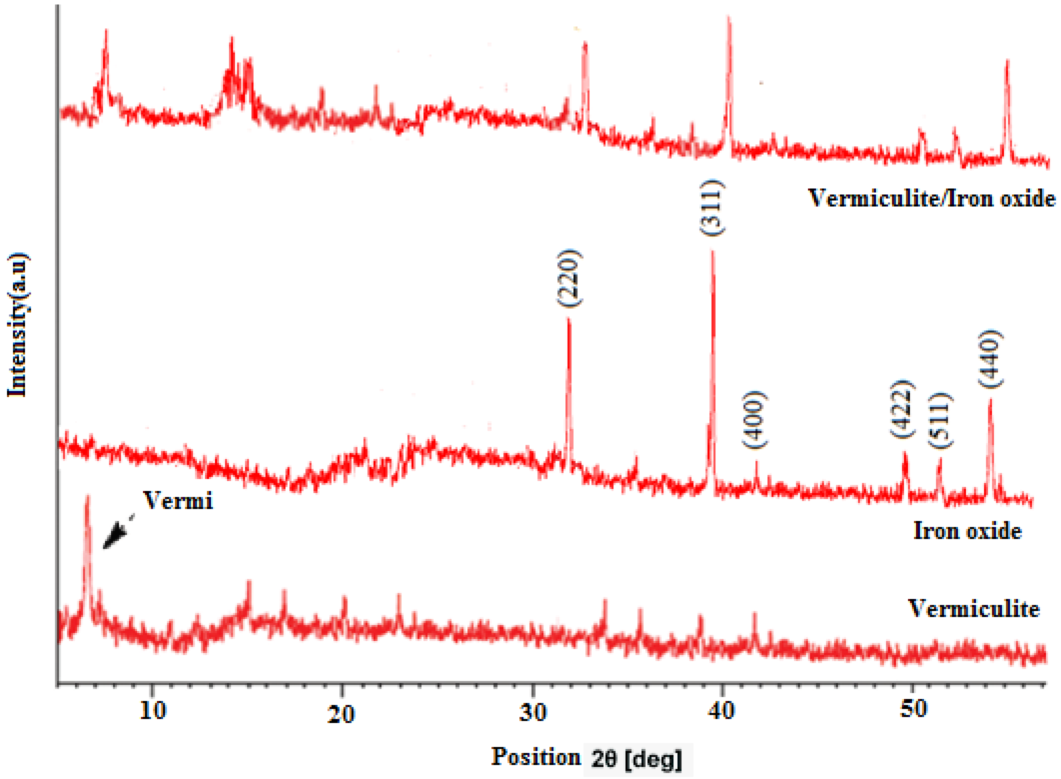
Daphnia pulex living organism was used to perform the toxicity test. First, a living organism is thrown into water and fed with yeast to reproduce. This process is repeated 3 times. Then we directly expose 18 living organisms to the process. Separately, we fed the organisms with deionized water (DI), sunset yellow, PMO, Ver/Fe and Ver/Fe@PMO. And finally, the number of active organisms was counted during 2, 4, 8 and 24 hours

RESULTS AND DISCUSSION

X-ray diffraction analysis (XRD)

Crystal structure of Vermiculite/iron oxide investigated by X-ray powder diffraction (XRD) pattern (**Fig.1**). The diffraction pattern shows the peak at an angle of 6.9 that corresponds to the vermiculite (JCPDS card 16–0613). A series of peaks is observed in the XRD pattern of vermiculite, which is related to the cations that exist in the layered structure of vermiculite (d = 12.1 Å). **Figure 1** also shows the XRD pattern of iron oxide, which matches the standard pattern (JCPDS file no: 65-3107). X-ray diffraction analysis for iron oxide display peaks at 2q = 31, 38.5, 42.3, 50.1, 52.8 and 56.9 that can be indexed to the (220), (311), (400), (422), (511) and (440). After the synthesis of the vermiculite/iron oxide composite, the results demonstrate that iron oxide particles were effectively incorporated onto the surface of the vermiculite mineral.

Figure 1. X ray diffraction patterns of Vermiculite, Iron oxide and Vermiculite/Iron oxide.



FE-SEM images

FE-SEM was used to investigate the surface morphology of vermiculites and vermiculites/iron oxide composite (**Figure 2**). According to the layered structure of vermiculites, which are formed due to strong ionic bonds, the FE-SEM images show the plate structure that is stuck together. It is clear that the size of Vermiculite/iron oxide particles is in the range of 23-35 nm. The adhesion between the layers of vermiculite can be diminished by the presence of surface-active substances. According to the FE-SEM image of iron oxide, it has indeed reduced the adhesion between layers. Additionally, the micrographs reveal that the structure possesses large pores and channels, thereby increasing its absorption capacity.

EDAX analysis was used to check the elemental composition and percentage of elements in the synthesized composite and to confirm the presence of iron oxide particles in the composite structure (**Fig.3**). A comparison of the EDAX images indicates that the content of elements such as Al and Si does not exhibit significant differences in the composite, whereas the iron content in the composite is five times higher compared to pure vermiculite.

Figure 2. SEM images of Vermiculite (A) and Vemiculite-Iron oxide (B).

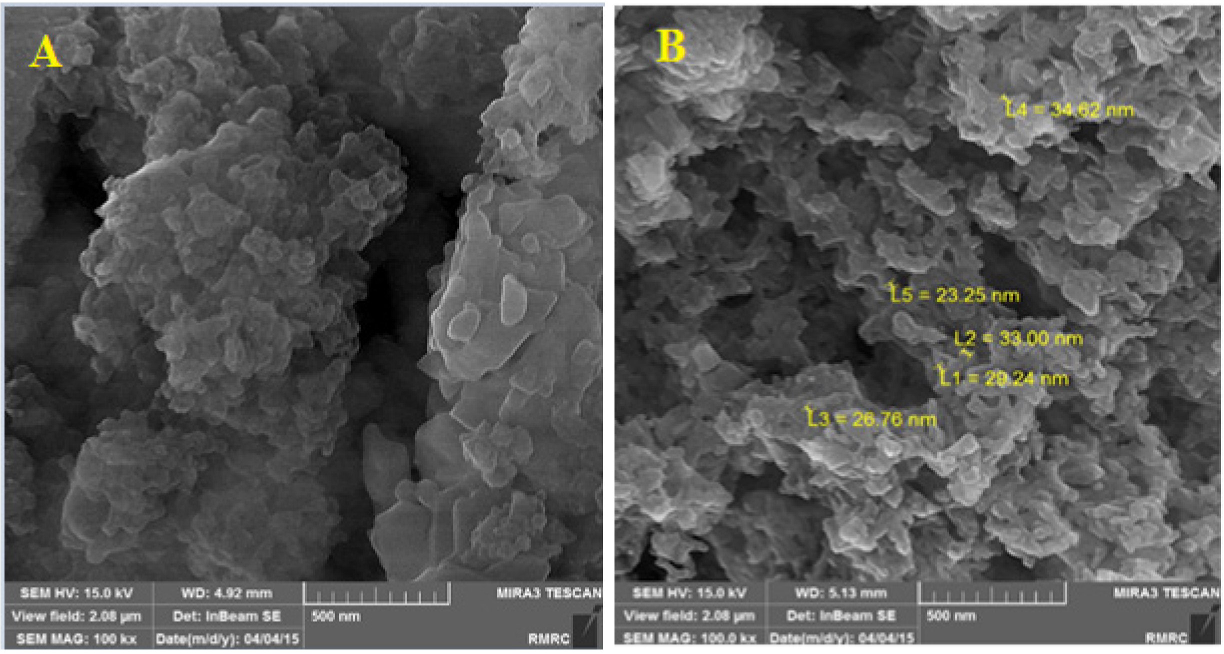
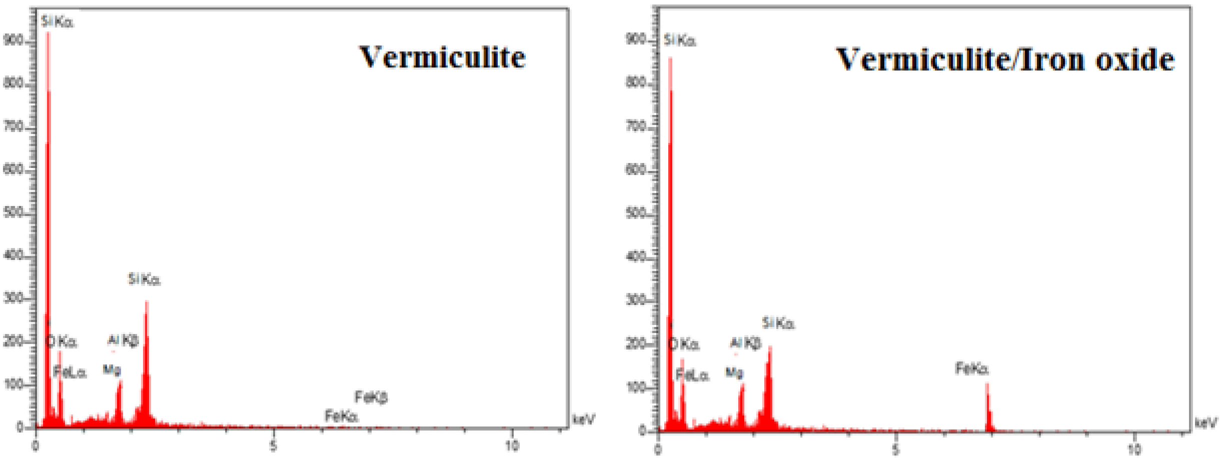


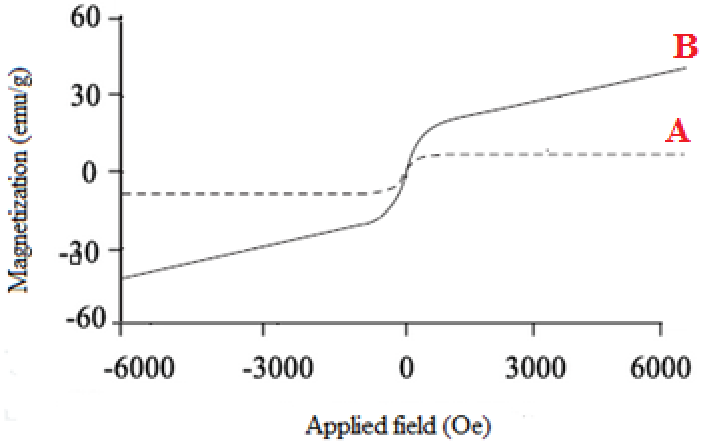
Figure 3. EDX analysis of Vemiculite and Vermiculite/Iron oxide.



VSM analysis

Magnetic properties of vermiculite and vermiculite/iron oxide composite were investigated by vibrating-sample magnetometer (VSM) analysis (**Fig.4**). Result shows a magnetic saturation (Ms) 42 emu g^{-1} and emu g^{-1} for vermiculite and vermiculite/iron oxide, respectively. Vermiculite has a low negative magnetic dipole interaction, while the vermiculite/iron oxide composite has a strong interaction, and this indicates that the magnetic moment is the main factor of particle interaction in the composite. At magnetic fields close to zero, both pure vermiculite and vermiculite/iron oxide exhibit nearly zero magnetization. These results, as depicted in the graph, indicate that iron oxide is well-incorporated into vermiculite and can be readily separated due to its paramagnetic properties.

Figure 4. VSM analysis of Vemiculite (A) and Vermiculite/Iron oxide (B).



Removal mechanism

The removal of sunset yellow color through the use of vermiculite/iron oxide composite involves two mechanisms: absorption and oxidation. Vermiculite possesses a structure comprising both trihedral and tetrahedral layers, where silicate sheets are interconnected by metals such as aluminum and magnesium.Vermiculite can create a bond between the M^+ present in Vermiculite minerals and the aromatic + Fe ring of sunset yellow color by using the π complexation (back donation effects).Also, Heteroatoms such as oxygen, nitrogen and sulfur located on the sunset yellow structure can act as Lewis bases and donate electrons to vermiculite metals (Lewis acid). In addition to the absorption process, the oxidation process with the production of .OH and SO.4 radicals also play a significant role in removing the sunset yellow color. In this process, the bond between the Fe^{3+} and metals is in the form of M-O-Fe. In this case, the 3 electrons in the d orbital of Fe^{3+} interact with the oxygen electrons, as well as the repulsion between the electrons of the vermiculite metals and Oxygen, transfers electrons to trivalent iron, all of process causes the synthesis of Fe^{2+} (eq. 1 and 2). Fe^{2+}in the vicinity of persulfate (radical production source) according to the following equations causes the production of .OH, SO.4 and O.2 radicals (eq. 3-7).

$$\mathrm{V(III) + Fe(III) \rightarrow V(IV) + Fe(II)} \tag{1}$$

$$\mathrm{V(IV) + Fe(III) \rightarrow V(V) + Fe(II)} \tag{2}$$

$$\mathrm{Fe(II)+S_2O_8{}^{2-} \rightarrow Fe(III) + SO_4{}^{\cdot -} + SO_4{}^{2-}} \tag{3}$$

$$\mathrm{SO_4{}^{\cdot -} + H_2\,O \rightarrow OH^{\bullet} + H^+ + SO_4{}^{2-}} \tag{4}$$

$$\mathrm{SO_4{}^{\cdot -} + OH^- \rightarrow OH^{\cdot} + SO_4{}^{2-}} \tag{5}$$

$$\mathrm{S_2O_8{}^{2-} + 2H_2O \rightarrow 2SO_4{}^{2-} + H_2\,O_2 + 2H^+} \tag{6}$$

$$\mathrm{S_2O_8{}^{2-} + HO_2{}^- \rightarrow O_2{}^{\cdot} + SO_4{}^{\cdot -} + SO_4{}^{2-} + H^+} \tag{7}$$

Response surface methodology

Statistical analysis

In this research, 30 experiments were conducted to check the amount of sunset yellow color removal with different levels of variables. Design Expert software and RSM-CCD method were used to analyze the results of sunset yellow color removal. According to the obtained results, the quadratic model with lower p-value (< 0.0001) and higher correlation coefficient (R2= 0.9178) shows the best description for the relationship between variables and responses (**Table.2**). These results show that the quadratic model with a high value, more than 90% of which can explain the variation in sunset yellow color removal with independent variables, and less than 10% cannot be explained by this model. Also, equation 8 shows the prediction of responses at certain levels, where the positive coefficient shows the positive effect of the variable on the removal of sunset yellow color, and the negative coefficient shows the negative effect of the variable on the removal.

$$\text{Sunset yellow removal} = 39.30 + 2.08\,A + 9.22\,B + 7.68\,C - 8.68\,D + 0.4250\,AB - 9.97AC + 1.75\,AD + 0.8125\,BC - 3.09\,BD + 5.91\,CD + 9.86\,A^2 + 1.68\,B^2\ 7.06\,C^2 + 8.80\,D^2$$

Table 2. Sequential model sum of squares.

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.0190	<0.0001	0.2635	0.1047	
2FI	0.4112	<0.0001	0.2766	-0.1556	
Quadratic	0.0008	<0.0001	0.8050	0.7824	Suggested
Cubic	0.1588	<0.0001	0.8318	-4.7916	

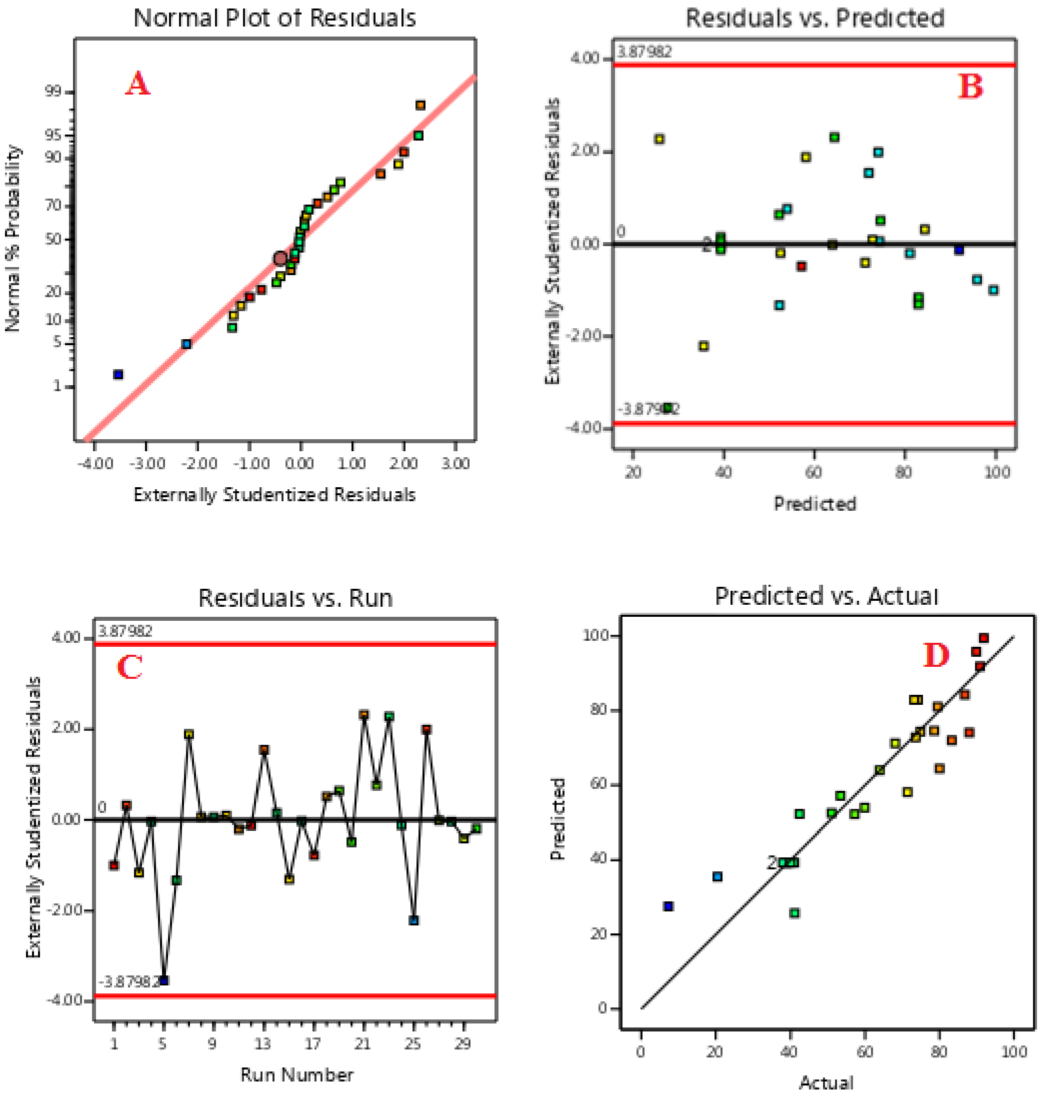
Based on the results, the high F-value and the low p-value (<0.0001), along with a low coefficient of variation (%C.V=8.28), indicate the suitability of the model and the high precision and reliability of the tests Furthermore, the lack of significance in the p-value indicates that the selected model effectively predicts the outcomes of the absorption and oxidation process in removing the Sunset yellow pollutant.The adequate precision ratio for the removal of sunset yellow color in the vermiculite/iron oxide process was obtained 38.83, which, due to being larger than 4, indicates a suitable signal for the quadratic model and the use of the model in the design space. The results derived from the analysis of the factors and their interactions reveal that the impact of the independent factors on sunset yellow color removal was more significant than the interactions between the variables themselves. Notably, among these variables, the quantities of oxidant and catalyst exerted the most substantial influence.

Table 3. ANOVA of the quadratic model for removal of sunset yellow.

SOURSE	SUM OF SQUARES	DF	MEAN SEQURE	F-VALUE	P-VALUE
MODEL	1608.89	18	200.64	316.46	< 0.0001
A-CAT	104.17	1	104.17	0.7474	< 0.0001
B-PMO	238.73	1	238.73	514.63	< 0.0001
C-TIME	113.73	1	113.73	310.14	0.0062
D-PH	109.61	1	109.61	212.98	0.0026
AB	2.89	1	2.89	0.0207	< 0.0001
AC	12.01	1	12.01	11.42	< 0.0001
AD	49	1	49	18.3516	0.05621
BC	10.56	1	10.56	9.0758	0.07869
BD	15.52	1	15.52	11.09	0.03121
CD	59.32	1	59.32	86.01	0.0636
A^2	269.07	1	269.07	219.15	< 0.0001
B^2	77.15	1	77.15	49.5535	< 0.0001
C^2	168.91	1	168.91	109.82	0.0068
D^2	225.07	1	225.07	115.25	< 0.0001
RESIDUAL	1090.71	27	39.38		
LACK OF FIT	1005.23	21	48.52	2.26	< 0.0001
PURE ERROR	105.48	6	19.1		
C.V%	8.28				
R2	0.9178				
R2ADJ	0.8050				
R2 PRED	0.7824				
ADEQ PRECISION	38.83				

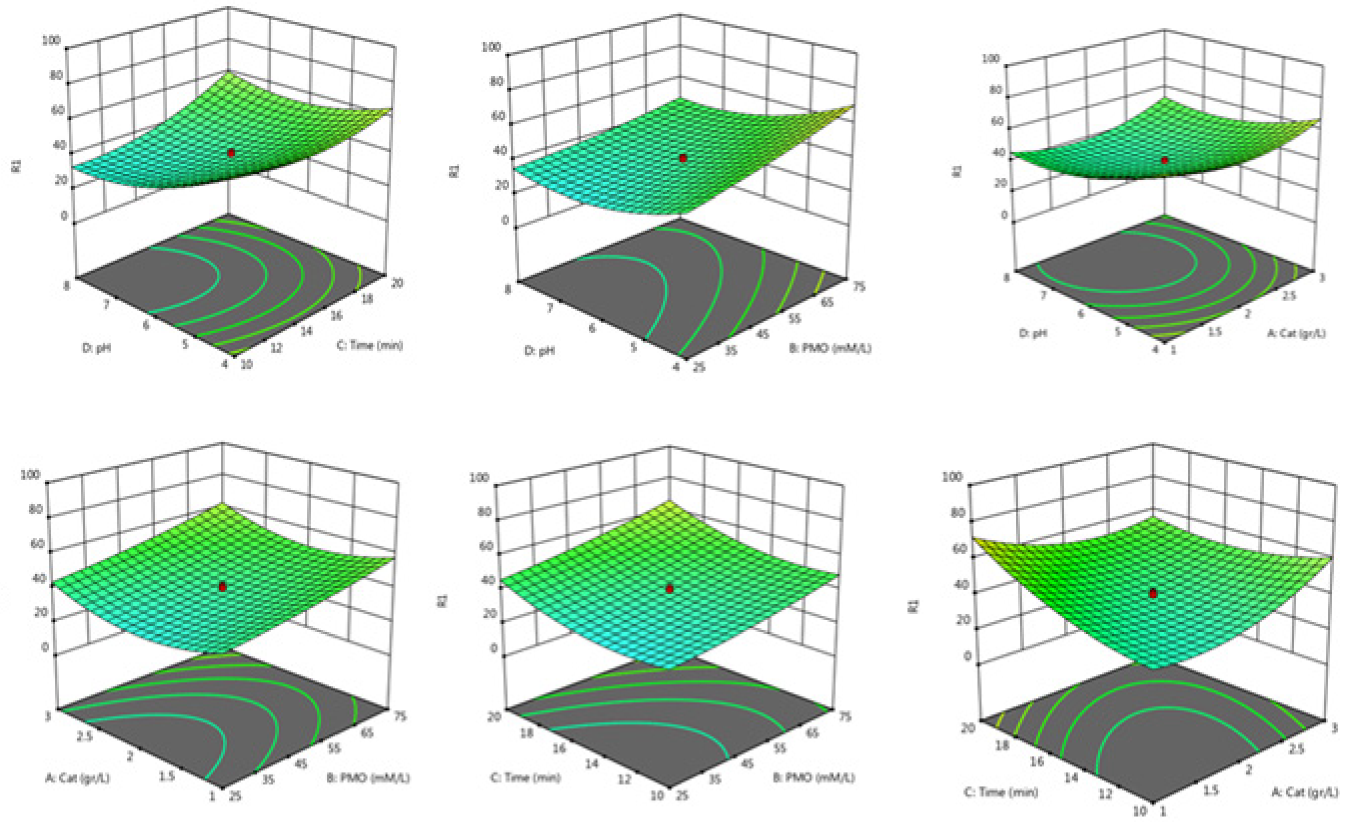
The distribution diagram of the residual was examined to check the model's suitability. The results show that the data have a uniform distribution. Furthermore, Chart B illustrates that the data are distributed almost evenly on both sides of the zero line. This distribution suggests that the average of the remaining data points is close to zero, indicating a lower likelihood of error in predicting the effect. Chart C confirms the validity of the model used by examining the random scatter of the residual versus the run. It can also be seen that the actual values versus the predicted values show a good agreement between the actual data and the data obtained from the model (Chart D). In summary, all the obtained results indicate that the quadratic polynomial model is adequate and appropriate for explaining and interpreting the data related to the removal process and the various operational factors.

Figure 5. (A) Normal probability plot, (B) residual versus predicted plot, (C) studentized residuals vs. run number plot and (D) predicted vs. actual values plot for sunset yellow degradation efficiency.



Three-dimensional response surface diagrams represent a relationship between two independent variables, providing insights into how these variables influence each other and their individual effects on the percentage of sunset yellow color removal. One of the important factors in the absorption and oxidation process is the pH of the solution (Figure A-C). The pH of the solution affects the surface charge characteristics of the vermiculite/iron oxide composite as well as its catalytic activity. The results indicate that the removal efficiency of sunset yellow is significantly higher at low pH levels. As pH increases, the removal efficiency decreases due to two factors: it saturates the surface of the composite (negatively affecting the adsorption process) and induces the hydrolysis of iron in the composite (negatively impacting the catalytic process). With the hydrolysis of iron, the role of the composite in the production of active radicals such as SO4•- and •OH decreases. At high and alkaline pH, sulfate radical reacts with H2O/OH- and produces hydroxyl radical. Although hydroxyl radicals have a higher oxidation potential, they are easily abducted by non-target species or converted into hydrogen peroxide due to the selective reaction. According to the figure 6 it can be seen that at pH 8, the removal efficiency has increased by almost a few percent. This effect can be attributed to the presence of numerous nucleophilic groups in alkaline solutions that attack the O-O bond in the oxidant, leading to the production of active radicals and thereby enhancing the removal efficiency. Finding the optimal amount of vermiculite/iron oxide composite is one of the most important parameters in the removal process. As the results show the removal efficiency also increases with an increase in the amount of composite. This effect is due to the increase in the amount of composite, the number of free radicals increases, which in turn increase the free radicals. Also, by increasing the amount of composite, more surface is available to remove sunset yellow color through chemical bonds (adsorption process). The effect of reaction time, as shown in **Figure 6**, indicates that the removal efficiency increased with increasing time. Because there has been enough time for the reaction between the oxidizing catalyst to produce SO4•- and •OH radicals, in addition, there has been enough time for the reaction and formation of a bond between the adsorbent and the sunset yellow pollutant.

Figure 6. 3D surface plots showing the interaction of different experimental parameters.



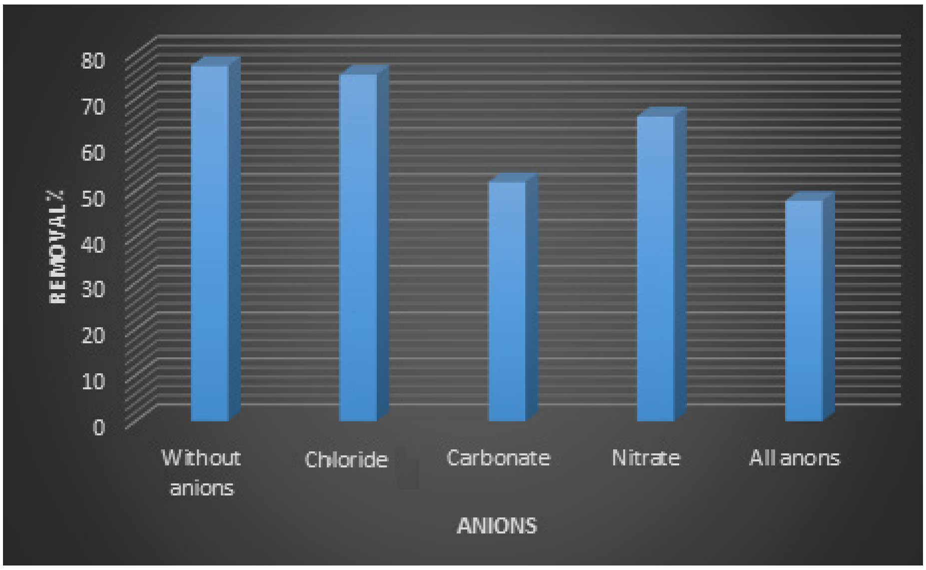
Process optimization

The results showed that the optimal conditions provided by Design Expert software are the best removal of sunset yellow color with 78.69% removal at pH 4, sunset yellow color concentration of 30 mg/L, persulfate oxidant dose of 75 mM, Vermiculite/iron oxide composite dose of 3 g/L and reaction time 20 minutes were obtained. To confirm the predicted model and increase the accuracy of the data, four experiments were conducted in optimal conditions, and the average results obtained (76.14%) are in good agreement with the results obtained from the software predictions, and a confirmation of the predicted model. In optimal reaction conditions, the percentage of removal and breakdown of sunset yellow color using vermiculite/iron oxide/PMO, vermiculite, iron oxide and PMO was investigated separately. The results showed that vermiculite/iron oxide/PMO had the highest removal percentage with 78% compared to the removal of 57% of vermiculite, 33% of iron oxide and 47% of PMO.

The effect of anions

The effect of bicarbonate, carbonate, nitrate and chloride anions on the removal of sunset yellow color is shown in **Figure 7**. The effect of different anions was investigated in the above-mentioned optimal conditions. The results show that the presence of other anions reduces the removal efficiency, which can be due to the consumption of SO4•- and •OH radicals and the production of radicals with lower oxidation power. Also, the results show that carbonate anions had the greatest effect in reducing the removal of sunset yellow color. This is because carbonate anions create a higher pH and a more alkaline environment compared to other anions used, resulting in a reduction in the quantity and potency of radicals.

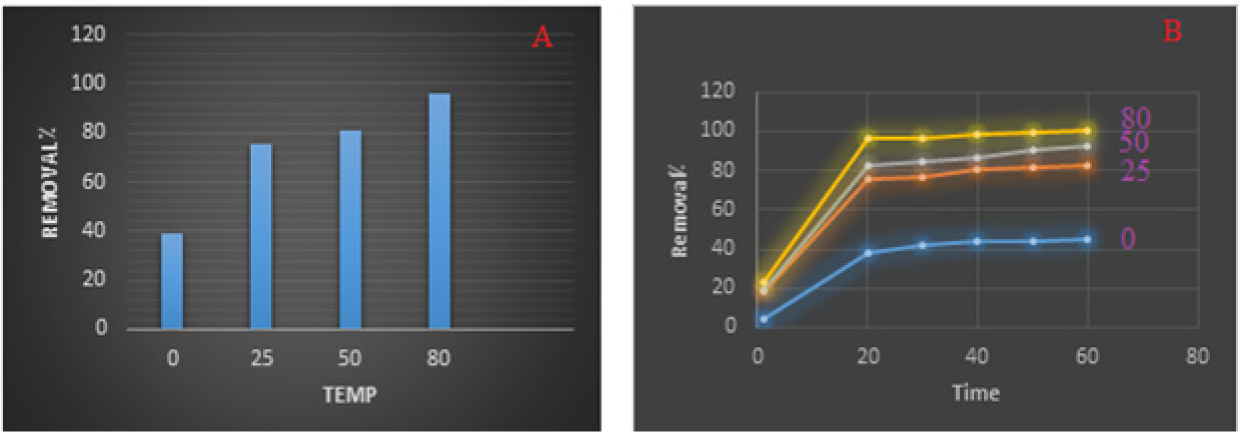
Figure 7. Effect of anions on the removal of sunset yellow.



Temperature effect

The effect of different values of temperature (0-80 °C) on the sunset yellow degradation efficiency was investigated in optimal conditions (**Fig.8**). As the temperature rises from 0°C to 80°C, the removal rate of sunset yellow increases from 38% to 96%, demonstrating the significant efficacy of thermal activation in the removal process (Fig. A). With increasing temperature, there is an elevated production rate of OH and SO4 radicals through the breaking of the O-O bond. Also, the effect of reaction time at different temperatures was investigated. As depicted in Figure (Fig. B), during the initial times (1-20 minutes), there is a notable increase in radical activation, leading to higher removal efficiency.The rate constant K was calculated in first-order kinetics for different temperatures. The results showed that by increasing the temperature from 1 to 80, the constant k reaches from 1.97 to 7.26 min-1, which is an indication of the effect of temperature on the reaction rate. Using the rate constant at different temperatures, the activation energy of the sunset yellow color removal reaction was found to be 0.009 J/mol using the Arrhenius equation.

Figure 8. Effect of temperatureon the removal of sunset yellow



The degradation pathways of sunset yellow

In order to better investigate the reaction mechanism and identify the intermediates during the sunset yellow dye breaking process, GC-Mass and UV-Vis analyses was used on the sample extracted after 20 minutes, and its results are shown in **Table 4**. **Figure 9** shows the results of UV-Vis analysis before and after the degradation process. According to the chemical structure of sunset yellow color, two peaks can be seen in the region of 315 nm and 480 nm, which are related to the aromatic ring and the azo bond. After the sunset yellow color degradation process, due to the breaking of the azo bond in the oxidation process, the intensity of the peak in the region of 480 nm is very low and almost disappears. In addition, the results show that the intensity of the peak in the region of 315 nm increases after the degradation process. This increase is attributed to the breaking of the naphthalene ring in the sunset yellow color structure, leading to the formation of new rings.

Table 4. GC–MS identification of the chemical structure and m/z of the sunset yellow dye and aromatic by-products formed during the degradation process.

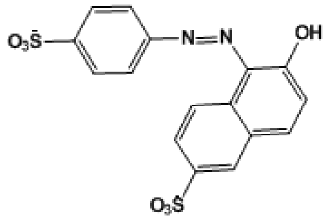
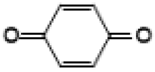
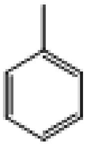
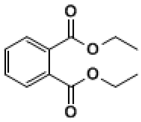
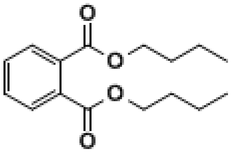
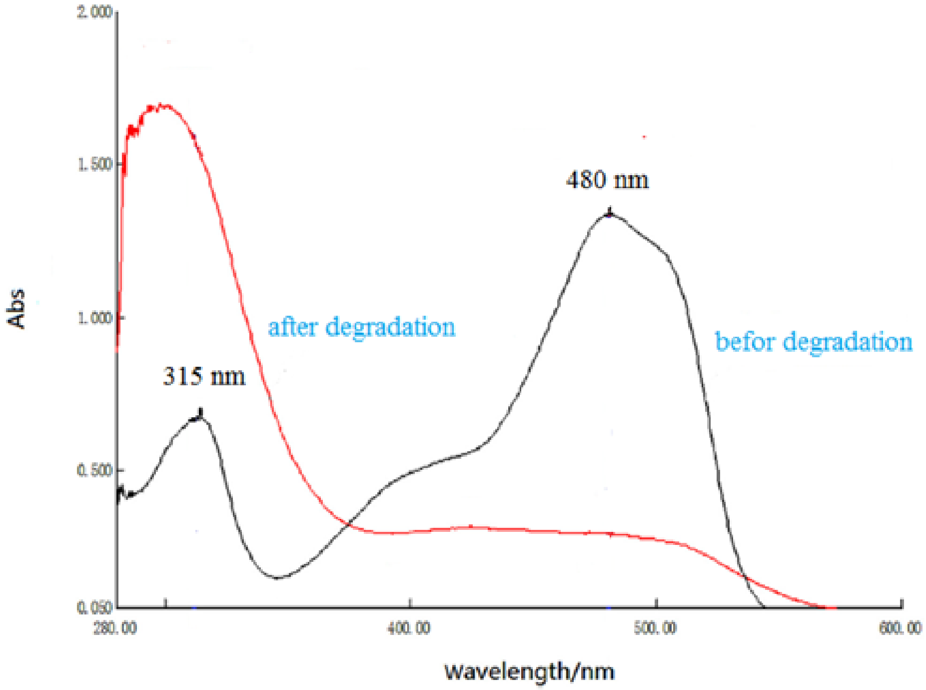
Compound	m/z	Formula	Proposed structures
Sunset Yellow	405.99	C16H10N2O7S2	
Benzoquinone	108	C6H4O2	
Methylbenzene	92	C7H8	
1,2-Benzene-dicarboxylic acid diethyl ester	222	C12H14O4	
1,2-Benzene-dicarboxylic acid dibutyl ester	278	C16H22O4	

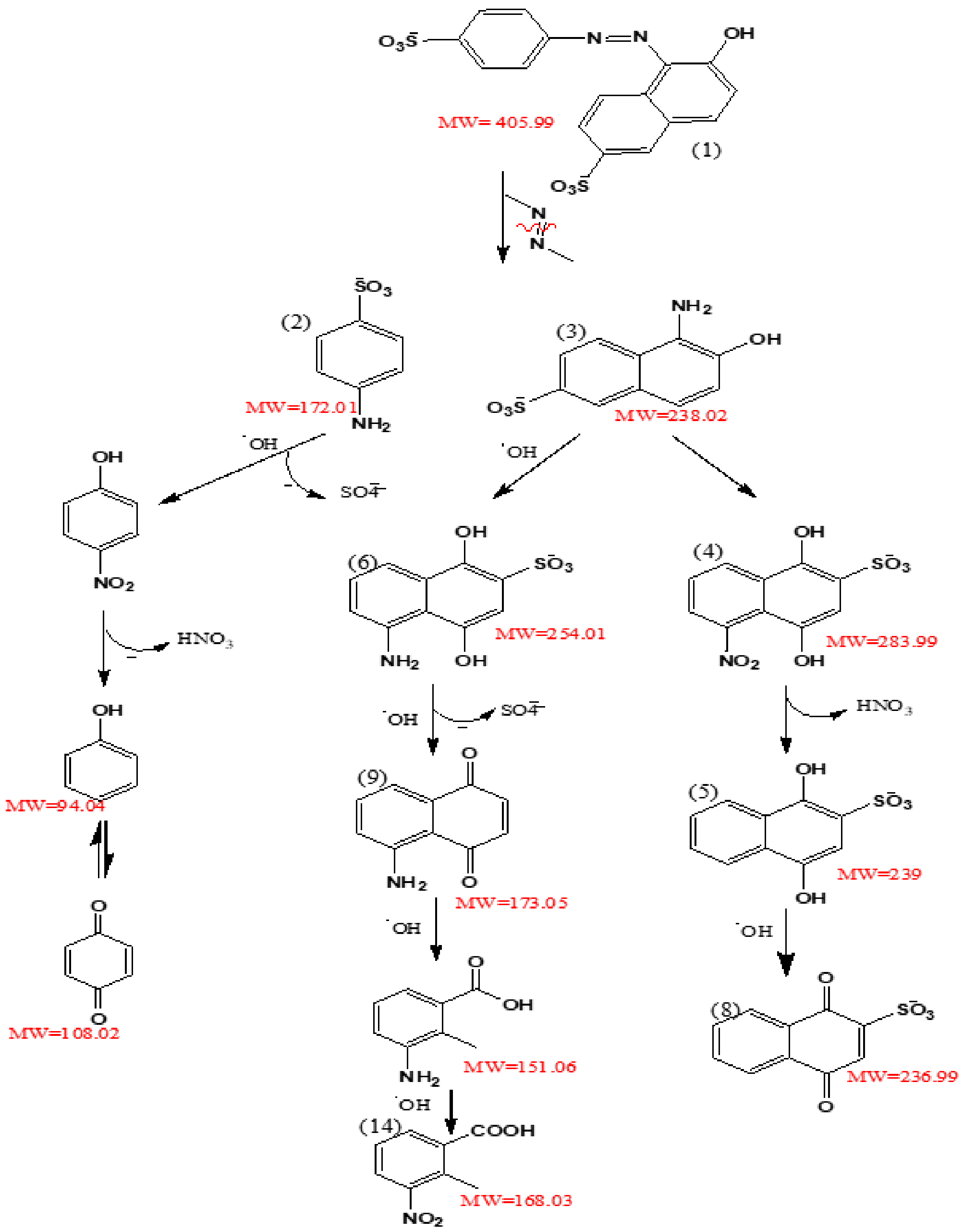
Figure 9. UV-Vis spectra changes during degradation process.

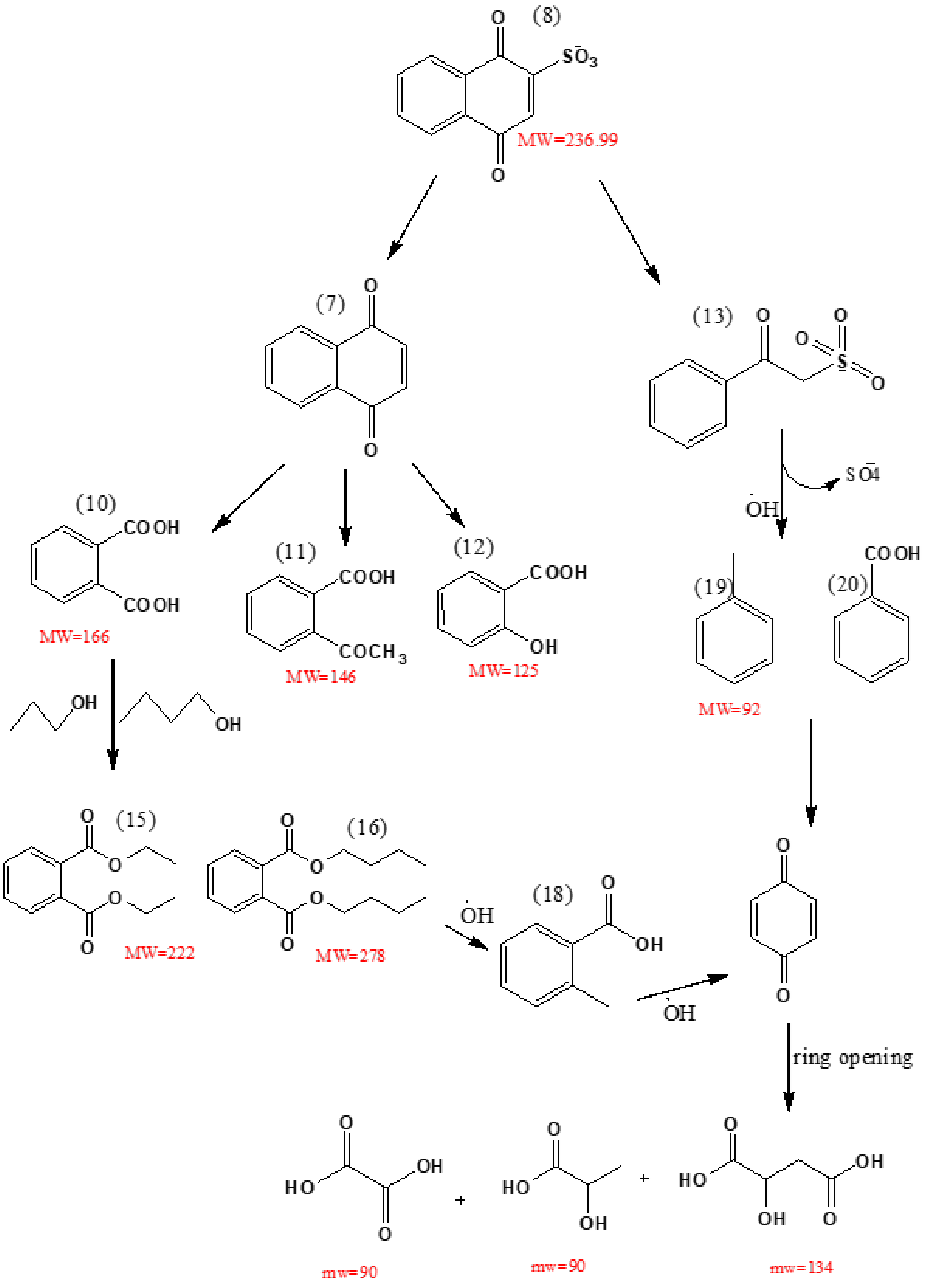


In the process of removing sunset yellow color by modified Vermiculite in this study, radicals such as OH. and SO.4 are produced, which can decompose sunset yellow into intermediates from different pathways. The break of azo bond (N N) in Sunset Yellow structure (1) results in the formation of 4-aminobenzenesulfonic (2) and 5-amino-6-hydroxy naphthalene-2-sulfonate (3), respectively. During the process of oxidation and hydroxylation, compound (3) turns into compound (4) and (6). Compound (4) turns into compound (5) during the process of oxidation and denitration, and then turns it into compound (8) during the oxidation process. In the continuation of the reaction path, the desulfonation of compound (8) is formed compound (7). Compound (7) after successive oxidations can favor the formation of compounds (10), (11) and (12) with naphthalene ring opening. Also, based on the obtained results, it can be predicted that a reaction occurred between compound (10) and an alcohol, which leads to the synthesis of compounds (15) and (16).

In the other way, it can be predicted that compound (3) will be converted to compound (6) and then to compound (9) during the oxidation and desulfurization process. Which after successive oxidations can favor the formation of compound (14) with naphthalene ring opening. In the continuation of the reaction path during the process of oxidation and denitration, compounds (14), (15) and (16) are converted into compound (18). Besides, the direct oxidation of compound (8) results in the formation of compound (13), which leads to the formation of compounds (19) and (20) by simultaneous oxidation and desulfonation. At the end, the aromatic rings of benzene and its derivatives are opened and during the oxidation process they are converted into compounds such as malic acid, oxalic acid and lactic acid.

Figure 10. Proposed degradation pathway of Sunset Yellow.





Toxicity test

The toxicity of the system and solutions containing modified Vermiculite was evaluated using Daphnia Pulex. The results show that in the presence of persulfate oxidant, daphnias die after 2 hours and become motionless (**Table. 5**). Persulfate, being an oxidizing compound, generates active species in the presence of UV light in the environment, ultimately leading to the demise of Daphnia. Also, the results show that in the presence of modified vermiculite, Daphnias die after 3 hours, which is due to the release of metal ions in the solution. In the case of the solution containing modified vermiculite and persulfate, the number of Daphnias remained constant for the first 2 hours, but their population gradually decreased over time, with no living Daphnias observed after more than 8 hours. This decline can be attributed to prolonged exposure to metal ions and persulfate.

Table 5. Daphnia live numbers in various systems Daphnia numbers.

System	2h	4h	8h	24h
DI water	16	16	16	16
Sunset yellow (50 ppm)	0	0	0	0
PMO (2.5 mM)	11	0	0	0
Ver/Fe (100 ppm)	15	3	0	0
Ver/Fe@PMS	13	9	4	0

Comparison with other sorbents

Table 6 shows the efficiency of the adsorbent and the removal method of sunset yellow color compared to other adsorbents that have been studied before. The results show that the adsorbent synthesized in this study has a higher efficiency than many adsorbents. Also, the data of previous studies show that the removal capacity of sunset yellow color is higher in acidic pH, which is a valid issue for the present study. The data in **Table 6** shows that the synthesized polymer absorbents have a higher absorption capacity than the studied absorbent, but such absorbents cause environmental concerns due to their long shelf life.

Table 6. Comparison of the various sorbents for sunset yellow removal.

NO	Sorbent	pH	Time (min)	Sorbent dosage (gL-1)	Qe (mg g-1)	Ref
1	m–CS–c–PAM	2-10	60	1	359.71	Jiang, 2023
2	PPy/mw nanocomposite	2	5	0.007	212.1	Aliabadi,2018
3	Activated carbon	1-2	90	0.1	44.9	Chukwuemeka-Okorie,2021
4	PDMAEMA grafted PS-DVB-VBC	2	40	0.4	312.5	Yayayürük,2020
5	ZnO NPs loaded on activated carbon	2	10	0.015	142.8	Maghsoudi,2015

Conclusion

In this study, vermiculite modified with iron ions was synthesized and used to activate the peroxymonosulfate compound to remove sunset yellow pollutant. All the influencing factors on the reaction conditions were optimized by RSM and the best result for sunset yellow removal was at pH 4, sunset yellow concentration 30 mg/L, dose of persulfate oxidant 75 mM, combined dose of vermiculite/iron oxide 3 g/L. liters and the reaction time was 20 minutes. vermiculite/iron oxide/PMO had the highest removal percentage with 78% compared to the removal of 57% of vermiculite, 33% of iron oxide and 47% of PMO. The presence of interfering substances such as anions leads to a decrease in the degradation efficiency, while an increase in temperature increases the degradation efficiency of sunset yellow. The results of the UV-Vis and GC-MS analysis showed that the intermediates formed from the degradation of Sunset Yellow were mostly done through the cutting of C-C and N-N bonds. The toxicity tests of treated effluent with Daphnia Pulex were evaluated, and the results showed that the system used required a long treatment time and better stabilization of the catalyst. Finally, the results of this study showed that the method used in this study is suitable for removing colored compounds from wastewater. However, more studies should be done to understand the different aspects of the wastewater treatment process.

Ethical Approval

Not applicable

Consent to Participate

All participants involved in the study provided their consent to participate in the research.

Consent to Publish

Consent has been obtained from all participants to publish the findings of this study.

Authors Contributions

Esmail Mohseni: Data curation, formal analysis, investigation, experiment execution, results interpretation, discussion enrichment, statistical methods application, initial draft writing, manuscript editing.

Habib Abbasi: Study conceptualization, methodology design, original draft preparation, project supervision, statistical methods application, manuscript revisions.

Zeinab Habibi: Results validation, visualization, manuscript review and editing, data accuracy assurance.

Funding

The authors thank the Larestan University of Medical Sciences for the financial support for this work (Project No. 149)

Competing Interests

The authors declare no competing interests.

REFERENCES

1. Aliabadi RS, Mahmoodi NO (2018). Synthesis and characterization of polypyrrole, polyaniline nanoparticles and their nanocomposite for removal of azo dyes; Sunset yellow and Congo red. J. Clean. Prod.179:235–245.

2. Ansari, R., et al. (2012). "Highly efficient adsorption of anionic dyes from aqueous solutions using sawdust modified by cationic surfactant of cetyltrimethylammonium bromide." Journal of Surfactants and Detergents 15: 557-565.

3. Bagal, M. V. and P. R. Gogate (2013). "Degradation of 2, 4-dinitrophenol using a combination of hydrodynamic cavitation, chemical and advanced oxidation processes." Ultrasonics sonochemistry 20(5): 1226-1235.

4. Chukwuemeka-Okorie HO, Ekuma FK, Akpomie KG, Nnaji JC, Okereafor AG (2021). Adsorption of tartrazine and sunset yellow anionic dyes onto activated carbon derived from cassava sievate biomass. Appl. Water Sci.11:1–8.

5. de Sá, F. P., et al. (2013). "Effect of pH on the adsorption of Sunset Yellow FCF food dye into a layered double hydroxide (CaAl-LDH-NO3)." Chemical Engineering Journal 215: 122-127.

6. Dezhampanah, H., et al. (2014). "Removal of an anionic dye from wastewaters by adsorption on modified rice husk and sugarcane bagasse." International Journal of Hybrid Information Technology 7(2): 309-320.

7. El-Ashtoukhy, E. Z. and N. Amin (2010). "Removal of acid green dye 50 from wastewater by anodic oxidation and electrocoagulation—A comparative study." Journal of hazardous materials 179(1-3): 113-119.

8. Fernández, I., et al. (2013). "Aerobic biodegradation of a mixture of monosubstituted phenols in a sequencing batch reactor." Journal of hazardous materials 260: 563-568.

9. Ghauch, A., et al. (2015). "Naproxen abatement by thermally activated persulfate in aqueous systems." Chemical Engineering Journal 279: 861-873.

10. Gupta, V., et al. (2011). "A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye—Acid Blue 113." Journal of hazardous materials 186(1): 891-901.

11. Ho, Y.-S., et al. (2005). "Removal of basic dye from aqueous solution using tree fern as a biosorbent." Process Biochemistry 40(1): 119-124.

12. Jiang, R.Shen, T. Zhu, H. Fu, Y. Jiang, S. Li, J. Wang, J (2023). Magnetic Fe3O4 embedded chitosan–crosslinked-polyacrylamide composites with enhanced removal of food dye: Characterization, adsorption and mechanism. Int. J. Biol. Macromol.227:1234–1244.

13. Khazri, H., et al. (2017). "Removal of ibuprofen, naproxen and carbamazepine in aqueous solution onto natural clay: equilibrium, kinetics, and thermodynamic study." Applied Water Science 7(6): 3031-3040.

14. Kong, Q., et al. (2017). "Kinetic and equilibrium studies of the biosorption of sunset yellow dye by alligator weed activated carbon." Desalin. Water Treat 66: 281-290.

15. Liu, H., et al. (2011). "Biodegradation of phenol at high concentration by a novel yeast Trichosporon montevideense PHE1." Process Biochemistry 46(8): 1678-1681.

16. Liu, Y., et al. (2010). "Fe2+-modified vermiculite for the removal of chromium (VI) from aqueous solution." Separation Science and Technology 46(2): 290-299.

17. Liu, Y., et al. (2006). "Adsorption of metal ions on natural vermiculite." JOURNAL-SICHUAN UNIVERSITY ENGINEERING SCIENCE EDITION 38(3): 92.

18. Liu, Y., et al. (2007). "Kinetics and thermodynamics of lead (II) adsorption on vermiculite." Separation Science and Technology 42(1): 185-202.

19. Maghsoudi M, Ghaedi M, Zinali A, Ghaedi A, Habibi M (2015). Artificial neural network (ANN) method for modeling of sunset yellow dye adsorption using zinc oxide nanorods loaded on activated carbon: Kinetic and isotherm study. Spectrochim. Acta Part A Mol. Biomol. Spectrosc.134:1–9

20. Mathialagan, T. and T. Viraraghavan (2003). "Adsorption of cadmium from aqueous solutions by vermiculite." Separation Science and Technology 38(1): 57-76.

21. Moghadasi M, Rahimi A, Heshmati A (2019). The prevalence of synthetic color in saffron and sweet products (yellow halvah, candy and crystallized sugar) supplied in store of Hamadan City using thin layer chromatography (TLC) Pajouhan Sci. J;17:31–36.

22. Mitter, E. and C. Corso (2012). “Acid dye biodegradation using Saccharomyces cerevisiae immobilized with polyethyleneimine-treated sugarcane bagasse.” Water, Air, and Soil Pollution 224: 1391.

23. Ramakrishna, K. R. and T. Viraraghavan (1996). “Dye removal using peat.” American Dyestuff Reporter 85(10): 28-34.

24. Sadaf, S. and H. N. Bhatti (2014). “Evaluation of peanut husk as a novel, low cost biosorbent for the removal of Indosol Orange RSN dye from aqueous solutions: batch and fixed bed studies.” Clean Technologies and Environmental Policy 16: 527-544.

25. Şenol, Z. M., et al. (2020). “Removal of food dyes from aqueous solution by chitosan-vermiculite beads.” International journal of biological macromolecules 148: 635-646.

26. Shokri, S. Shariatifar, N. Molaee-Aghaee, E. Khaniki, G.J. Sadighara, P. Faramarzi, M.A (2024). “Modeling sunset yellow removal from fruit juice samples by a novel chitosan-nickel ferrite nano sorbent”. 14: 208.

27. Sharma, P. and H. Kaur (2011). “Sugarcane bagasse for the removal of erythrosin B and methylene blue from aqueous waste.” Applied Water Science 1: 135-145.

28. Tan, C., et al. (2015). “Kinetic oxidation of antipyrine in heat-activated persulfate.” Desalination and Water Treatment 53(1): 263-271.

29. Tayyab, M. Liu, Y. Liu, Zh. Xu, Z. Yue. W. Zhou, L. Lei, J. Zhang, J (2023). A new breakthrough in photocatalytic hydrogen evolution by amorphous and chalcogenide enriched cocatalysts. Chem. Eng. J;455:140601.

30. Walker, G. and L. Weatherley (2000). “Biodegradation and biosorption of acid anthraquinone dye.” Environmental pollution 108(2): 219-223.

31. Yayayürük O, Yayayürük AE, Özmen P, Karagöz B (2020). PDMAEMA grafted microspheres as an efficient adsorbent for the removal of Sunset yellow from pharmaceutical preparations, beverages and waste water. Eur. Polym. J.141:110089.

32. Zhang, J., et al. (2012). “Kinetic, isotherm, and thermodynamic studies of the adsorption of methyl orange from aqueous solution by chitosan/alumina composite.” Journal of Chemical & Engineering Data 57(2): 412-419.

33. Zhang, M., et al. (2015). “Degradation of p-nitrophenol by heat and metal ions co-activated persulfate.” Chemical Engineering Journal 264: 39-47.