Environmental Win–Win Management: Using Aluminum-Based Solid Waste for Synozol Red-KHL Dye Oxidation

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Abstract: The awareness of the concept of the “Circular Economy” is motivating scientists to convert drinking water treatment plant by-products, which are based on aluminum waste, into a valorized material for wastewater treatment. Alum sludge from a local waterworks plant in Egypt was collected and dewatered using chitosan-coated magnetic nanoparticles. The role of the conditioned sludge in wastewater treatment was then examined. Chitosan (Ch) augmented with magnetite nanoparticles (MNs), labeled as ChMNs, was prepared by means of a simple co-precipitation route with mixing ratios of 1:1, 2:1, and 3:1 of chitosan and magnetite nanoparticles to form the ChMN catalyst. The ChMNs were shown to beneficially enhance alum sludge conditioning and dewaterability. The conditioned and dried aluminum-based sludge (AS) loaded with ChMNs was then used as a source of Fenton’s catalyst for Synozol Red-KHL textile dyeing wastewater. The characteristics of the AS-ChMN sample were investigated using Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The photocatalytic activity of the AS-ChMN composite was assessed by examining its diffuse reflectance spectra (DRS). Response surface methodological analysis was applied to optimize the operational parameters in order to reduce the use of chemicals and improve dye oxidation to form a complete (99%) dye oxidation strategy. The experiments demonstrated that the optimal operating parameters included doses of 1.5 g/L and 420 mg/L for AS-ChMNs and hydrogen peroxide, respectively, as a source of Fenton’s reaction at a working pH of 3.5. Kinetic and thermodynamic analyses for potential full-scale applications were conducted, showing the reaction to be exothermic and spontaneous in nature and following second-order reaction kinetics. Hence, the novelty of this work lies in the introduction of conditioned and dewatered alum sludge waste as a photocatalyst for textile dye effluent oxidation, which could be considered a “win–win” strategy.

Keywords: alum sludge; textile dye; industrial ecology; catalytic oxidation; dual waste management

1. Introduction

A global increase in the development of domestic areas and industrial advances is usually linked to a considerable water demand. The result associated with such a massive water requirement is that a considerable amount of wastewater is attained that requires significant and intensive treatment [1–3]. As a result, massive amounts of sludge are produced by drinking water treatment plants, forming an inevitable by-product of aluminum-based waste [4]. Water in the alum sludge increases both its transportation and disposal costs [5]. Hence, sludge dewatering is a vital step to reduce its water content, for the purposes of both recycling the water and easily managing the solid sludge waste [6,7].
Therefore, efficient sludge conditioning prior to mechanical dewatering is essential in waterwork plants. In particular, polymeric substances are introduced to the sludge as a binder material to bind water molecules to the solid surface by forming sludge flocs. The flocs trap water, and the result is the formation of a highly compressible aluminum-based sludge matrix. Thus, the attained waste is prepared for disposal [8–10].

 Massive amounts of industrial effluents are also discharged due to industrial activities [11]. Conventional wastewater treatment technologies associated with secondary wastes include filtration, physical separation, and adsorption, which require further treatments or may be expensive; thus, developing appropriate treatment technologies is a hot research topic [12–15]. The emergence of advanced oxidation processes (AOPs) as a superior wastewater management technique has attracted great attention. Such treatments are rapid and possess high performance in mineralizing organic substances to reach environmentally friendly end products (CO\textsubscript{2} and H\textsubscript{2}O) [16]. Fenton’s oxidation reaction is an AOP that involves hydrogen peroxide and iron ions [17]. However, the costs of the treatments and the fresh chemicals used still stand as a barrier to practical applications. Classical Fenton’s reagent is a homogenous technology, and iron is the rate-limiting factor [18,19]. However, after a treatment using this process, iron precipitate is formed as a final sludge, which is difficult to separate from the medium [20]. This is one of the limiting steps of this process. Therefore, to overcome such disadvantages, conversion to a heterogeneous catalyst is required to improve upon the homogenous Fenton system. Furthermore, the application of a nanoscale photocatalyst is favorable for efficient treatments, and searching for other sources of catalysts is essential to reduce processing costs [21].

 Of great urgency worldwide is the replacement of toxic and highly concerning chemicals with ecologically benign substances. As a part of this concept, the incorporation of new environmentally benign substances, especially in waste management strategies, is gaining further attention and interest due to modernization [22–24]. For instance, the use of magnetic materials has shown pronounced effects on treatments, such as magnetic composites integrated with plasmatic metals [23], biometric urchin-like photocatalysts [24], and metal–organic frameworks [16,19]. Ferrites decorated with various metals such as zinc and alumina have shown positive effects on eliminating dyes contained in wastewater [20]. Additionally, the biomass-synthesized biopolymers cellulose and chitin are the two most abundant biopolymers on the planet [25]. Win–win waste control is a worldwide concept for a greener and more sustainable ecosystem. In this regard, there have been some very recent but limited developments in the search for greener photocatalyst, particularly from waste [25–27]. In particular, alum sludge is produced in large volumes daily, and after dewatering, it still poses concerns regarding its final disposal. Thus, converting such waste into a viable photocatalyst is an alternative and greener opportunity. In the pursuit of overcoming the use of new chemicals and limiting the generated waste, using alum sludge is a cradle-to-cradle waste management opportunity. Previous research articles [11–13] have concluded that alum sludge can be applied in its original form without conditioning as a source of an adsorbent material or catalyst [6]. However, research is still needed on the use of the conditioned sludge as a photocatalyst.

 According to the research articles studied and cited, to the best of the authors’ knowledge, there is a gap in the research on the modulation of alum sludge conditioned with a chitosan–magnetite composite material as a catalyst source for the Fenton-like reaction. The present work examines a win–win technology through the use of alum sludge conditioned and dewatered with chitosan–magnetite nanoparticles (ChMNs) as a source of a catalyst for Fenton-like oxidation, as one of the AOPs. The combination of ChMNs and hydrogen peroxide is used to oxidize Synozol Red-KHL dye, which is used to simulate textile dyeing wastewater. The system operational variables, such as ChMN and H\textsubscript{2}O\textsubscript{2} loadings, as well as the effect of pH and temperature, are examined, and the dye oxidation is monitored. The response surface methodology is also applied to maximize the system yield and optimize the chemicals added for oxidation. Finally, the thermodynamics and kinetics of the oxidation reaction are assessed.
2. Materials and Methods

2.1. Wastewater

The dye-containing aqueous media were prepared using a water-soluble reactive dye named Synozol Red-KHL, supplied by Kisco Int., Adana, Turkey. A specific weighed amount of dye was dissolved in distilled water to produce the stock aqueous medium solution that was then diluted further, as required, to the desired values.

2.2. Fenton-Like “AS-ChMN” Catalyst

Alum sludge that was augmented with chitosan magnetite after being conditioned using chitosan–magnetite conditioner was applied as a Fenton-like catalyst source. Initially, the conditioned sludge solids, after the water was decanted, were subjected to overnight drying in an electric oven at 105 °C to eliminate any remaining water from the conditioned and dewatered AS. AS-ChMN material was then obtained and applied as the catalyst source for the Fenton-like system.

2.3. Methodology

Synozol Red-KHL dye-containing wastewater containers were filled with 100 mL of 20 ppm dye aqueous solution. Diluted sulfuric acid and sodium hydroxide solutions were used to adjust the pH to the desired values when needed. All chemicals were of analytical grade and were used as received without extra purification or treatment. AS-ChMN material was added to the dye solution, followed by the addition of hydrogen peroxide (30%/30% w/v) to initiate the Fenton-like oxidation test. The oxidation reaction was initiated by exposing the sample to ultraviolet (UV) illumination, produced by a UV lamp (15 W, 230 V/50 Hz, with 253.7 nm wavelength). Subsequently, the samples were withdrawn periodically at selected time intervals for micro-filter separation prior to spectrophotometric analysis to inspect the remaining Synozol Red-KHL dye in the solution. A graphical illustration representing the experimental set-up is exhibited in Figure 1.

![Figure 1. A graphical illustration of the experimental technique.](image-url)
2.4. Analytical Determination and Characterization

Spectrophotometric analysis was applied to investigate the remaining dye in the solution using a Unico model UV-2100, manufactured in the Triad Scientific, Manasquan, NJ, USA. The test was checked and conducted at 525 nm, the maximum absorbance wavelength of the Synozol Red-KHL dye. For the pH adjustment, a digital pH meter (Model AD1030, Adwa instrument, Bonaduz, Switzerland) was used to check that the desired values had been obtained. The characteristics of the AS-ChMN sample were also explored by means of FTIR analysis, which was performed in the wavenumber region of 400–4000 cm$^{-1}$ using a Jasco FTIR-4100 spectrometer (Jasco Inc., Easton, MD, USA). Furthermore, the morphology of the AS-ChMN catalyst was displayed using a field-emission scanning electron microscope (FE-SEM) (model Quanta FEJ20). Finally, a Bruker–Nonius Kappa CCD diffractometer (Bruker, Billerica, MA, USA) equipped with Cu Kα radiation ($\lambda = 1.5406$ Å) with 2θ ranging from 10 to 80° was used to investigate the XRD pattern of the AS-ChMN catalyst.

2.5. Factorial Design

In order to produce a sensible process with higher efficiency and more effective oxidation, with a suitable understanding of the role of the independent variables in the outcome of the Synozol Red-KHL oxidation system, measured as the dye removal percentage (dependent variable), a three-level factorial design (Box–Behnken design) with triplicates of the central values was applied. A Box–Behnken factorial design model based on the response surface methodology (RSM) analysis type was applied to optimize the effective variables. Such a Box–Behnken model is applied to optimize the most operative working parameters. The preliminary results of the experiments were used to investigate the levels of the three variables. SAS software, version 5 (SAS, 1990) was applied to identify the optimum values of the selected parameters. The designated variables were the hydrogen peroxide dose, AS-ChMN concentration, and operational pH value. Afterwards, the experimental responses were explored with regard to the Synozol Red-KHL dye oxidation efficacy. The coded and original values of the process operating parameters used in the designed matrix are displayed in Table 1. Fifteen experimental runs to cover the full experimental matrix were designed (according to SAS software, version 5), as tabulated in Table 2. Furthermore, to avoid experimental errors, the design of the experimental matrix was conducted in random order and in duplicate. Subsequently, a second-order polynomial quadratic model was constructed, affording Equation (1). To examine the model’s implications, a statistical analysis using an analysis of variance (ANOVA) was implemented in SAS software version 5; additionally, Mathematica software (V 5.2) was used to define the optimized variables and responses in terms of numerical values.

$$\gamma (\%) = \beta_0 + \sum \beta_i \varepsilon_i + \sum \beta_{ij} \varepsilon_i^2 + \sum \sum \beta_{ij} \varepsilon_i \varepsilon_j$$

(1)

where $\gamma$ is the Synozol Red-KHL dye concentration removal response; $\beta_0$, $\beta_i$, $\beta_{ij}$, and $\beta_{ij}$ are the model coefficients of the linear effect and double interactions; $\varepsilon_i$ and $\varepsilon_i^2$ are the independent parameters.

Table 1. Kinetic parameters for different reaction order models for Synozol Red-KHL oxidation by the modified AS-ChMN Fenton-like system *.

<table>
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<tr>
<th>Kinetic Model</th>
<th>Parameters</th>
<th>$T$ (°C)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>Zero-order</td>
<td>$C_t = C_0 - k_0t$</td>
<td>$k_0$ (min$^{-1}$)</td>
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<td></td>
<td>$t_1/2$ $R^2$</td>
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<td>$R^2$</td>
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Table 1. Cont.

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<td>$C_t = C_0 - e^{k_1 t}$</td>
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<td></td>
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<td>$k_1 (\text{min}^{-1})$</td>
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<td>Second-order</td>
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<td>$\left( \frac{1}{C_t} \right)$</td>
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<td></td>
<td>$\left( \frac{1}{k_2 t} \right)$</td>
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<tr>
<td></td>
<td>$k_2 (L/\text{gm.min})$</td>
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<td>$t_{1/2}$</td>
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</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.60</td>
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* $C_0$ and $C_t$: Synozol Red-KHL doses initially and at time $t$ (mg/L); $t$: time (min); $k_0$, $k_1$, $k_2$: the kinetic rate constants of the zero-, first-, and second-order kinetic models.

Table 2. Thermodynamic data of acetaminophen oxidation via the Chit@Fe$_3$O$_4$-based Fenton system.

<table>
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<th>50 °C</th>
<th>60 °C</th>
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<td>$E_a$ (kJ/mol)</td>
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<td>$\Delta G'$ (kJ/mol)</td>
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<td>76.74</td>
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<tr>
<td>$\Delta H'$ (kJ/mol)</td>
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<td>92.31</td>
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<td>$\Delta S'$ (kJ/mol)</td>
<td>92.47</td>
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3. Results and Discussion

3.1. The Characterization of the “AS-ChMN” Catalyst

3.1.1. SEM-EDX and TEM Morphological Analyses

Initially, SEM was performed to examine the morphology of the prepared ChMNs (with mixing ratios of 1:1, 2:1, and 3:1 of chitosan and magnetite nanoparticles) and the alum sludge material; the micrographs are presented in Figure 2a–d, respectively. The SEM micrographs of all the ChMN composites with different proportions revealed agglomerated nanoparticles with a particle size of about 10–40 nm. The chitosan crosslinker has a noteworthy role in giving nanoparticles a more spherical morphology. Homogeneous, spherical nanoparticles with a narrow grain size distribution characterized the magnetite nanoparticles prepared in different proportions (Figure 2a–c). Additionally, the SEM micrographs in Figure 2a–c show that the presence of more cumulative chitosan than magnetite in the composite caused a decay in the appearance of spherical particles of magnetite-decorated chitosan, as displayed in Figure 2c. Varied shapes with predominant semi-hexagonal sheets of agglomerated alum sludge particles appeared in the alum sludge sample, as shown in Figure 2d.

The morphology of the obtained conditioned and dewatered AS-ChMN photocatalyst, before and after use, was evaluated through SEM analysis augmented with energy-dispersive X-ray (EDX) analysis; the micrographs are displayed in Figure 3a,b. The microstructure in the SEM micrographs (Figure 2) reveals mostly quasi-spherical particle dots with a few irregular particles and a particle size distribution range of 30–46 µm. This is due to the compaction of the sludge particles in the conditioned sludge with chitosan and magnetite nanoparticles, revealing agglomerated particles that enhanced the dewaterability of the conditioned sludge and increased the particle size [14]. A quantitative EDX analysis was performed before and after calcination, and the results are presented in terms of atomic % and weight % (Figure 3 and the inset table). Both samples (before and after) had the same elements but with different compositions and were comparable. The sample after dye oxidation showed significant impacts and increases in most of its element percentages after the oxidation and dye treatment. This might be attributed to the reaction of the dye...
with the catalyst which might increase the elements’ composition. Exceptions were noted for the C and N elements, which totally disappeared, and for the removal of volatile gases (including CO$_2$ and NO$_x$ ($x = 2/3$) gases).

![SEM micrographs of various ChMN composite materials with different chitosan–magnetite ratios of (a) 1:1, (b) 2:1, and (c) 3:1 and (d) alum sludge.](image)

Figure 2. SEM micrographs of various ChMN composite materials with different chitosan–magnetite ratios of (a) 1:1, (b) 2:1, and (c) 3:1 and (d) alum sludge.

Figure 4 displays TEM images of the AS-ChMN composite material. The micrograph clearly displays mixed hexagon-like particles, as well as spherical shapes with the exception of small edges attached to definite nanoparticles. The particles with a clear dark spherical shape represent magnetite, as seen in the label in Figure 4. The spherical particles of magnetite and the hexagon-like sheets of alum sludge are accompanied by chitosan and are mounted on this polymer. Also, the pale spheres of chitosan appear attached with magnetite dark spheres. The inset of Figure 4 illustrates the particle size distribution of the AS-ChMN composite which displays an average particle size distribution of 5.65 µm.

3.1.2. XRD Analysis

Figure 4 presents the characteristic XRD spectrum of the AS-ChMN composite material. The peaks that appear at 20 values of 30.0° (220), 35.3° (311), 43.0° (400), 56.9° (511), and 62.8° (440) reflect the standard XRD data for the pure cubic spine crystal structure of magnetite in the sample (JCPDS No. 89-4319) [23]. Such data are compared with previous published data by authors [10] for the XRD pattern of the chitosan–magnetite composite, which confirmed the presence of chitosan and magnetite in the alum sludge–chitosan–magnetite composite. Furthermore, the XRD spectrum reflects the presence of alum sludge, which is well defined with sharp diffraction peaks that identify the complex phases of graphite, quartz, sodium aluminum silicate, and calcium aluminum silicate, showing a good crystalline phase [11]. This XRD pattern shown in Figure 5 proves the simultaneous
presence of magnetite, chitosan, and alum sludge in the hybrid substance, confirming that the material is a multiphase system including crystalline and amorphous phases, as indicated by the presence of both the sharp diffraction peaks and the background. This verifies that the crystallinity of the magnetite and alum sludge is still retained in the nanocomposite after sludge dewatering.

**Figure 3.** SEM-EDX analysis results of area scan of AS-ChMN composite material (a) before and (b) after dye oxidation.
3.1.3. FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) analyses were conducted to illustrate the links to the functional groups of the AS-ChMN composite material before and after
the Fenton-like oxidation reaction. FTIR analysis is a valuable tool for understanding the changes in the catalyst’s structure and the degradation mechanism of the dye, and the results are displayed in Figure 6. The FTIR analysis results can provide valuable information about the changes in the functional groups of the catalyst before and after dye degradation. The FTIR spectra can reveal the presence or absence of specific peaks associated with the catalyst’s composition, which can indicate the degradation of the dye and the interaction between the catalyst and the dye.

![FTIR analysis results for AS-ChMN composite material](image)

**Figure 6.** FTIR analysis results for AS-ChMN composite material (a) before and (b) after dye oxidation.

In both the curves exhibited for the AS-ChMN composite (a) before dye oxidation and (b) after dye oxidation, the bands at around 1427, 1631, and 3427 cm\(^{-1}\) can be assigned to C-O, C=C, and O-H stretching vibrations, respectively. Furthermore, the peak at 490 cm\(^{-1}\) signifies the presence of Fe-O stretching. This peak solely reflects the vibration of cationic vacancy ordering [26–28]. The band at 470–444 cm\(^{-1}\) is linked to the C-H and Si-O-Si bending modes. The band at 458 reflects the presence of a C-N bond. All the peaks after 3500 cm\(^{-1}\) represent the OH group [29]. However, weak bond deformation is observed due to the asymmetric stretching bonds of –CH- at wavenumbers of 3122 and 2550 cm\(^{-1}\); this is due to dye loading and oxidation, since it only appeared in the AS-ChMN composite after oxidation [28].

### 3.1.4. BET Surface Area Analysis

The specific surface area of the AS-ChMN composite material was calculated from N\(_2\) adsorption–desorption isotherms measured using the Brunauer–Emmett–Teller (BET) surface area analysis technique (Quantachrome Instrument, version 1.21). The data revealed that the BET surface area was 66.63 m\(^2\)/g (Figure 7). This indicates that after the aluminum-based sludge was conditioned using chitosan decorated with magnetite nanoparticles, then dewatered and dried, it was porous in nature. The surface area of the AS-ChMN composite has a fundamental role in the Synozol dye’s adsorption onto the AS-ChMN surface, since the increase in surface area has a pronounced positive effect on the adsorption tendency.
and activity. The photocatalytic activity is subsequently improved due to the improved contact between the pollutant and the catalyst surface, allowing the composite to oxidize the dye more efficiently than a non-porous photocatalyst would [30].

![Graph](image)

**Figure 7.** BET surface area obtained from N\\textsubscript{2} adsorption–desorption isotherms for AS-ChMN composite.

3.1.5. DRS Analysis

The absorption spectrum of the diffuse reflectance spectra (DRS) of the AS-ChMN composite material was obtained in order to examine the optical characteristics of the substance; the spectrum is displayed in Figure 7. The broad peak in the range of 400 to 600 nm verified the presence of magnetite nanoparticles [14]. This confirms the appropriateness of the material for use as a photocatalyst.

Furthermore, the diffuse reflectance spectra (DRS) were applied to investigate a simple method for the calculation of the optical band gap of the ChMN substance. Figure 8a shows the plot obtained from the Kubelka–Munk equation. The Kubelka–Munk equation, \( F(R) = \frac{(1 - R)^2}{2R} \) [31], signifies the behavior of light traveling inside a light-scattering sample, where \( R \) is the diffuse reflectance, \( F(R) \) is called the Kubelka–Munk function, \( E_g \) is the optical band gap, \( v \) is the light frequency, \( h \) is Planck’s constant, and \( A \) is the proportionality constant. The band gap is estimated from the plot of \( (F(R) \nu)^2 \) vs. \( \nu \) of the Kubelka–Munk function (Figure 8b). The band gap can be obtained by extending the straight line from the straight segment of the graph touching the \( hv \) axis. Hence, the band gap of the substance is 2.01 eV. This confirms the possibility of using this material as a photocatalyst in the infrared and visible region, particularly for applications involving photocatalytic activity under solar irradiation. The use of such a catalyst in a modified Fenton system under the infrared and visible light irradiation, particularly under solar...
irradiance, could contribute to the infrared and visible light absorption and result in a high photocatalytic tendency.

**Figure 8.** Plots of (a) the UV–Vis DRS absorption spectrum and (b) the corresponding Kubelka–Munk plot for the indirect band gap energy of the AS-ChMN composite.

3.2. The AS-ChMN Composite in a Fenton-Like Oxidation System

3.2.1. Effect of Reaction Time through Different Systems

Figure 9 presents the oxidation reaction times and the effectiveness of the various oxidation systems based on the various AS-ChMNs, namely AS-ChMNs-(1:1), AS-ChMNs-(2:1), and AS-ChMNs-(1:3). As an object of comparison, the results for pristine magnetite and AS systems are also presented to illustrate and explore the effect of the novel oxidation system. All the systems were conjugated with 400 mg/L of added H2O2 in order to initiate the Fenton oxidation reaction system.

The data exhibited in Figure 9 demonstrate that all the applied systems attained almost complete Synozol Red-KHL dye removal, with removal rates as high as 98%. However, a shorter reaction time was achieved when the AS-ChMN-based Fenton-like catalysts were applied. For the pristine AS system with no conditioner, a 70 min reaction time was required. However, a shorter reaction time of only 25 min was needed for oxidation when the AS-ChMN (1:3)-based Fenton-like catalyst was used with UV illumination. It is essential to note that for all the applied Fenton-like systems, an initial rapid oxidation rate was observed, followed by a steady oxidation rate. However, for the AS-ChMN-based catalysts, the rate of oxidation was faster than that for the pristine AS. This might be due to the limited amounts of OH radical species that are produced in the pristine AS-based Fenton-like system, in comparison to the AS-ChMN-based systems. This can be explained by the extra Fe2+/3+ present in such composites due to the presence of magnetite nanoparticles in the alum sludge conditioner. These iron nanoparticles react with hydrogen peroxide in the solution, and extra OH radicals are thereby generated, providing the main driving factor of the oxidation system. The greater availability of these radicals in the reaction medium is reflected in an enhancement in the Synozol Red-KHL oxidation reaction. Furthermore, the presence of chitosan in the sample could lead to an adsorption system; thus, the treatment is a dual treatment through adsorption–oxidation reactions.
Previous studies [1,4,31–34] confirmed the possibility of a dual adsorption–oxidation reaction through the Fenton-like reaction. Additionally, according to the data in Figure 9, the magnetite solo oxidation system showed an efficacy of only 64%. This verifies the function of alum sludge as the catalyst source for the photo-Fenton oxidation system and confirms that the presence of the augmented Al$^{3+}$/Fe$^{2+}$/Fe$^{3+}$ catalyst improves the Fenton system, as described previously. The system is enhanced by the dual composite, but it is noteworthy to also mention that the used catalyst is a waste material that is usually dewatered for disposal. However, in this study, we redirected this waste for use as a photocatalyst. Our investigations confirmed the role of each catalyst in the system, since the presence of both magnetite and alum sludge incorporated with chitosan showed a pronounced effect, due to the presence of Al$^{3+}$/Fe$^{2+}$/Fe$^{3+}$, in enhancing the Fenton oxidation [30]. Thus, it might be concluded that the presence of magnetite alone leads to the Fenton reaction through the Fe$^{2+}$/Fe$^{3+}$ catalyst reacting with hydrogen peroxide to generate OH radicals, which are the driving factor of the oxidation system. However, the use of AS alone as the Fenton catalyst source, comprising aluminum in excess relative to iron, resulted in an oxidation rate less than that for the magnetite-based system. This could be due to the decline in the amount of OH radicals produced by the system, since the aluminum-based Fenton system is less active than the iron-based system [24]. However, the co-existence of magnetite and alum sludge with chitosan in the dewatered and conditioned alum sludge led to a higher efficiency due to the hybrid characteristics of the composite material. The alum sludge contained various metals according to the EDX results displayed in Figure 3; the sample contained carbon, aluminum, and iron, which all might lead to an oxidation–adsorption reaction. Furthermore, the presence of chitosan as a crosslinker in the composite also leads to an adsorption reaction [31]. However, the composition ratio of ChMNs and AS influenced the oxidation rate. A greater amount of ChMNs relative to AS resulted in a higher oxidation rate due to the higher amount of OH radicals produced [23]. However, it is noteworthy that although the presence of excess AS in the composite hindered the oxidation rate, the oxidation tendency was still higher than that in the solo system. This verifies the importance of valorizing waste material, such as conditioned alum sludge, for use as a photocatalyst.

Figure 9. The reaction times of the various oxidative systems.
The catalytic Fenton reaction system basically comprises the oxidation of Fe$^{2+}$ and Fe$^{3+}$ through H$_2$O$_2$ as an oxidizing agent, in addition to triggering the highly reactive •OH species. These hydroxyl radicals are the driving factor required to initiate the reaction between Fe$^{2+}$ and H$_2$O$_2$ in an acidic environment, generating non-selective •OH to attack the persistent dye molecules and then oxidize them into non-toxic carbon dioxide and water [16]. The rate-limiting factor in this reaction is iron, and further radicals are produced through the chain cyclic reactions involving OH$^-$ and OH$_2$; the oxygen radicals and these reactions are categorized as a catalytic cyclic system [1,7]. Such generated radicals lead to chain reactions, but the presence of dissolved oxygen in the reaction medium reduces H$_2$O$_2$ decay. In parallel, the hydrolysis of Fe$^{2+}$/Fe$^{3+}$ also occurs. Hydrogen peroxide further reacts with the generated radicals present in the reaction medium, and extra hydroxyl radicals are generated. Furthermore, chitosan is well known for its chelating characteristics with metal ions. The generation of (OH) radicals might occur closer to the polysaccharide backbone to further generate extra macroradicals. Then, hydrogen abstraction occurs due to the presence of (OH) hydroxyl radicals that afford macroradicals along the polysaccharide, introducing the growth of attached monomers. Overall, such radicals present in the reaction medium hydroxylate the dye molecules and build up hydroxycyclohexadienyl radicals by proton abstraction. The result is the production of highly reactive organic radicals that might be extra oxidized. It is also important to mention that the alum sludge acts as an adsorbent material, as well as a catalyst source. This further increases the dye removal efficiency [31].

3.2.2. The Effect of the AS-ChMN Composite Concentration

The main species responsible for oxidizing Synozol Red-KHL dye is the strongly oxidative •OH radical. The strongly oxidizing species are mainly associated with the different Fenton variables, such as transition metal alteration, which represents an energetic role in the oxidation system. Thus, to verify the function of the AS-ChMNs’ catalytic effect on the Fenton-like system, the AS-ChMN catalyst doses were changed, ranging from 0.25 to 1.5 g/L, while the other variables were kept at constant values of pH 3.0 and H$_2$O$_2$ 400 mg/L. Notably, it is clear from the data displayed in Figure 10 that increasing the AS-ChMN catalyst dose resulted in an enhancement in the oxidation rate, corresponding to 100% removal. However, this phenomenon was associated with a dose concentration of 1 g/L; a further increase in the AS-ChMN catalyst concentration to 1.5 g/L resulted in a decline in the dye oxidation performance. This could be linked to the available •OH radicals generated in the oxidation medium, where the excess AS-ChMN catalyst above the optimal dose results in a decline in the overall oxidation efficacy. The excess catalyst in the aqueous medium controls hydroxyl radical formation and function since the catalyst is precipitated in the medium. Numerous authors [35–37] have confirmed this result.

3.2.3. The Effect of the H$_2$O$_2$ Concentration

Figure 11 presents the influence of increased hydrogen peroxide loading on the Synozol Red-KHL reaction rate when the remaining operating system variables were kept at constant levels (i.e., AS-ChMNs at 1 g/L and pH 3.0). The data in Figure 6 reveal an enhancement in the Synozol Red-KHL oxidation and removal tendency, reaching 98%, corresponding to 400 mg/L of hydrogen peroxide. However, a further increase in the reagent concentration to 800 mg/L resulted in a decline in the oxidation process. This could be attributed to the excess peroxide reagent itself acting as an •OH radical scavenger, rather than a generator. Hence, the Synozol Red-KHL oxidation rate was reduced.
Nonetheless, it is observed that an increase in the amount of reagent resulted in a reduction in OH radicals, reducing the dye oxidation rate. Thus, an enhancement in Synozol Red-KHL oxidation is expected. Nevertheless, hydrogen peroxide behaves more efficiently in the reduction of the dye concentration, as shown in the figure. The role of hydrogen peroxide is to decompose the dye into non-harmful species, thereby reducing its concentration. The presence of hydrogen peroxide in an optimal range enhances the dye oxidation process, as shown in the figure.

**Figure 10.** The effects of the AS-ChMN concentration on the Fenton-like reaction performance.

**Figure 11.** The effects of H₂O₂ loading on the Fenton oxidation system.

The effect of increased hydrogen peroxide is unsurprisingly linked to the generation of a high yield of OH radicals, representing the main species responsible for the oxidation reaction. Thus, an enhancement in Synozol Red-KHL oxidation is expected. Nevertheless, an increase in the amount of reagent resulted in a reduction in OH radicals, reducing the Synozol Red-KHL dye oxidation yield. This might be linked to excess hydrogen peroxide in the reaction medium producing HO₂ radicals, rather than OH radicals. Such radicals cause a decline in the oxidation rate, rather than enhancing Synozol Red-KHL removal. Excess HO₂ radicals might react with hydroxyl radicals and thereby reduce their activity [38,39]. Thus, predictably, the presence of hydrogen peroxide in an optimal...
loading amount improved the oxidation rate, but the removal reaction’s efficiency was reduced when peroxide was overdosed into the system due to the excessive concentration of this reagent resulting in a decline in dye oxidation. The radicals generated were instead perhydroxyl radicals (HO$_2^-$), which are less reactive as compared to OH radicals [38].

### 3.2.4. Effect of pH

A Fenton-like reaction is a pH-dependent system since the pH of the aqueous wastewater environment plays a momentous role in the reaction yield. To examine this role, the Fenton-like oxidation reaction carried out to oxidize the Synozol Red-KHL dye was conducted at various dye solution pH values. Although the Fenton system might work at an acidic pH (3.0), some Fenton systems work at various pH values due to changes in the catalyst’s nature [1]. Thus, the pH was examined within various pH ranges, including acidic (3.0 and 5.0), alkaline, and the original pH of the wastewater (6.3).

The optimal operational pH was examined by changing the dye-containing solution’s pH from 3.0 to 5.0, 6.3, and 8.0, whereas the other operational parameters—the AS-ChMN catalyst dose (1 g/L) and hydrogen peroxide level (400 mg/L)—were kept constant. The data displayed in Figure 12 show that changing the wastewater pH from its original natural value (6.3) to within the acidic range (5.0 and 3.0) enhanced the oxidation efficiency rate. An alkaline pH of 8.0 was not preferred since the resulting removal rate was only 92%. However, even though an acidic pH is favorable, it is noteworthy that all the pH values examined led to the generation of OH radicals. It is notable that pH 3.0 led to complete dye oxidation. This might be associated with the H$_3$O$_2^+$ species, which could be produced within the acidic pH range. This might lead to an increase in peroxide stability. Nonetheless, with an increasing pH value, FeOOH precipitate formed; hence, hydroxyl radical generation was reduced. Accordingly, the data showed that the examined Synozol oxidation was significant and more efficient at pH 3.0. Consequently, pH 3.0 was kept as an optimal value for the remaining experiments of the present investigation. The optimality of this value might be attributed to the *OH radicals being severely scavenged by H$^+$. Hydrogen peroxide is unstable in alkaline media, and it rapidly decomposes to oxygen and water at neutral and higher pH levels. Hence, it loses its capacity to oxidize more efficiently. This was observed in the reduction in the overall oxidation rate from 100% to 92% with an increasing pH. Such results are in agreement with previous data in the literature on treating aqueous effluent using the Fenton reaction [39,40].

### 3.2.5. Effect of Temperature

For industrial and real-world concepts, it is essential to consider the treatment of wastewater discharged at different temperatures, since it might be within various temperature ranges when it is disposed of. Thus, it is crucial to conduct the Fenton-like reaction at various temperature ranges; in this study, the temperature was varied from 28 to 60 °C. According to the data from these experiments, displayed in Figure 13, an elevation in temperature resulted in the deterioration of the Synozol Red-KHL removal rate, which might be linked to the OH yield in the aqueous medium. Room temperature (28 °C) exhibited the highest oxidation yield, extending to complete dye removal (100%) within 25 min of irradiance. Such data could be associated with the temperature elevation causing the rapid reduction of H$_2$O$_2$ to O$_2$ and H$_2$O, rather than generating OH radicals. Such radicals are the main species responsible for the oxidation, and thus, the overall reaction yield is deduced. Also, it is notable that the reaction is exothermic in nature. A previous study [40] showed that an increment in temperature presented a pronounced effect on the oxidation yield; however, others showed that the reaction is exothermic and that a temperature increase results in a decline in the overall efficacy.
3.2.6. Catalyst Stability and Recyclability

In considering the sustainability of the Fenton reaction, verifying the AS-ChMN catalysts’ reusability is essential. The life cycle of the catalytic reaction system was therefore assessed through the AS-ChMN catalysts’ recyclability. AS-ChMNs were recycled after the Fenton-like oxidation test. After each use, AS-ChMNs were collected via filtration and exposed for successive cleaning with distilled water three times, then dried at 105°C in an electric furnace for a duration of 1 h. After drying, the material was ready for reuse. Synozol Red-KHL was oxidized with the recycled material, the remaining dye was examined, and

Figure 12. The effect of pH on the Fenton oxidation reaction.

![Figure 12](image-url)

Figure 13. The effect of temperature on the Fenton oxidation reaction.

![Figure 13](image-url)
the removal percentage was recorded to investigate the treatment adequacy of the recycled material. The data presented in Figure 14 show the sustainability of the AS-ChMN catalysts; the oxidation efficacy decreased from 99% for the fresh catalyst to 90 and 77% after the first and second cycles of reuse, meaning that the AS-ChMN catalyst could still be used to treat the Synozol Red-KHL dye. However, notably, the material became loaded with Synozol Red-KHL dye molecules, which was reflected in the reduction in activity. The activity of the composite until the second cycle shows reasonable sustainability and stability. Such results are in accordance with a previous study [40] that explored the recyclability of a clay substance after use, showing a reduction in its activity. Another previous study [37] showed that copper could be used as a photocatalyst for six successive cycles of use, with a reduction in its activity of only 15% in comparison to its fresh catalyst use.

![Figure 14](image_url)

**Figure 14.** The activity of recycled catalysts in Synozol Red-KHL oxidation.

3.2.7. Kinetic and Thermodynamic Studies

Exploring the reaction kinetics is essential for full-scale applications in a real-world facility. Reaction kinetic statistics supply estimations for both reactor design and process finances. Thus, the dependence of a reaction’s kinetics on temperature effects is established to explore the consideration of an Arrhenius-type reliance on the global kinetic constant on temperature. Zero-, first-, and second-order kinetic models were constructed to fit the experimental data, and the results are tabulated in Table 1. According to the data (Figure 14), a temperature increase resulted in an unfavorable impact on the Synozol Red-KHL removal rate. As seen from Table 1, the highest $R^2$ values (regression coefficient values), used to indicate the significance of the model, corresponded to the second-order kinetic model. Hence, the second-order kinetic model is the most appropriate model to represent the experimental data. The kinetic constants of the second-order model increased and ranged from 0.0092 to 1.0334 L/mg.min as the temperature increased from 28 to 60 °C. Furthermore, the half-life time ($t_{1/2}$) declined as the temperature rose. The lowest $t_{1/2}$ for Synozol Red-KHL oxidation was recorded at a high temperature. Consequently, the second-order model projected the oxidation reaction. Hence, the second-order kinetic model can well describe Synozol dye removal for the examined system. This appropriate fit with the second-order kinetic model reveals that the oxidation reaction between the dye and the AS-ChMN photocatalyst is dependent on the amount of dye adsorbed on the AS-ChMNs’ surface. Furthermore, the second-order kinetic model is not very sensitive to random errors [35]. The model also showed that the half-life time ($t_{1/2}$) increases with
increasing temperature. This might be explained by the increasing temperature enhancing the catalytic activity of the AS-ChMN photocatalyst in the oxidation of Synozol dye and completion of the oxidation reaction [35]. Previous reports in the literature verified that the second-order kinetic model well represents the Fenton-like system.

In order to extend this study to field applications, supportive thermodynamic parameters may be calculated. The thermodynamic variables of oxidation in the modified Fenton-like system based on AS-ChMNs are presented in Table 2 based on the second-order kinetic rate constant. The Arrhenius equation is \( k_2 = Ae^{-\frac{E_a}{RT}} \). Negative values of \( \Delta H' \) demonstrate an exothermic type of reaction. These data confirm a decline in the degree of freedom of the Synozol Red-KHL molecules in addition to a high production yield of OH radicals, thus reducing the oxidation efficiency. The oxidation system reduces the degree of freedom of the dye molecules while maintaining an excess ·OH radical species yield. This is in agreement with results from prior research [37].

3.2.8. The RSM Model Optimization of the Operating Parameters

Initially, a model was established to attain higher Synozol Red-KHL oxidation efficiency in a rational time period with minimal reagent doses. The independent variables and their three levels are displayed in Table 3 according to the preliminary work. Then, statistical analysis software, version 5 (SAS, Institute USA) was applied to explore the full factorial design (as seen in Table 4). Hence, the design was constructed, and the second-order polynomial model was obtained (Equation (2)).

\[
Y(\%) = 97.67 + 4.12\varepsilon_1 + 2.735\varepsilon_3 - 3.08\varepsilon_1^2 + 1.75\varepsilon_1\varepsilon_2 - 2.5\varepsilon_1\varepsilon_3 - 0.833\varepsilon_2^2 - 1.25\varepsilon_2\varepsilon_3 + 0.41\varepsilon_3^2
\]  

(2)

Table 3. The boundaries of the model design for the coded and natural experimental domains and the corresponding levels’ spacing.

<table>
<thead>
<tr>
<th>Experimental Variable</th>
<th>Symbols</th>
<th>Range and Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>( \varepsilon_1 )</td>
<td>Natural</td>
</tr>
<tr>
<td>( H_2O_2 ) (mg/L)</td>
<td>( \varepsilon_2 )</td>
<td>200</td>
</tr>
<tr>
<td>As-ChMNs (mg/L)</td>
<td>( \varepsilon_3 )</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Here, \( Y \) is the predicted Synozol Red-KHL dye oxidation and removal efficiency (dependent parameter response) (%); \( i = 1, 2, 3 \), and \( j = 1, 2, 3 \); \( \beta_{ij}, \beta_i, \beta_j \), and \( \beta_{ij} \) are the model regression coefficient variables; and \( \varepsilon_i \) is the input calculating the coded parameters.

An analysis of variance (ANOVA) was conducted to check the model’s adequacy. In the ANOVA, all model terms, i.e., the sum of squares (SS), mean square (MS), estimated coefficient, standard error, and corresponding \( F \)-value and \( p \)-values, were examined by means of a statistical t-test and are displayed in Table 5. Normally, the model is considered significant and accepted when the \( F \)-value is greater than unity with a small \( p \)-value (<0.05) and a high \( R^2 \) value (coefficient of determination). The recorded \( R^2 \) was 93%, resulting in an assessment of model approval.

To further understand the effect of interacting variables, 3D response surface and 2D contour plots of the Synozol Red-KHL oxidation process were designed. The data are displayed in Figure 15a–c. According to the illustrated plots, the Synozol Red-KHL removal efficacy was steadily enhanced with elevations in both the \( H_2O_2 \) and AS-ChMN reagent doses. This might be attributed to the presence of highly reactive species (·OH radicals) in the aqueous reaction medium with an increase in these reagents’ concentrations. However, after reaching a certain concentration limit for both reagents, the Synozol Red-KHL removal and oxidation were reduced. A proper explanation for this result is linked to the extra dosing of these reagents leading to their action as an OH radical scavenger, rather
than a producer [4]. It is also noteworthy that an acidic pH value is required to produce such radicals. OH radicals are the driving species of oxidation, and their presence is thus required for an optimal reaction rate.

Table 4. The Box–Behnken factorial design in coded and natural values and the corresponding Lanox 90 response of removal by means of effluent oxidation.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Variables</th>
<th>Response (Y)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>H₂O₂ Dose</td>
</tr>
<tr>
<td></td>
<td>Coded</td>
<td>Natural</td>
</tr>
<tr>
<td>1</td>
<td>−1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>−1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>−1</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>−1</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 5. Evaluations of the model regression for Synozol Red-KHL oxidation via AS-ChMN catalyst-based photo-Fenton oxidation *.

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F-Value</th>
<th>p-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>9</td>
<td>6.5</td>
<td>2.090154</td>
<td>9.329449</td>
<td>1.021026</td>
</tr>
<tr>
<td>Linear</td>
<td>3</td>
<td>−0.70833</td>
<td>2.418978</td>
<td>0.402297</td>
<td>1.048941</td>
</tr>
<tr>
<td>Quadratic</td>
<td>3</td>
<td>1.04167</td>
<td>2.707569</td>
<td>2.17839</td>
<td>0.184818</td>
</tr>
<tr>
<td>Cross Product</td>
<td>3</td>
<td>262.9833</td>
<td>29.22037</td>
<td>7.524559</td>
<td>0.019377</td>
</tr>
<tr>
<td>Model</td>
<td>5</td>
<td>19.41667</td>
<td>3.883333</td>
<td>7.524559</td>
<td>0.019377</td>
</tr>
<tr>
<td>Error</td>
<td>14</td>
<td>282.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* R² = 93%; adj R² = 81.

After the main experimental work was conducted, the optimal results were investigated using Mathematica software (V 5.2). The optimal values estimated were 420 mg/L for hydrogen peroxide and 1.5 g/L for AS-ChMNs; the corresponding optimal pH was recorded at a pH of 3.5, with a predicted response of 98% removal. Then, three more replicates of experimental work were conducted to verify the predicted model; these further experiments confirmed the results, and the Synozol Red-KHL removal efficiency reached 99%.

Consequently, the optimum point, as investigated and calculated through the suggested empirical model, was successfully confirmed. Thus, the Box–Behnken design might be a powerful tool for optimizing Synozol Red-KHL oxidation through novel modified photo-Fenton oxidation systems that use recycled waste.

Additionally, to assess the significant species that govern the Fenton reaction’s oxidation system, various scavengers were added to the reaction medium separately to check their independent roles. A scavenger’s solo effect is dependent on its ability to trap and remove a specific active species by its addition. Primarily, the effect of ammonium oxalate was checked by its addition to the reaction medium. The role of ammonium oxalate is to
deteriorate the holes ($h^+$) available in the substance. Such an addition led to a scavenging effect in the reaction, and the oxidation efficiency was reduced to 61%, as compared to 99% removal with no scavenger in effect. Further, isopropanol was added to the reaction medium to evaluate the role of the superoxide radical ($\bullet O_2^−$) in the oxidation reaction. The oxidation reaction rate was reduced to 89%. This is attributed to the terminal effect of the superoxide radical affecting the oxidation reaction. The effect of the hydroxyl radical species was evaluated by scavenging them from the reaction medium by the addition of a benzoquinone scavenger. The result was a strong scavenging effect, and the oxidation reaction reached only 22% in this case. This dramatic decrease in the oxidation reaction is attributed to the significant role of the hydroxyl radicals in photo-oxidation activity. Thus, the major role in dye oxidation is associated with the hydroxyl radical, but a minimal effect is related to the $\bullet O_2^−$ radical. The presence of holes in the photocatalyst might also increase the efficiency.

![Figure 15](image_url)

**Figure 15.** Factorial model design for optimal Synozol Red-KHL oxidation: 3D surface and 2D contour plots of the (Y) response and the interacting effects of (a) the pH and $H_2O_2$ dose, (b) the pH and AS-ChMN catalyst dose, and (c) the $H_2O_2$ dose and AS-ChMN catalyst.

4. Conclusions

In the present investigation, a feasible way to treat wastewater containing Synozol Red-KHL was introduced based on a win–win strategy. Aluminum-based sludge conditioned with chitosan coated with magnetite nanoparticles, then dewatered and dried (AS-ChMNs), was used as a catalyst source for Fenton’s reaction. The reaction time, reagent doses, and pH were investigated, and the response surface methodology was applied to optimize the dependent parameter. The photocatalyst oxidation reaction revealed that a pH of 3.5 and amounts of 420 mg/L and 1.5 g/L for hydrogen peroxide and the AS-ChMN catalyst,
respectively, are the optimal operating conditions, resulting in 99% Synozol Red-KHL dye removal. The results show that although an acidic pH is favorable, the reaction can still proceed within various pH ranges. However, a cumulative dye concentration in the reaction medium results in a reduction in the overall oxidation rate. The kinetics and thermodynamics of the reaction were assessed, and the data signified that the reaction displays second-order kinetics with an energy barrier of \(-89.71 \text{ kJ/mol}\). Thus, this work confirms that conditioned alum sludge can be used as a sustainable photocatalyst for the green treatment of textile effluent. The experimental results derived from this study may lead to great advances in the future for real industrial application prospects and are believed to be a valuable addition to the knowledge base for real-world textile facilities. However, further research is required on the initiative fabrication of composite substances with targeted properties for real-world applications; such research was not within the scope of this study but is currently underway.

Author Contributions: Conceptualization, M.A.T.; Methodology, M.M.N., Z.A.E. and M.A.T.; Validation, Z.A.E.; Writing—original draft, M.M.N. and Z.A.E.; Writing—review & editing, M.M.N. and M.A.T. All authors have read and agreed to the published version of the manuscript.

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