ABSTRACT: Catalytic degradation of organic water pollutants has emerged as a cost- and energy-effective technique to treat wastewater. In this work, new silver and magnetite nanoparticles (NPs) were prepared with a protic poly(ionic liquid) (PIL) based on a quaternized diethylethanolamine cation combined with 2-acrylamido-2-methylpropane sulfonate-co-vinylpyrrolidone (QAMPSA/VP) as a capping and a reducing agent. The morphology, particle size, surface charge, thermal stability, and magnetic properties of QAMPS/VP-Ag and Fe₃O₄ NPs were investigated to determine the efficiency of the PIL as a reducing and a capping agent to protect the produced NPs from oxidation or thermal degradation. The activation energy, enthalpy, and entropy of the catalytic degradation of the cationic methylene blue (MB) dye in the presence of QAMPS/VP-Ag and Fe₃O₄ NPs were determined. The data elucidated that MB was completely degraded in 8 min in the presence of QAMPS/VP-Fe₃O₄ NPs as a Fenton oxidation catalyst. Moreover, their good magnetic properties allowed their easy separation and reuse for five cycles without losing their magnetic or catalytic properties.

1. INTRODUCTION

Ionic liquids (ILs) and their polymers (PILs) are environmentally friendly organic salts with low vapor pressure and melting temperature, high thermal stability, and no toxicity. They are widely used to prepare inorganic metal and metal oxide nanoparticles (NPs) with controlled sizes and shapes. They are used as solvents or cosolvents as well as reducing and capping agents. They are used to prepare nanomaterials using different techniques, such as coprecipitation, sol−gel, hydrothermal, and ray-mediated methods (ultrasound, microwave, ultraviolet (UV), and γ irradiation). The widely used ILs and PILs are based on dialkyl imidazolium cations combined with fluoroborate, fluorophosphate, or bis-(trifluoromethylsulfonyl) imide anions because they possess good transport properties and low viscosity. They also have low melting temperatures. It is reported that the formation of nanoparticles depends on the types of cations and anions for both ILs and PILs. Amphiphilic ILs and PILs have attracted great attention due to their strong interaction with nanomaterials. Also, they act as cosolvents in the synthesis of nanomaterials via an IL-assisted synthesis route. ILs and PILs having quaternary ammonium cations combined with acrylate anions are widely used as amphiphiles to prepare nanomaterials.

Nanomaterials based on metal and metal oxides and their nanocomposites are widely used as adsorbents, filters, membranes, and fibers for water treatment and desalination. They have advantages over other materials due to their higher surface area, selectivity, and photocatalytic and antimicrobial activity. The lower energy cost, chlorine-free water treatment, superparamagnetism, and growth inhibition of microorganisms are preferred characteristics for applying metals and metal oxides instead of organic nanostructured materials for water desalination and purification. Nanostructured materials based on metals, metal oxides, and metal−organic frameworks that are capable of adsorptive and photocatalytic removal of organic and inorganic pollutants have emerged as energy- and cost-effective materials.
nanomaterials that are responsive to the surrounding environmental stimuli (pH, temperature, and magnetic and electric fields) are favored for application in wastewater remediation, purification, and desalination.\textsuperscript{22–25} In this respect, iron oxide, silver, graphene, and titanium nanomaterials have received much attention for wastewater treatment due to their biocompatibility, large surface area, good dispersibility in aqueous systems, high adsorption and catalytic activity, and their easy separation by applying an external electric or magnetic field. It was previously reported that magnetite and silver nanomaterials have catalytic activity to oxidize and degrade organic water pollutants with the formation of side products.\textsuperscript{26–28} Moreover, magnetic polymer composites were used as adsorbents to purify water from organic and inorganic pollutants.\textsuperscript{30–33} In this work, a new protic poly(ionic liquid) (PIL) based on a quaternized dialkylethanolamine cation combined with 2-acrylamido-2-methylpropane sulfonate-co-vinylpyrrolidion (QAMPSA/VP) was used as a capping and a reducing agent to prepare silver and magnetite nanoparticles with high catalytic activity to degrade the cationic methylene blue (MB) dye, an organic water pollutant. The work aims to use the prepared QAMPSA/VP as a reducing agent due to the presence of the VP moiety, which can act as a capping and a reducing agent to prepare silver and magnetite nanoparticles without using toxic reducing agents. It is also expected that QAMPSA/VP-Fe3O4 and QAMPSA/VP-Ag NPs will have negative surface charges on their surfaces due to the presence of sulfonate groups of the AMPsA moiety. These charges will facilitate the electrostatic attraction of MB and improve the catalytic activity of Ag NPs or magnetite. Moreover, the good thermal and chemical stability, and the antimicrobial activity of Ag NPs based on QAMPSA/VP-Ag as PILs will enhance their catalytic activity to reduce MB. The investigation of optimum conditions applied to produce nanoparticles having high catalytic activity to degrade MB without the formation of intermediates in a short time is the main aim of this study. Moreover, the MB degradation mechanism, kinetics, and thermodynamics in the presence of magnetite or silver nanomaterials are investigated to determine the catalytic activity of QAMPSA/VP as a PIL.

2. EXPERIMENTAL SECTION

2.1. Materials. N-Vinylpyrrolidone (VP), diethyleneamine (DEEA), and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) monomers were purchased from Sigma-Aldrich Chemical Co. and used as received. Anhydrous FeCl3, KI, and AgNO3 were used as reagents and sources for iron and silver cations. N,N-Azobisisobutyronitrile (AIBN) was used as a radical initiator.

2.2. Preparation Technique. 2.2.1. Synthesis of Poly(ionic liquid). A mixture of equal molar ratios (1:1 mol %) of AMPS and VP (6 mmol of each monomer) was vigorously stirred with 6 mmol DEEA under a nitrogen atmosphere at 10 °C in a flask for 5 h to complete dissolution of AMPS in VP and DEEA solutions. The formation of the quaternized DEEA organic salt with the AMPS monomer was confirmed by the formation of a transparent solution. The AIBN initiator (0.08 mmol) was added to the reaction mixture under nitrogen bubbling, and the mixture was heated to 443 K for 24 h. The viscosity of the mixture increased with the appearance of a transparent light yellow oil. The mixture was precipitated from acetone into cold diethyl ether (dry ice/acetone bath) and the milky solution formed was centrifuged at 15 000 rpm for 20 min. The obtained precipitate was washed several times with ethanol to remove aggregates and organic impurities.

2.2.2. Synthesis of QAMPSA/VP-Fe3O4 Nanoparticles. Silver nitrate (0.25 g) was dissolved in 100 mL of water. QAMPSA/VP (1 g) was dissolved in 40 mL of water and added dropwise to the silver nitrate solution under stirring for 1 h. The reaction temperature was increased to 323 K and maintained for another 1 h to produce a reddish brown colored solution. The reaction mixture was cooled at room temperature, and the mixture to determine the residual concentration (C0) of MB at 313 K to remove any residual volatile materials to obtain the QAMPSA/VP polymer with high yield (98.7%).

2.2.3. Synthesis of QAMPSA/VP-Ag Nanoparticles. A solution of iron cations was prepared by mixing KI solution (0.33 g dissolved in 1.5 mL of distilled water) with an anhydrous FeCl3 (1 g dissolved in 30 mL of distilled water) solution for 1 h under a nitrogen gas atmosphere. The precipitated iodine was filtered from the reaction mixture. QAMPSA/VP (2 g) was dissolved in 10 mL of water and added dropwise to the filtrate of iron cations, and the reaction temperature was increased to 333 K to produce a black solution after 3 h. The QAMPSA/VP-Fe3O4 NPs were separated after the black solution was centrifuged at 15 000 rpm for 20 min, washed several times with ethanol, and air-dried at room temperature.

2.3. Characterization. The chemical structure of QAMPSA/VP was confirmed by 1H and 13C NMR analyses using a 400 MHz Bruker Avance DRX-400 spectrometer. The morphology of QAMPSA/VP-Fe3O4 and QAMPSA/VP-Ag NPs was investigated using a transmission electron microscope (TEM, JEOL JEM-2100 F). The TEM sample was prepared by placing a dilute drop of aqueous particles onto copper grids and allowing it to dry. The particle sizes were determined by dynamic light scattering (DLS) using a Malvern Instruments Zetasizer (model 2000) in aqueous solution in the presence of KCl (0.01 M) in solutions of different pH values. The ζ-potentials were determined using a laser zeta meter (Malvern Instruments model 2000 Zetasizer). The thermal stability and Ag or Fe3O4 contents of QAMPSA/VP-Fe3O4 and QAMPSA/VP-Ag were evaluated by thermogravimetric analysis (TGA; TGA-50 Shimadzu) using a nitrogen gas atmosphere at a flow rate of 50 mL min\(^{-1}\) and a heating rate of 283 K min\(^{-1}\). A vibrating sample magnetometer (VSM; USALD9600-1) was used to evaluate the magnetic properties of QAMPSA/VP-Fe3O4.

A double-beam ultraviolet–visible (UV–vis) spectrophotometer (Shimadzu model UV-1208) was used to determine the surface plasmon resonance (SPR) peak at maximum wavelength \(\lambda_{\text{max}}\) (400 nm) of QAMPSA/VP-Ag NPs.

2.4. MB Catalytic Degradation. The QAMPSA/VP-Fe3O4 NPs were used as the catalyst for Fenton oxidation of MB. In this respect, QAMPSA/VP-Fe3O4 (2.5 g L\(^{-1}\)) was suspended into water (100 mL containing 10 mg L\(^{-1}\) MB, 0.029 mol L\(^{-1}\) as initial concentration \(C_0\) using ultrasonication. HCl (0.5 mL of 6 M) and hydrogen peroxide (4 mL of 30%) were added to the QAMPSA/VP-Fe3O4 suspension. The flask containing the MB solutions was closed and stirred with a magnetic stirrer over a time period, and samples (1 mL) were withdrawn after separation of QAMPSA/VP-Fe3O4 particles with an external magnet every 2 min from the mixture to determine the residual concentration (C) of MB at 662 nm. The catalytic efficiency (CE%) was determined
as CE% = [(C0 − Ct)/C0] × 100/C0. The reproducibility of the results was tested randomly under the experimental conditions.

The reusability of QAMPSA/VP-Fe3O4 for several cycles was evaluated after separation of the catalyst by an external magnet followed by washing with distilled water and ethanol. The solid QAMPSA/VP-Fe3O4 was dried in air and reused in another cycle, as mentioned above.

The QAMPSA/VP-Ag NPs were used as the catalyst for the reduction of MB. In this respect, QAMPSA/VP-Ag NPs (40 μL of 1400 mg L−1) were dispersed in water (100 mL) using ultrasonication. NaBH4 (4 mL of 1000 mg L−1) and MB (40 μL of 500 mg L−1 solution) were added to the QAMPSA/VP-Ag NP suspension. The conversion of MB from the oxidized to the reduced form was monitored using a UV−vis spectrometer at 662 nm.

A blank sample was prepared in the absence of QAMPSA/VP-Fe3O4 or QAMPSA/VP-Ag NPs under the same experimental conditions.

3. RESULTS AND DISCUSSION

The PILs produced from the copolymerization of polymerizable QAMPSA, quaternized diethylethanolamine 2-acrylamido-2-methyl propane sulfonate, with VP using AIBN as the initiator are represented in Scheme 1. The quaternization of DEE with AMPS is carried out to prevent the hydrolysis of the VP monomer during copolymerization with AMPS.34 The mixing molar ratio of QAMPSA and VP is 1:1 (mol/mol). The chemical structure of QAMPSA/VP is elucidated from 1H and 13C NMR spectra, as represented in Figure 1a,b, respectively. The 1H NMR spectrum, Figure 1a, elucidates the disappearance of vinyl protons of AMPS or VP peaks at chemical shifts (δ) 6.03 (dd, 1H, J = 17.1 Hz), 5.94 (dd, 1H, J = 17.1 Hz), and 5.49 ppm (dd, 1H, J = 3.06 Hz) and the appearance of new peaks of polymerized protons −CH2−CH− at δ 1.2 and 3.2 ppm, respectively. It is also confirmed from the disappearance of peaks from its 13C NMR spectrum, Figure 1b, at 122−130 ppm with the appearance of the new peaks of methylene protons (CH2) at 32.8 ppm and methine group (CH−) at 42.3 ppm.35 The new peak at 60.06 ppm (Figure 1b; C−N+) implies the quaternization of DEEA with AMPS. The 1H NMR spectrum of QAMPSA/VP, Figure 1a, also confirms the appearance of a new broad peak at δ 9.11 and the disappearance of a peak at 7.16, attributed to cationic NH glass-transition (Tg; °C) and melting temperatures (Tm; °C) are −68.9 and 41.3 °C, respectively. The low Tg and Tm values below zero and 100 °C elucidate the formation of the PIL of QAMPSA/VP rather than polyelectrolyte PAMPS and AMPS/VP, which have Tg values at 108 and 120 °C, respectively.35 The flexible AMPS/VP chains of the prepared PIL confirm the absence of hydrogen bonding of AMPS with VP due to
quaternization that shields the Coulombic interactions of the QAMPSA/VP polymer backbone.36,37

3.1. Synthesis and Characterization of Coated Magnetite and Ag NPs with QAMPSA/VP. Magnetite and Ag NPs are prepared without using a reducing or an oxidizing agent, and QAMPSA/VP is used as a capping and a reducing agent, as reported in Section 2 and represented in Schemes 2 and 3. The mechanism for producing magnetite nanoparticles without using an alkaline solution is represented in Scheme 2. Ultrapure water produced hydroxyl ferrous, and the ferric cations linked with the sulfonate anions and amide groups of QAMPSA/VP as a stable ligand to surround their surfaces.38 The gentle heating of QAMPSA/VP facilitated the hydrolysis of the hydroxyl iron cations to form the Fe₃O₄ NPs. HCl (Scheme 2) stabilized the protic QAMPSA/VP, which acted as an acid acceptor.39 The sulfonate groups interacted with the positive charges of either iron cations or Ag cations by ionic interactions followed by the oxidation of the hydroxyl groups of DEEA to aldehyde groups, and the Ag cation reduced to Ag(0) NPs (Scheme 3). The presence of VP facilitated the chemical capping of Ag(0) NPs by O−Ag bonding.40,41

The chemical structure of QAMPSA/VP-Fe₃O₄ was elucidated from the Fourier transform infrared (FTIR) spectrum represented in Figure 3. The formation of magnetite nanoparticles without oxidation to other iron oxides is confirmed from the appearance of a strong band at 585.2 cm⁻¹, attributed to Fe−O stretching.42 The formation of the hydroxyl groups on the surface of magnetite is confirmed from the appearance of broad bands at 3414.87 and 1630.3 cm⁻¹, attributed to OH stretching vibrations.42 The appearance of bands at 2924.23, 1706.37, 1516.97, and 1052 cm⁻¹ assigned for CH₂, CONH, C=N, and S=O stretching confirms the capping of magnetite nanoparticles with QAMPSA/VP, as represented in Scheme 2. The formation of Ag NPs without Ag₂O is confirmed by using UV−vis analysis, as represented in Figure 4. The presence of a strong absorption band at 415 nm is assigned to an Ag surface plasmon, without a shoulder band below 400 nm. The sharp band elucidates the formation of dispersed Ag NPs without the formation of aggregates or Ag₂O nanoparticles.43

The crystal lattice structures of QAMPSA/VP-Ag and QAMPSA/VP-Fe₃O₄ are confirmed from X-ray diffraction (XRD), as shown in Figure 5a,b. The diffraction peaks of QAMPSA/VP-Fe₃O₄ (Figure 5b) assigned to the (220), (311), (400), (422), (511), (440), and (533) planes reflect the formation of pure magnetite without the formation of other iron oxides, such as maghemite or hematite.42 These data confirm the stability of magnetite nanoparticles against oxidation with oxygen in air due to their capping with QAMPSA/VP. It is also elucidated that the appearance of diffraction peaks as the (111), (200), (220), (311), and (331) planes for the QAMPSA/VP-Ag diffractogram (Figure 5a) confirms the formation of near-spherical of face-centered cubic (fcc) Ag NPs without silver oxide nanoparticles.43 The overwhelmingly intense peak at a 2θ value of 38.02° is related to the (111) fcc plane, whereas other peaks related to other lattice planes are quite weak, indicating that the (111) planes of Ag NPs are highly oriented, parallel to the supporting substrate.43 These data elucidate that the PIL based on QAMPSA/VP can control the shape dimensions of the prepared Ag NPs and protect them from oxidation or silver ion formation.

It is important to determine the percentage of capping of magnetite or silver nanoparticles with QAMPSA/VP, which can be estimated from their TGA thermograms, as shown in

Scheme 2. Synthesis of QAMPSA/VP-Fe₃O₄ NPs
Scheme 3. Synthesis of QAMPSA/VP-Ag NPs

Figure 3. FTIR spectrum of QAMPSA/VP-Fe₃O₄ NPs.

Figure 4. UV–vis spectrum of QAMPSA/VP-Ag NPs.

Figure 6. The remaining weight above 650 °C is used to determine the nondegraded or oxidized magnetite and silver by thermal heating under a nitrogen atmosphere (Figure 6). The contents of magnetite and silver are 19.2 and 39.4 wt %, respectively (Figure 6). The free water content of QAMPSA/VP increased from 3.6 to 5.8 and decreased to 2.8 wt % with
incorporation of Fe$_3$O$_4$ and Ag NPs, respectively (Figure 6), as observed from their weight losses below 100 °C. This observation confirmed the formation of hydroxyl groups at the surface of magnetite and the interaction of Ag NPs with the amide groups of QAMPSA/VP, as shown in Schemes 2 and 3.

The morphologies of QAMPSA/VP-Ag and QAMPSA/VP-Fe$_3$O$_4$ are further examined by TEM, as shown in Figure 7a,b. The TEM micrograph of QAMPSA/VP-Ag (Figure 7a) shows a near-spherical morphology with a mean diameter of 35 ± 10 nm and with numerous phases. The TEM micrograph of Ag NPs (Figure 7a) confirms the good dispersion of QAMPSA/VP-Ag to elucidate their capping with the charged PIL based on QAMPSA/VP. QAMPSA/VP-Fe$_3$O$_4$ (Figure 7b) shows a spherical morphology with some agglomerates and networks to confirm the linking of iron cations of magnetite inside the PIL, which has a flexible network by polar interactions to produce a stable hydrosol (Scheme 2). The particle sizes of QAMPSA/VP-Fe$_3$O$_4$ and QAMPSA/VP-Ag were measured in aqueous solutions at different pH values and are represented in Figure 8a–c. The polydispersity index (PDI) and particle size diameters are determined using DLS, as summarized in Figure 8a–c, to confirm that the QAMPSA/VP-Ag NPs are more dispersed than QAMPSA/VP-Fe$_3$O$_4$ NPs, which agrees with the TEM data (Figure 7).

The effect of pH on the stability, particle size, and surface charge of the QAMPSA/VP-Fe$_3$O$_4$ and QAMPSA/VP-Ag NPs is investigated from their DLS and $\zeta$-potential measurements, as represented in Figures 8a–c and 9a,b respectively. The low particle size and PDI of both Ag and Fe$_3$O$_4$ NPs at pH 4 (Figure 8a) verify the high stability of the prepared materials at low pH. This kind of stability is due to the strong capping of the protic PIL (QAMPSA/VP), which prevents the degradation of nanomaterials in acidic medium. The increasing PDI and diameters of both QAMPSA/VP-Fe$_3$O$_4$ and QAMPSA/VP-Ag NPs above pH 7 elucidated the capping of the prepared nanoparticles with protic QAMPSA/VP, which deprotonated in basic medium and agglomerated the magnetite and silver nanoparticles, as represented in Figure 7c. It is also observed that magnetite NPs were highly agglomerated compared to Ag NPs due to the lower content of QAMPSA/VP on the surface of magnetite, as determined from TGA thermograms (Figure 6). The values of $\zeta$-potential of QAMPSA/VP-Fe$_3$O$_4$ and QAMPSA/VP-Ag NPs at pH 7 are −31.21 and −41.82 mV, respectively, which prove the good dispersion of the coated nanoparticles in aqueous medium because they possess a more negative value than 25 mV. The negative charges of both QAMPSA/VP Fe$_3$O$_4$ and QAMPSA/VP-Ag NPs (Figure 9a,b) indicate that the sulfonate anions of QAMPSA/VP are oriented to the exterior surface of nanoparticles and DEE ammonium cations are oriented to the interior surfaces of nanoparticles.

The magnetic characteristics of the prepared QAMPS/VP-Fe$_3$O$_4$ NPs were evaluated using a vibrating sample magnetometer (VSM) at room temperature, and their magnetic hysteresis loop is shown in Figure 10. Their saturation magnetization (emu g$^{-1}$), remanent magnetization (emu g$^{-1}$), and coercivity (G) values are 73.41, 0.190, and 9.04, respectively. The higher value of saturation magnetization and lower values of remanent magnetization and coercivity elucidate the formation of superparamagnetic magnetite nanoparticles in the presence of QAMPSA/VP as the PIL. The higher magnetite content of QAMPSA/VP-Fe$_3$O$_4$ (80.8 wt %; Figure 6) elucidates the superparamagnetic characteristics in the presence of QAMPSA/VP. The good superparamagnetic characteristics of QAMPSA/VP-Fe$_3$O$_4$ facilitate its application and rapid separation with the assistance of an external magnet in different environments.

3.2. Catalytic Activity of QAMPSA/VP-Ag for MB Reduction. The cationic MB dye is one of the water pollutants, which consumes the dissolved oxygen in water and endangers the aquatic system. In the present work, negatively charged magnetite and Ag NPs capped with the PIL based on QAMPSA/VP are used as catalysts to remove a low concentration of MB by the degradation, reduction, or oxidation reaction. Silver nanoparticles, embedded into polymeric microgels or coated with extracts, were previously used as a catalyst in the reduction reaction of MB using NaBH$_4$. The kinetics of the catalytic reduction of MB using QAMPSA/VP-Ag NPs is investigated using UV–vis spectroscopy by following the complete disappearance of the maximum absorption wavelength of MB ($\lambda_{max} = 662$ nm), which does not overlap with the SPR peak of Ag NPs at 415 nm. The catalytic performance of QAMPSA/VP-Ag was investigated using the UV–vis spectra of MB, as plotted in Figure 11a,b. The spectra indicate that the presence of
QAMPSA/VP-Ag reduces the intensity of the MB bands at a λ\textsubscript{max} of 662 nm and the band disappears completely in 12 min. It was also noticed that the MB color changed from blue to colorless. In the absence of QAMPSA/VP-Ag NPs, the MB concentration was reduced by 50 wt % in 24 h without discoloration of the MB aqueous solution, confirming the catalytic performance of QAMPSA/VP-Ag NPs. Pseudo-first-order kinetics is used to determine the catalytic rate as explained in eq 1

\[ \ln(C_t/C_0) = k_{app}t \]  

where \( C_0 \) and \( C_t \) are the initial MB concentration and the MB concentration at different time intervals, apparent reaction rate constant, and time taken for MB removal in the presence of NaBH\(_4\) and QAMPSA/VP-Ag NPs. The relations between \( \ln(C_t/C_0) \) and \( t \) at different temperatures (\( T; K \)) are plotted in Figure 12; the \( k_{app} \) (min\(^{-1}\)) values are determined from the slope of the curves and are summarized in Table 1. The relation between \( \ln(k_{app}) \) and \( 1/T \) is plotted in Figure 13a to determine the catalytic activation energy \( (E_a; \text{kJ mol}^{-1}) \) according to the Arrhenius eq 2

\[ \ln(k_{app}) = \ln A - (E_a/RT) \]  

where \( A \) and \( R \) are the pre-exponential factor and ideal gas constant \((R = 1.897 \times 10^{-3}\text{ kcal K}^{-1}\text{ mol}^{-1})\), respectively. The \( E_a \) value for the catalytic reduction of MB in the presence of QAMPSA/VP-Ag NPs is 28.95 kJ mol\(^{-1}\), which is smaller than the reported values in the literature\(^{47,48}\). This value confirms the fast catalytic reduction reaction rates (Table 1), which increase with increasing reaction temperature. The relation between \( \ln(k_{app}/T) \) and \( 1/T \) is plotted in Figure 13b to calculate the activation enthalpy \( (\Delta H^\#; \text{kJ mol}^{-1}) \) and entropy \( (\Delta S^\#; \text{J mol}^{-1} \text{ K}^{-1}) \) using the Eyring eq 3

\[ \ln(k_{app}/T) = \ln(k_b/h) + (\Delta S^\#/R) - (\Delta H^\#/RT) \]  

where \( k_b \) and \( h \) are the Boltzmann and Planck constants, respectively. The calculated \( \Delta H^\# \) and \( \Delta S^\# \) values (Figure 13b; from the slope and intercept) are 26.65 kJ mol\(^{-1}\) and \(-168.8\); J mol\(^{-1}\) K\(^{-1}\), respectively. The lower \( E_a \) and \( \Delta H^\# \) and more negative \( \Delta S^\# \) values of the present system using QAMPSA/VP-Ag NPs as a catalyst for catalytic reduction compared with the reported values using Ag NPs in the literature\(^{47-49}\) elucidate the simplicity of the present system to act as a fast

**Figure 7.** TEM micrographs of (a) QAMPSA/VP-Ag and (b) QAMPSA/VP-Fe\(_3\)O\(_4\) NPs.
reducing catalyst. It can also be concluded that the QAMPSA/VP-Ag NPs act as an electron relay, where BF$_4^-$ acts as an electron donor to Ag NPs and MB accepts the electron from Ag NPs to convert into the colorless reduced form. The presence of QAMPSA/VP as the PIL facilitates the interactions of both BF$_4^-$ anions and MB as cations with the PIL since it contains both sulfonate anions and DEE ammonium cations (Schemes 2 and 3). The presence of amide groups of VP and QAMPS in the chemical structure of QAMPSA/VP facilitates the transfer of electrons from BF$_4^-$ anions to MB cations, which increases with increasing temperature due to the higher thermal activity of PILs. Accordingly, it can also be concluded that the $k_{app}$ of the QAMPSA/VP-Ag NPs follows an Arrhenius-type dependence on temperature.

3.3. Fenton Oxidation of MB Using QAMPSA/VP-Fe$_3$O$_4$. Application of magnetite-based materials as a catalyst for the oxidation of organic pollutants in the presence of H$_2$O$_2$ using the Fenton mechanism was previously reported. The produced hydroxide or peroxide radicals from the oxidation of ferrous or the reduction of ferric cations, respectively, were used as initiators to decompose the organic pollutants to intermediates or to degrade the organic pollutants to carbon dioxide, water, and inorganic salts if the pollutants contained heteroatoms such as MB. In the present system, the pH and temperature of the MB aqueous solution are adjusted at pH 4 and desired temperatures (298–333 K), followed by the addition of magnetite and hydrogen peroxide of different concentrations. The concentration of QAMPSA/VP-Fe$_3$O$_4$ ranged from 2500 to 3500 mg L$^{-1}$, and the concentration of H$_2$O$_2$ ranged from 0.155 to 0.456 M. The complete degradation of MB without the formation of any intermediate is examined by the disappearance of the peak at 662 nm related to MB without the formation of other peaks, as represented in Figure 8. 

![Figure 8. DLS data of QAMPSA/VP-Fe$_3$O$_4$ and QAMPSA/VP-Ag NPs at different pH values of (a) 4, (b) 7, and (c) 9 in aqueous solutions with 0.001 M KCl at a temperature of 298 K.](https://dx.doi.org/10.1021/acsomega.9b03610)
the UV–vis spectra in Figure 14a,b. The degradation results of MB in the absence and presence of QAMPSA/VP-Fe₃O₄ at a temperature of 318 K in aqueous solution (Figure 14a,b)
revealed that MB was not degraded even after 24 h in the absence of QAMPSA/VP-Fe₃O₄ and completely degraded in 35 min in the presence of QAMPSA/VP-Fe₃O₄ (Figure 14b). The optimum QAMPSA/VP-Fe₃O₄ and H₂O₂ concentrations and catalytic reaction temperature for the degradation of MB can be determined from Figure 15a. The data elucidate that the optimum QAMPSA/VP-Fe₃O₄ (Figure 15a) and H₂O₂ (Figure 15b) concentrations to completely degrade MB in aqueous solution are 3500 mg L⁻¹ and 0.31 M, respectively. The data (Figure 15c) also elucidate that MB was degraded in the presence of QAMPSA/VP-Fe₃O₄ and H₂O₂ to a greater extent than with QAMPSA/VP-Fe₃O₄ and only H₂O₂. The effect of catalytic temperature on the degradation of MB in aqueous solution using QAMPSA/VP-Fe₃O₄ (3500 mg L⁻¹) and H₂O₂ (0.31 M) (Figure 15d) confirms that the optimum temperature of 318 K is enough to degrade MB in 10 min.

Kinetics of MB catalytic degradation in the presence of different concentrations of QAMPSA/VP-Fe₃O₄ and at different temperatures are estimated according to pseudo-first-order kinetics (eq 1) and are summarized in Figure 16a,b. The k_{app} (min⁻¹) values for catalytic MB degradation in the presence of QAMPSA/VP-Fe₃O₄ are summarized in Table 1. The values of E_a (kJ mol⁻¹), ΔH° (kJ mol⁻¹), and ΔS° (J mol⁻¹ K⁻¹) were determined from eqs 2 and 3 derived from the relations plotted in Figure 17a,b. The E_a, ΔH°, and ΔS° values for MB degradation in the presence of QAMPSA/VP-Fe₃O₄ are 88.93 kJ mol⁻¹, 86.30 kJ mol⁻¹, and 0.665 J mol⁻¹ K⁻¹, respectively. By comparing the present system with reported data for using magnetite-based catalysts for dye degradation.

**Table 1. Catalytic Degradation Constant k_{app} of MB Using QAMPSA/VP-Fe₃O₄ and QAMPSA/VP-Ag NPs at Different Temperatures and Concentrations**

| catalyst          | temperature (K) | k_{app} (min⁻¹) | concentrations (mg L⁻¹) | k_{app} (min⁻¹) |
|-------------------|-----------------|-----------------|-------------------------|-----------------|
| QAMPS/VP-Fe₃O₄   | 303             | 0.0237          | 2500                    | 0.0032          |
| QAMPS             | 318             | 0.3296          | 3000                    | 0.0038          |
| QAMPS/VP-Fe₃O₄   | 323             | 0.3829          | 3500                    | 0.0037          |
| QAMPS/VP-Fe₃O₄   | 333             | 0.5075          |                         |                 |
| Fe₃O₄ QAMPS/VP-Ag| 298             | 0.101           | 50                      | 0.0053          |
| Fe₃O₄ QAMPS/VP-Ag| 303             | 0.138           | 100                     | 0.1011          |
| Fe₃O₄ QAMPS/VP-Ag| 308             | 0.164           | 200                     | 0.1125          |
| Fe₃O₄ QAMPS/VP-Ag| 313             | 0.205           | 250                     | 0.1354          |
| Fe₃O₄ QAMPS/VP-Ag| 318             | 0.260           |                         |                 |

Figure 12. Plot of ln(Ct/C₀) against reaction time for the catalytic reduction of MB with QAMPSA/VP-NPs at different temperatures.

Figure 13. Plots of (a) ln k_{app} and (b) ln(k_{app}/T) versus 1/T for QAMPSA/VP-Ag NPs in the temperature range of 303–333 K.

Figure 14. UV–vis curves of MB solution in the presence of H₂O₂ (a) absence and (b) presence of QAMPSA/VP-Fe₃O₄ at 25 °C.
degradation, it is found that the presence of QAMPSA/VP on the surface of Fe₃O₄ NPs increases their chemical and thermal stability to completely degrade MB in a short time of 8−12 min at 318 K. Moreover, the presence of HCl combined with protic QAMPSA/VP (Scheme 2) enhances the catalytic degradation rate of MB. The recovered QAMPSA/VP-Fe₃O₄ by an external magnet is reused to degrade MB. The catalytic activity of QAMPSA/VP-Fe₃O₄ was not changed for four cycles and decreased with magnetite leaching and loss of magnetic characteristics after seven cycles. The present QAMPSA/VP-Fe₃O₄ system achieved promising results although the research in this field is still incipient. These data elucidate that the capping of magnetite NPs with

Figure 15. Plot of $C_t/C_0$ against reaction time for the catalytic reduction of MB at different concentrations of (a) QAMPSA/VP-Fe₃O₄ NPs and (b) H₂O₂, (c) optimum concentrations of QAMPSA/VP-Fe₃O₄ NPs and H₂O₂, and (d) different temperatures.

Figure 16. Plot of ln($C_t/C_0$) against reaction time for the catalytic reduction of MB at different (a) QAMPSA/VP-Fe₃O₄ NP concentrations and (b) temperatures.

Figure 17. Plots of (a) $ln(k_{app})$ and (b) $ln(k_{app}/T)$ versus $1/T$ for QAMPSA/VP-Fe₃O₄ in the temperature range of 303−333 K.
QAMPSA/VP prevents their leaching and improves their thermal and chemical stability.

3.4. Reusability and Mechanism of MB Degradation Using QAMPSA/VP-Fe₃O₄. The reusability of QAMPSA/VP-Fe₃O₄ for the catalytic degradation of MB was evaluated for seven cycles under the same conditions as mentioned in the Section 2. The relation between CE% and reuse time of QAMPSA/VP-Fe₃O₄ for the catalytic degradation of MB is presented in Figure 18. The data confirm that the CE% of QAMPSA/VP-Fe was not affected and it retains a high CE% after seven cycles. These data elucidate that the presence of QAMPSA/VP as capping for magnetite NPs protects their oxidation and leaching as iron cations, which stabilizes the remaining active sites of the QAMPSA/VP-Fe₃O₄ catalyst.

It is previously reported that the possible mechanism for degradation of MB in the presence of H₂O₂ and Fe²⁺ is based on the production of hydroxyl radicals (•OH) followed by the oxidation of Fe(II) to Fe(III) (Fenton process). The very reactive oxidizing free radicals, hydroxyl radicals, are responsible for the degradation of the double bonds of reactive dyes. The presence of the VP moiety in the chemical structure of QAMPSA/VP-Fe₃O₄ increases the stability of magnetite for an extensive period of time due to the formation of chemical bonds between VP and magnetite. The presence of VP reduces Fe(III) to Fe (II) as an effective reducing agent and stabilizes their ratios in magnetite during the Fenton oxidation reaction.

4. CONCLUSIONS

A new PIL of quaternized diethylethanol ammonium combined with sulfonate of the AMPS/VP copolymer was used as a capping and a reducing agent to synthesize a new catalyst based on Fe₃O₄ and Ag NPs. The QAMPSA/VP-Ag and QAMPSA/VP-Fe₃O₄ NPs show good thermal and chemical stability to protect Ag and Fe₃O₄ from further oxidation. The thermal stability data elucidate that the contents of magnetite and silver were 19.2 and 39.4 wt %, respectively. The spherical morphology of QAMPSA/VP-Ag and QAMPSA/VP-Fe₃O₄ confirms their capping with the charged PIL based on QAMPSA/VP as a network. The negative surface charges of QAMPSA/VP-Ag and QAMPSA/VP-Fe₃O₄ at acidic and neutral pH values confirm the formation of protic QAMPSA/VP as a shell, which increases the dispersion of both QAMPSA/VP-Fe₃O₄ and QAMPSA/VP-Ag NPs in water. Moreover, the negative charges indicate that the sulfonate anions of QAMPSA/VP are oriented toward the exterior surface of nanoparticles and DEE ammonium cations are oriented toward the interior surfaces of nanoparticles. The formation of superparamagnetic Fe₃O₄ NPs and their capping with QAMPSA/VP facilitate their application as a Fenton oxidation catalyst to completely degrade MB without the formation of any intermediate in a short time of 8 min. Moreover, the formation of highly dispersed Ag NPs and their capping with QAMPSA/VP facilitate their application as a catalyst for discoloration of MB by converting its oxidized form to the reduced form in a short reaction time. It is found that the lower E° and ΔH° and more negative ΔS° values of 28.95 kJ mol⁻¹, 26.65 kJ mol⁻¹, and –168.8 J mol⁻¹ K⁻¹, respectively, confirm the higher catalytic reduction efficiency of QAMPSA/VP-Ag NPs for MB than that of other catalysts reported in the literature.

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Notes

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