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ARTICLE

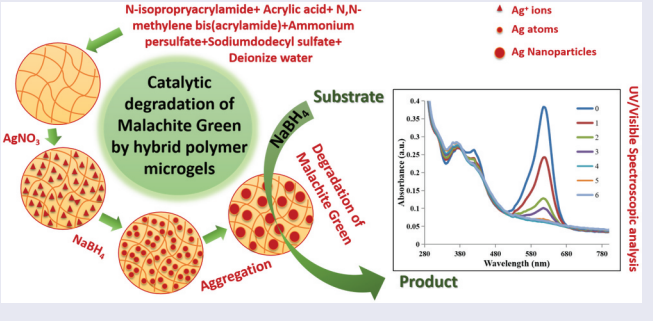
Catalytic degradation of malachite green using a crosslinked colloidal polymeric system loaded with silver nanoparticles

Zahoor H. Farooqi [a], Hamadia Sultana [a,b], Robina Begum [a], Muhammad Usman [b], Muhammad Ajmal [c], Jan Nisar [d], Ahmad Irfan [e,f] and Muhammad Azam [a]

[a]Institute of Chemistry, University of the Punjab, Lahore, Pakistan; [b]Department of Chemistry, Government College University, Faisalabad, Pakistan; [c]Department of Chemistry, University of Education, Attock Campus, Pakistan; [d]National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan; [e]Research Center for Advanced Materials Science, Faculty of Science, King Khalid University, Abha, Saudi Arabia; [f]Department of Chemistry, Faculty of Science, King Khalid University, Abha, Saudi Arabia

ABSTRACT

Aim of this work is to investigate the catalytic efficiency of silver nanoparticles loaded poly(*N*-isopropylacrylamide-co-acrylic acid)[Ag-P(NAA)] microgel system towards degradation of an organic dye (malachite green (MG)) in aqueous medium. Ag-P(NAA) system was synthesised by free-radical precipitation polymerisation followed by *in-situ* reduction of silver nitrate in the presence of reducing agent. Fourier transform infrared, UV-Visible Spectroscopy and transmission electron microscopy were employed for characterisation of synthesised catalytic system. Measurement of surface Plasmonic property of the silver nanoparticles was used to study the stability of the hybrid system as a function of time of storage and pH of the medium. Catalytic potential of Ag-P(NAA) towards reductive degradation of MG in aqueous medium was investigated. The experiments were performed at various concentrations of reducing agent, dye and catalyst for the evaluation of a kinetic parameter called apparent rate constant (k_{app}) using pseudo first-order kinetic model. The results revealed that hybrid microgels can degrade dye completely in few minutes. Values of k_{app} under different reaction conditions suggested that the catalytic process takes place through Langmuir–Hinshelwood mechanism. Ag-P(NAA) system is highly useful for the treatment of industrial waste water containing organic dyes.



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CONTACT Zahoor H. Farooqi zhfarooqi@gmail.com

1. Introduction

The field of nanotechnology is multidisciplinary and has been an area of global interest since many decades. Large variety of the available nanomaterials such as nanoparticles, nanotubes, nanorods, nanocomposites and nanocrystals have countless applications in various fields. Metal nanoparticles have many attractive properties, the most significant among those is their good catalytic behaviour [1]. Stabilisation of nanoparticles by a suitable stabiliser is crucial particularly for their application in catalysis. Different stabilising agents like surfactants [2], dendrimers [3] and microgels [4] have been used to achieve stability of the nanoparticles over the time of storage and even during catalysis. Microgels are potential candidates for the said purpose [5].

Microgels are utilised as nano-sized reactors for nanoparticles fabrication to encapsulate them inside the sieves of their network. The microgels-based stabilising systems have many exceptional features that made them superior over the other systems [2]. These are small cross-linked polymeric three-dimensional structures dispersed in the solvent. They are usually spherical in shape with diameter ranging from sub-microns to several microns. Nature of the monomers used in the fabrication of microgels makes them able to respond to particular external stimuli like pH, ionic strength and temperature of the medium [6]. In response to variation in a particular external stimulus, they show a sudden change in their size. Extensive interior network of the microgel particles can also entrap other materials in their voids. Nanomaterials like metal oxide magnetic nanoparticles [7], metal sulphide nanoparticles [8,9] and metal nanoparticles [10,11] can be loaded inside the microgels to accomplish various tasks as per requirement.

Microparticles made of crosslinked poly(*N*-isopropylacrylamide) [P(NA)] are sensitive towards change in temperature of the medium. They exhibit volume phase transition at 32°C in water which is known as volume phase transition temperature (VPTT). Below this temperature, the P(NA) microgel particles are in swollen state because of hydrogen bonding of amide groups of P(NA) with solvent (water) molecules. While at temperature ≥VPTT, these microgel particles exist in shrunken state [12,13] owing to breakage of hydrogen bonding between amide groups of P(NA) and water molecules. Shrinkage of P(NA) microparticles at T ≥VPTT restricts loading of inorganic nanomaterials into the microgels and use of resulting hybrid microgels as catalyst at high temperature. The value of VPTT must be increased to load high contents of metal nanoparticles and effective use of resulting hybrid materials as catalyst. One of the best strategies to increase the VPTT is copolymerisation of *N*-isopropylacrylamide with some hydrophilic (ionic) monomer [14,15]. In the present study, we have copolymerised *N*-isopropylacrylamide with acrylic acid in the presence of *N,N*-methylenebisacrylamide in aqueous medium to obtain multi-responsive P(NAA) polymer microgel system using slightly modified strategy already reported by us [14]. P(NAA) microgel system has been widely reported for a wide range of applications due to its various attractive features including temperature sensitivity, pH responsiveness [16,17], high stability, good water dispersity, open network, good ability to be used as an effective micro-reactor for in-situ fabrication of metal nanoparticles [18,19] and excellent catalytic activity [20] of the resulting metal-P(NAA) hybrid system [21,22]. We have recently reviewed synthesis, properties and applications of this widely reported microgel system [23]. Fabrication of different metal nanoparticles including silver nanoparticles in P(NAA) microgels for different applications including

catalysis has been reported by our group [18,24] and others [25,26]. To the best of our information, silver nanoparticles loaded into the P(NAA) system have not been reported for catalytic degradation of highly toxic malachite green (MG) dye.

Silk, wool and leather dyeing industries involve a wide use of MG (tri-phenyl methane dye). It has been also used as antiseptic and fungicide in fish farming industry. MG is highly dangerous and has cytotoxic effects on mammalian cells. It also enhances the chances of liver tumour. The presence of dyes in aquatic environment blocks out penetration of sunlight which inhibits the development of aquatic life [27]. Therefore, it is very important to degrade MG dye present in industrial effluent before its discharge to the ecosystem. Various methodologies for removal of the dye from aqueous medium including adsorption [28,29], Fenton process [30], photochemical degradation [31], biological treatment [32] and catalytic degradation [33] have been reported in the literature. Only a few reports are available on noble metal catalysed reduction/degradation of MG without any additional photo-catalyst (metal oxide/metal sulphide) [34,35]. All aforementioned reports deal with catalytic reduction of MG in the presence of nanoparticles of highly expensive metals like gold, palladium and platinum. We are going to report catalytic degradation of MG using nanoparticles of comparatively cheap metal (Ag) loaded into P (NAA) system without any additional photocatalyst.

In the present work, Ag-P(NAA) hybrid system was synthesised and characterised for catalytic degradation of MG. The stability of the synthesised system was also studied. Catalytic degradation of carcinogenic dye, MG system was carried under different conditions to optimise catalysis parameters and to elucidate catalysis mechanism.

2. Experimental

2.1. Chemicals

The *N*-isopropylacrylamide (NA), acrylic acid (A), *N,N*-methylene bis(acrylamide) (NN-BA) and sodium dodecylsulfate (SodS) and ammonium persulphate (ApS) were purchased from Sigma-Aldrich, Germany. Silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were purchased from Gemistone chemicals and Scharlau, Spain, respectively. A total of 12,000–14,000 MCWO molecular porous membrane, obtained from Fischer Scientific, UK, was employed in dialysis process for purifying P(NAA) and Ag-P(NAA) systems. MG oxalate salt commercially available in market was used in all degradation experiments. All chemicals, employed in these experiments, were used without any further purification and are listed in Table 1. Water used for synthesis, dialysis and preparation of solutions was deionised.

Table 1. Percentage purities and amounts of chemicals used in the synthesis of P(NAA) and Ag-P (NAA).

Chemical Reagents	% Purity	Mol %	Amounts (g)
N-Isopropylacrylamide ($C_6H_{11}NO$)	98%	93	1.0509
Acrylic acid ($C_3H_4O_2$)	98%	4	0.0288
N,N-methylene bis(acrylamide) ($C_7H_{10}N_2O_2$)	99%	3	0.0462
Ammonium persulphate ($(NH_4)_2S_2O_8$)	99%	–	0.5705
Sodium dodecylsulfate ($CH_3(CH_2)_{11}SO_4Na$)	98%	–	0.0580
Precursor ($AgNO_3$)	97%	–	0.4200
Reductant ($NaBH_4$)	98%	–	0.0240

2.2. Synthesis of P(NAA) microgels

Free-radical precipitation polymerisation method reported by us in our previous work with slight modification was used for fabrication of P(NAA) system of colloidal particles [14]. Feeding contents of all reagents used in the preparation of P(NA) system are listed in Table 1. Measured contents of surfactant (SodS), crosslinker (NN-BIS), *N*-isopropylacrylamide (NA) were stirred in 95.00 mL deionised water in a three-necked round bottom flask (250 mL) connected with a condenser and nitrogen gas (N_2) inlet placed in paraffin-oil-based heating system. Stirring of the mixture was carried out for 30 min in the presence of nitrogen purging to displace dissolved oxygen. The temperature of the mixture was raised to 75°C and was maintained on the same value in the presence of continuous nitrogen supply. Given amount of acrylic acid was added into the flask using microsyringe. The inhibitor was removed from acrylic acid via vacuum filtration by passing it through Al_2O_3 before its addition to the reaction mixture. Then, 5.00 mL ApS (50 mM) was injected dropwise into the reaction mixture to start the process of polymerisation. Turbidity that appeared in the reaction mixture was an indication of on-set of polymerisation. Polymerisation process was continued for 5 h to complete the reaction. Purification of P(NAA) microgel dispersion was carried out by subjecting it to dialysis using distilled water for 4 days within macromolecular porous membrane provided by Fischer Scientific. Water was changed thrice a day for successful removal of surfactant, unreacted monomers and initiator from P(NAA) dispersion.

2.3. Synthesis of Ag-P(NAA) hybrid microgels

Ag-P(NAA) system was synthesised by reduction of silver salt within P(NAA) dispersion at room temperature. For this purpose, 37.8 mL deionised water and 9.5 mL P(NAA) dispersion was stirred for half an hour in a three-necked round bottom flask (250 mL), equipped with nitrogen inlet and condenser. Then, 0.2 mL precursor salt ($AgNO_3$) solution (0.1 M) was added into reaction mixture. After 30 min stirring, 2.5 mL reducing agent ($NaBH_4$) solution (0.13 M) was added dropwise to silver ions loaded P(NAA) dispersion. The appearance of brownish colour in the reaction mixture was the sign of successful loading of Ag nanoparticles into P(NAA) system. Hybrid microgels Ag-P(NAA) dispersion was also purified through dialysis for half an hour.

2.4. Characterisation

Synthesis of P(NAA) and incorporation of Ag nanoparticles into P(NAA) were analysed by spectroscopic measurements using double beam UV-Visible Spectrophotometer (UVD 3500). Fourier transform infrared spectroscopy (FTIR) analysis of P(NAA) and Ag-P(NAA) systems was carried out on RXI FTIR spectrometer (Perkin Elmer, USA). Stability of the system and impact of various parameters on the reduction of MG were also evaluated using the same UV-Visible spectrophotometer. Morphology of Ag-P(NAA) system was analysed through FEI TECNAI transmission electron microscope (TEM) working at 120 kV accelerating voltage. Dilute dispersion of Ag-P(NAA) was placed and dried over carbon-coated copper grid for 2 days before TEM measurements.

2.5. Catalytic reduction of MG

UV-Visible Spectrophotometry was applied to study the activity of the synthesised Ag-P (NAA) hybrid microgel system. For monitoring the reduction of MG, 0.48 mL of deionised water, 1.6 mL MG solution (0.03 mM), 0.02 mL Ag-P(NAA) hybrid dispersion and 0.4 mL $NaBH_4$ solution were taken in a cuvette to scan spectra of ongoing reaction as a function of time. Deionised water was used as a reference for spectroscopic measurements. Spectra were obtained after every minute in range of 200–800 nm at room temperature.

3. Results and discussion

3.1. Synthesis of P(NAA) microgels

For synthesising, mono-dispersed microgel system, free-radical precipitation polymerisation is a reliable and highly useful method. It requires temperature up to 70–75°C which is necessary for successful polymerisation. Thermal decomposition of APS at this temperature forms sulphate radicals. These radicals activate both monomers to start the process of polymerisation. Growth of the small polymer chains occurs as the reaction progresses [36]. Initially, small P(NAA) particles are generated which ultimately start to agglomerate with each other to stabilise themselves in the system. The addition of surfactant (SodS) further helps in stabilising the system and controlling the size of agglomerated colloidal particles. The appearance of turbidity in the reaction mixture is usually taken as an indication of onset of polymerisation [37,38]. Light scattering due to the difference between the refractive index value of water and that of growing crosslinked polymer particles is the major cause of appearance of turbidity. Dialysis has become an effective method for purification of polymer microgels as reported previously [39,40]. Therefore, P(NAA) microgel dispersion was cooled and then was poured into macromolecular membrane tubing for its dialysis for 3 days against deionised water. Surfactant, initiator and unreacted species are diffused out through porous membrane because of concentration gradient between outer water medium and P (NAA) microgel dispersion.

3.2. Preparation of Ag-P(NAA)

Ag nanoparticles were loaded in polymer framework of P(NAA) by reduction of metal salt ($AgNO_3$) within the reaction mixture at pH higher than pK_a value of acrylic acid [41]. Under this condition of pH value of medium, deprotonation of carboxyl groups (–COOH) of acrylic acid units of P(NAA) system causes swelling in the microgel particles to increase the diffusion of Ag^+ ions from outside bulk water to crosslinked polymer network. Moreover, in the aforementioned condition of pH, positively charged metal ions are attracted by the negatively charged carboxylate groups ($–COO^–$) because of electrostatic attractive forces. Mass transfer of Ag^+ ions from bulk water to the polymer network occurs due to both modes of mass transfer, diffusion as well as migration. As a result, Ag^+ ions are entrapped inside the network. Addition of $NaBH_4$ reduces Ag^+ ions to zerovalent Ag atoms. Ag atoms present in each void of polymeric network agglomerate to form Ag nanoparticles. The size and number of Ag nanoparticles depend upon the size of voids/sieves of P(NAA) microgel system and charged density of the microgel

particles. Discussion on factors affecting the size and number of nanoparticles loaded into P(NAA) microgels is out of scope of the present study and has been already discussed in our previous publications [42]. Turning the milky white dispersion into brownish was due to surface plasmon resonance property of silver nanoparticles formed in microgels particles [42,43].

3.3. Characterisation of P(NAA) and Ag-P(NAA) and study of their stability

UV-Visible spectroscopic analysis has become an excellent tool of characterisation of noble metal nanoparticles. The appearance of peak/peaks in UV-Visible region of spectra of dispersion is taken as a confirmatory test for the formation of Plasmonic nanoparticles. Information regarding size, size distribution and even shape of Plasmonic nanoparticles can also be obtained from UV-Visible analysis. Our group has recently published a tutorial review on utility of UV-Visible spectroscopy in characterisation of noble metal nanoparticles and in monitoring of their catalytic activity [44]. Therefore, in the present work, loading of silver nanoparticles into P(NAA) was confirmed by UV/Visible Spectroscopic analysis of dilute aqueous dispersion of Ag-P(NAA). Figure 1 shows the spectra of both P (NAA) microgels and Ag-P(NAA) hybrid microgels. There was no band in P(NAA) dispersion while a sharp peak at 435 nm was observed in case of spectra of Ag-P(NAA) dispersion. A sharp single peak at 435 nm can be attributed to Plasmonic nature of nearly monodisperse spherical silver nanoparticles formed in P(NAA) dispersion [45].

FTIR analysis of polymer microgel system gives information on the presence of various functionalities in polymer network. Comparison of FTIR spectra of pure and hybrid microgels can be used to figure out interaction between metal nanoparticles and functionalities of microgel system. FTIR Spectra of P(NAA) and Ag-P(NAA) recorded for the said purpose are given in Figure 2. Both spectra are almost similar with only slight differences in the position and intensity of some peaks. It means that loading of silver nanoparticles into the microgel

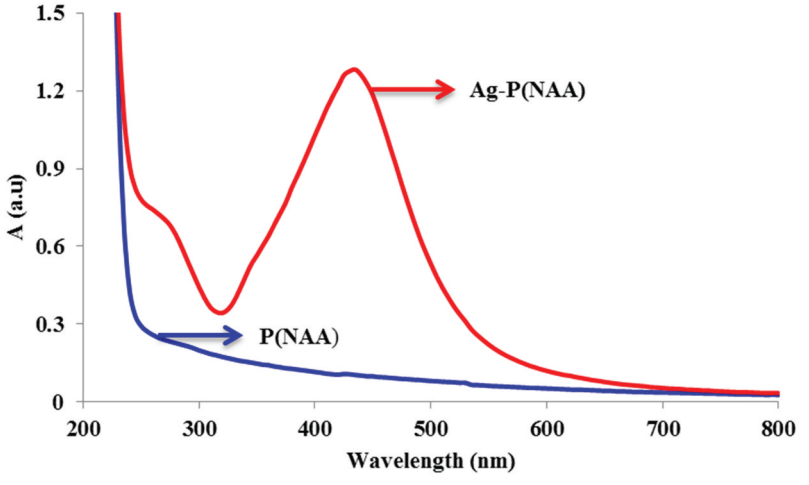

Figure 1. UV-Visible spectra of colloidal aqueous dispersion of P(NAA) and Ag-P(NAA) at room temperature.

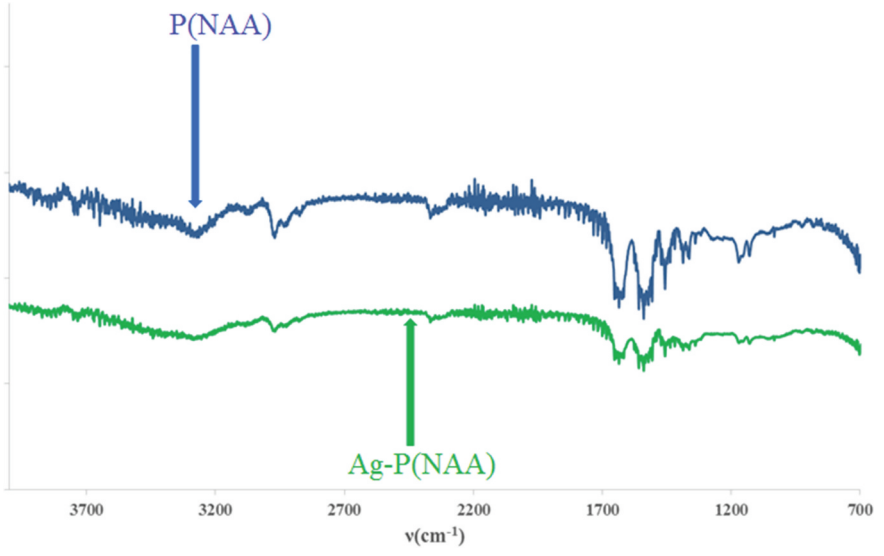

Figure 2. FTIR spectra of P(NAA) and Ag-P(NAA) systems.

Table 2. Data of FTIR analysis of P(NAA) and Ag-P(NAA) systems.

Functionality with mode of vibration	FTIR bands in P(NAA) (cm^{-1})	FTIR bands in Ag-P(NAA) (cm^{-1})
O-H (stretching)	3272	3282
N-H (stretching)	2970	2971
NH_2 (bending)	1539	1540
CH_2 (bending)	1456	1458
C=O (stretching)	1633	1623
C–O (stretching)	1366	1366

does not have any effect on chemical structure of microgels. Values of wavenumber (cm^{-1}) associated with stretching/bending of various functionalities of P(NAA) microgels are summarised in Table 2. Significant shift in the value of C=O stretching band was observed upon loading of silver nanoparticles into P(NAA) microgels. This shift may be attributed to some sort of interaction between carbonyl groups and silver nanoparticles. No peak in 1600 cm^{-1} range reveals the absence of carbon–carbon double bond and confirms polymerisation [46].

TEM image of Ag-P(NAA) dispersion is shown in Figure 3. It exhibits the shape of microgel particles, shape of metal nanoparticles and uniformity in distribution of these nanoparticles. Particle encapsulated in large blue circle in the TEM image is microgel particle while prominent black dots encircled by peach colour within large blue circle are silver nanoparticles. Results revealed that both P(NAA) and Ag nanoparticles are nearly spherical in shape. Ag nanoparticles are present throughout the P(NAA) network but their sizes are not exactly the same. Estimated average diameter of Ag nanoparticles was 6–9 nm while that of hybrid microgel particles was estimated to be about 50 ± 8 nm. Ag nanoparticles stabilised in P(NAA) are actually true catalysts due to possessing large surface area because of their small size.

The catalyst to be used for the reduction of dyes with sodium borohydride must be stable in a wide pH range to retain its catalytic activity. It is well known that $NaBH_4$ has

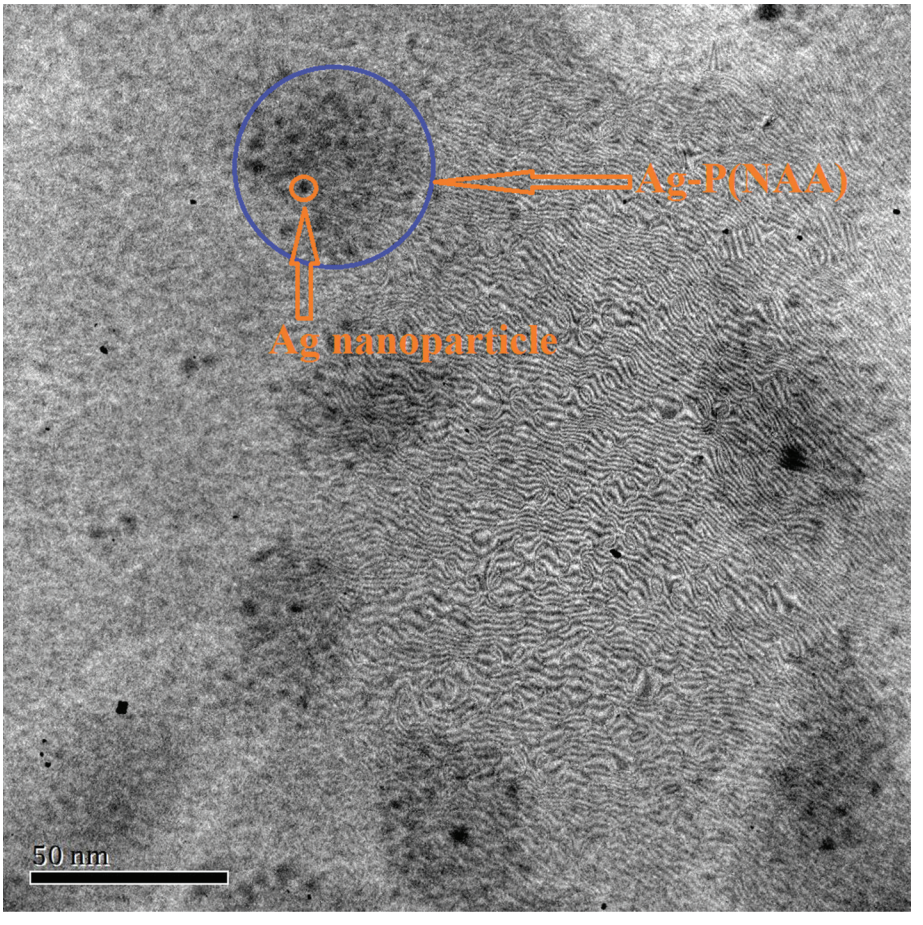

Figure 3. TEM analysis of Ag-P(NAA) hybrid microgels.

basic pH in aqueous medium. Its addition into dispersion of P(NAA)-containing dye increases the pH of the medium. Moreover, pH of the medium may be a function of extent of the reaction. Catalyst will be supposed to be active if it is stable in pH window of the reaction. Therefore, the stability of silver nanoparticles loaded into pH-sensitive P (NAA) microgels as a function of pH of the medium was investigated before their use as a catalyst for the degradation of MG. Surface plasmon resonance property of silver nanoparticles loaded into P(NAA) system measured by UV-Visible spectroscopy was employed to investigate the stability of Ag-P(NAA) system over the wide pH range. UV-Visible spectra of Ag-P(NAA) microgel dispersions at various values of pH is given in Figure 4. The surface plasmon resonance band (λ_{spr}) remains alive in the pH ranging from 6.60 to 12.01 with a slight shift in the value of (λ_{spr}) and absorbance at λ_{spr} which reflects the stability of nanosilver in a broad pH range. It is worth mentioning that Ag-P(NAA) was not stable at pH ≤2.5. However, our catalytic system was found to be stable in pH range of our interest (pH variation during the progress of catalytic reduction of MG). Variation in value of absorbance at λ_{spr} and that of λ_{spr} may be attributed to the variation of refractive index of the medium around nanoparticles due to swelling/deswelling of P(NAA) system,

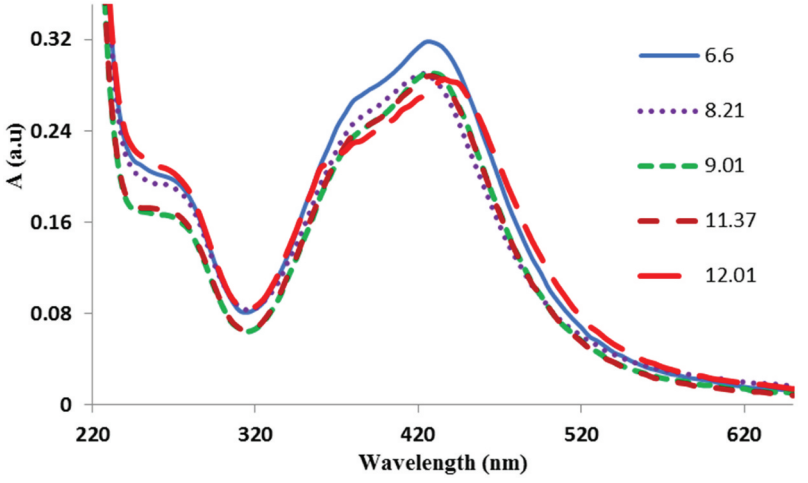

Figure 4. UV-Visible spectra of dispersion of Ag-P(NAA) at different pH values of the medium at room temperature.

Table 3. Plasmonic parameters of dispersion of Ag-P(NAA) at different values of pH of the medium at room temperature.

pH of medium	Plasmonic wavelength (nm)	Absorbance at λ_{spr}
6.6	425	0.318
8.21	425	0.29
9.0	425	0.29
11.37	430	0.288
12.0	435	0.285

change of inter-nanoparticles distance because of change in pH of the medium and even due to change of concentration of dispersion because of the addition of small volume of NaOH/HCl (one–two drops) to adjust pH values [47,48]. The values of λ_{spr} and corresponding absorbance of Ag-P(NAA) at different pH values are given in Table 3.

Another important feature of an effective and excellent catalytic system is its stability over the time of storage. It should remain stable on its storage to be a sustainable catalyst. Dilute dispersion of Ag-P(NAA) was placed in dark at room temperature and its UV-Visible spectra was scanned at different time of storage. Figure 5 shows the spectra of fresh Ag-P(NAA) and stored Ag-P(NAA) dispersions after 7, 21 and 42 days of storage. It can be inferred that value of λ_{spr} remains constant with a slight decrease in absorbance. Constant value of λ_{spr} of silver nanoparticles confirms their long-term stability in Ag-P(NAA) particles while a slight decrease in corresponding absorbance value may be due to attachment of some particles with internal wall of vial used for storage [13].

3.4. Ag-P(NAA) catalysed degradation of MG

After investigating the stability of Ag nanoparticles loaded into P(NAA) microgels, catalytic activity of Ag-P(NAA) system towards the reduction of MG with sodium borohydride in aqueous medium was investigated. UV-Visible spectra of aqueous solution (0.03 mM) of

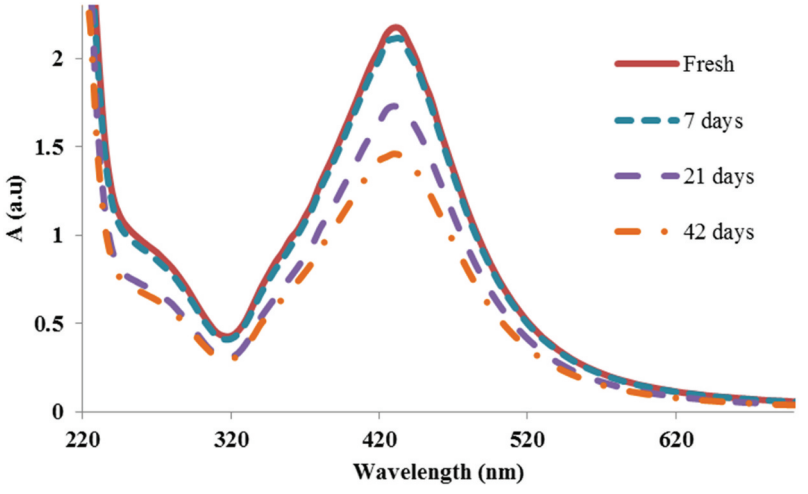

Figure 5. UV-Visible spectra of dispersion of Ag-P(NAA) saved in dark for different time after synthesis at ambient temperature.

MG was scanned in wavelength range of 200–750 nm for determination of its wavelength of maximum absorption (λ_{max}) which is shown in Figure 6 (a). The value of λ_{max} of MG was found to be 615 nm which suggested the utility of UV-Visible spectrophotometry to monitor the progress of catalytic degradation of the dyes in aqueous medium. The value of λ_{max} of MG was far away from that of λ_{spr} of silver nanoparticles. So, surface Plasmonic resonance property of silver nanoparticles do not interfere in the measurement of change in absorbance due to reduction of MG. Therefore, UV-Visible Spectrophotometry was employed to measure the progress of catalytic degradation of MG. Ag-P(NAA) catalyst and $NaBH_4$ solution were added into MG solution in a quartz cuvette and was subjected to UV-Visible spectrophotometric measurements as a function of time. UV-Visible scans taken at regular intervals during the progress of the reaction are shown in Figure 6(b). A gradual decrease in the value of absorbance at 615 nm with time confirms decrease in concentration of MG due to its catalytic reductive degradation. At the end of reaction, reaction mixture becomes colourless and values of absorbance become constant indicating the complete degradation of the dye. Interestingly, the intensity of the peak at 380 nm was not found to be changed during the reaction progress. It may be associated with some aromatic part of MG which is not being consumed during the progress of the reaction but we do not have any evidence to support this claim.

The concentration of reductant was kept very large in comparison to that of MG to fulfil the requirement of application of pseudo first-order kinetic model for determination of parameters of kinetics. The mathematical expression of pseudo first-order kinetic modelling applied is given in Equation (1).

$$\ln(C_t/C_o) = -k_{app}t \tag{1}$$

It is a straight line equation, in which C_o is the concentration of MG at $t = 0$ and C_t is its concentration at time = t [49]. Slope of the $\ln(C_t/C_o)$ versus time gives the value of

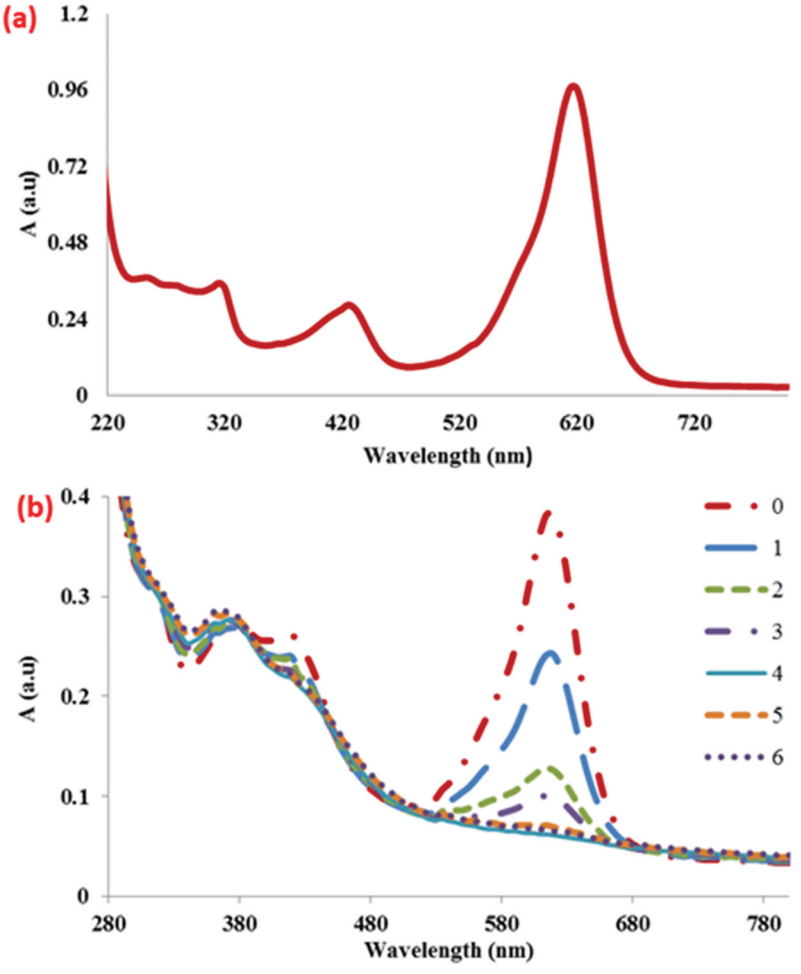

Figure 6. UV-Visible spectra of (a) aqueous solution of malachite green (b) Time dependent UV-Visible spectra of ongoing catalytic degradation of malachite green using Ag-P(NAA) catalyst = 0.02 mL and [NaBH4] = 1.5 mM at 25 ± 1° C].

apparent rate constant (k_{app}). The ratio of concentration (C_t/C_o) was determined by calculating the ratio of absorbance (A_t/A_o) at 615 nm using UV-Visible spectrophotometry.

3.5. Study of parameters affecting catalytic reduction of MG

Catalytic degradation of MG with $NaBH_4$ using Ag-P(NAA) was carried out under different reaction conditions to understand the scenario of catalysis. Effect of each parameter on the value of k_{app} for the reduction of MG was investigated by keeping all other parameters constant. To explore the effect of reductant concentration on k_{app}, the contents of MG and catalyst were kept constant while that of $NaBH_4$ was changed from 0.6 mM to 2.1 mM. The values of absorbance were noted after regular time intervals. The plot of $\ln(A_t/A_o)$ vs. time at various concentrations of the reductant is given in Figure 7 and the values of k_{app}

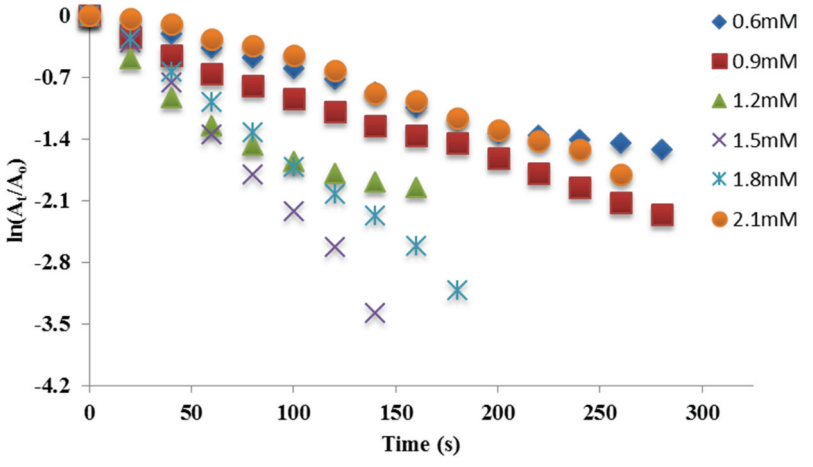

Figure 7. Kinetic analysis of Ag-P(NAA) catalyzed degradation of MG using first order kinetic model at different concentrations of NaBH4 at[MG] = 0.03 mM, [Catalyst] = 0.02 mL and temperature = 25 ± 1° C.

Table 4. Values of k_{app} for catalytic degradation of malachite green under different reaction conditions at 25 ± 1°C.

Varying factor	[Ag-P(NAA] (mL)	[MG] (mM)	[Reductant] (mM)	Rate constant (min^{-1})
$NaBH_4$	0.02	0.03	0.6	0.0058
	0.02	0.03	0.9	0.007
	0.02	0.03	1.2	0.0118
	0.02	0.03	1.5	0.0239
	0.02	0.03	1.8	0.017
	0.02	0.03	2.1	0.0071
Malachite green	0.02	0.01	1.5	0.0021
	0.02	0.02	1.5	0.0038
	0.02	0.03	1.5	0.0071
	0.02	0.04	1.5	0.0131
	0.02	0.05	1.5	0.0042
	0.02	0.06	1.5	0.0016
Catalyst	0.01	0.03	1.5	0.0198
	0.02	0.03	1.5	0.0206
	0.03	0.03	1.5	0.0233
	0.04	0.03	1.5	0.0295
	0.05	0.03	1.5	0.0376

evaluated from the slope of the plot are listed in Table 4. Table 4 Results revealed that the value of k_{app} increases gradually up to 1.5 mM concentration of $NaBH_4$ then decreases. The increase of concentration of $NaBH_4$ gives a large number of BH_4^- ions in the reaction mixture which enhances their rate of diffusion towards the surface region and ultimately their rate of adsorption on the surface of silver nanoparticles loaded in P(NAA). As a result, rapid reaction between adsorbed substrate and BH_4^- ions occurs. Therefore, the value of k_{app} increases with increase in $NaBH_4$ contents up to a certain extent after which the reaction rate falls due to retardation caused by competition between adsorption of BH_4^- ions and dye molecules on the same catalyst surface. At [$NaBH_4$] ≥1.5 mM, most of the catalytic sites are occupied by BH_4^- ions. As a result, adsorption of dye molecules is

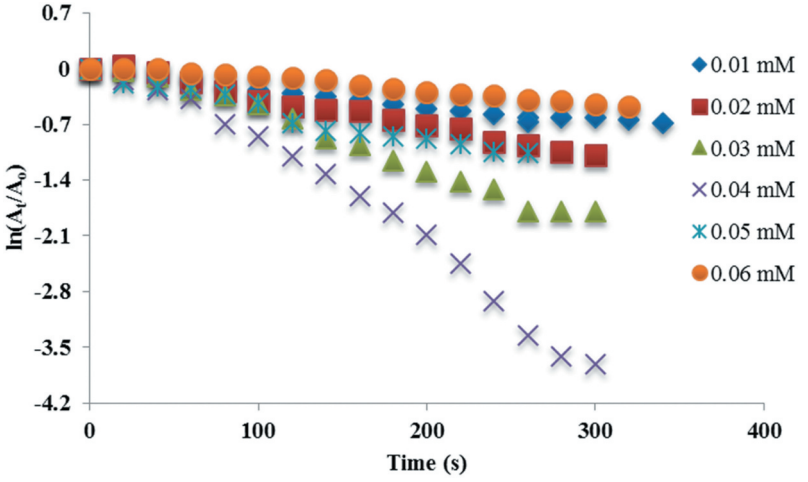

Figure 8. Kinetic analysis of Ag-P(NAA) catalyzed degradation of MG using first order kinetic model at different concentrations at A-P(NAA) = 0.02 mL, [NaBH4] = 1.5 mM and temperature = 10 ± 1° C.

hindered which result in decrease in the reaction rate. The trend of [$NaBH_4$] dependence of k_{app} indicates that reaction proceeds with Langmuir–Hinshelwood mechanism where the reaction occurs due to interaction between already adsorbed species (both dye and reductant). It has been already reported that most of the nano catalysed reduction reactions occurs according to Langmuir–Hinshelwood mechanism [50].

Amounts of catalyst and reducing agent were kept constant while the concentration of MG was varied from 0.01 mM to 0.06 mM for evaluating the effect of this parameter on the rate of its own degradation. Figure 8 shows the gradual decrease in $\ln(A_t/A_o)$ with time for different values of MG concentration. The decreasing trend of $\ln(A_t/A_o)$ with time reveals the continuous reduction of MG with time. The values of k_{app} determined from the slope of the plot are given in Table 4. The k_{app} value of degradation of MG increases up to specific concentration of MG and then decreases. This trend of [substrate] dependence of k_{app} has been already observed in literature dealing with catalytic degradation of different dyes [51,52]. The increase of rate up to a certain level reveals that degradation of MG can be enhanced by increasing its concentration up to a specific limit. It is thought that increase in the concentration of dye up to optimum concentration causes an increase in the rate of adsorption of dye molecules on the catalytic surface which results in the enhancement of the reaction rate. The decrease in value of k_{app} with increasing [MG] at [MG] ≥0.04 mM is because of the unavailability of surface for adsorption of BH_4^- ions due to complete surface coverage by adsorption of MG only. This may occur only if [MG] is much higher than that of BH_4^- ions or if adsorption ability of dye is much greater than that of BH_4^- ions. The first possibility is not possible because $NaBH_4$ concentration was much large in comparison to MG concentration throughout the catalytic study. The second possibility needs further investigation. Another reason for decrease of k_{app} with an increase of [MG] at [MG] ≥0.04 mM is the diffusional barrier faced by dye molecules to access the surface of Ag nanoparticles, particularly at its high concentration because of its bulky size [52].

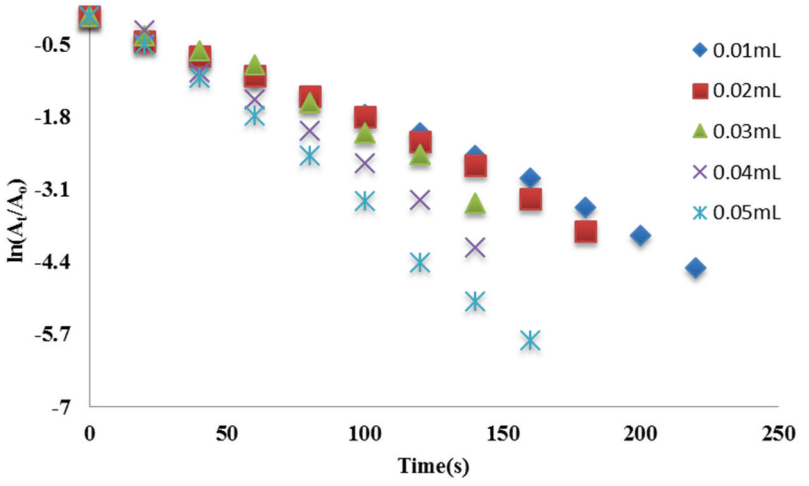

Figure 9. Kinetic analysis of Ag-P(NAA) catalyzed degradation of MG using first order kinetic model at different amounts of Ag-P(NAA) at [MG] = 0.03 mM, [NaBH4] = 1.5 mM and temperature = 25±1o C.

Effect of content of Ag-P(NAA) on k_{app} for degradation of MG at particular reaction conditions is highly useful to identify true catalyst in system as well as to understand the role of catalyst in enhancement of the rate of reaction. Linear regions of the plot of $\ln(A_t/A_o)$ versus time (t) for different amounts of catalyst at a constant concentration of dye and reducing agent are shown in Figure 9. Catalytic dose was varied from 0.01 to 0.05 mL. Values of $\ln(A_t/A_o)$ gradually decrease with time depending upon the amount of Ag-P(NAA) added. The values of apparent rate constant at different Ag-P(NAA) contents are listed in Table 4. A regular increasing trend depicts that the rate of degradation increases on increasing the amount of catalyst because high amount of catalyst provides greater number of available adsorption site of dyes and reducing agent to carry out catalysis. This trend indicates that Ag-P(NAA) is the true catalyst and reaction is occurring on its surface. The results are in accordance with the previously reported literature [6].

4. Conclusion

In summary, Ag-P(NAA) hybrid system was successfully fabricated using facile and economical in-situ reduction approach for rapid degradation of MG in aqueous medium. Free-radical precipitation polymerisation in environmentally benign solvent was used to obtain P(NAA) crosslinked polymeric system. Spherical silver nanoparticles were loaded in voids of crosslinked polymeric system by reducing silver ions with sodium borohydride within aqueous dispersion of P(NAA) through *in-situ* reduction of silver nitrate. Ag-P(NAA) system was stable at different pH values as well as on its long-term storage in dark. Ag-P (NAA) system has an excellent catalytic potential to degrade MG. Value of k_{app} for degradation of MG was found to be adjustable by varying the contents of any one of the catalysts, dye and reductant under similar reaction conditions. Kinetic data collected under various reaction conditions reveal that both reactants (dye and reductant) are

adsorbed on Ag surface to interact with each other before going to degradation products. We believe that Ag-P(NAA) system may be used for degradation of other organic dyes or mixture of dyes for waste water treatment in future.

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Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

Zahoor H. Farooqi http://orcid.org/0000-0003-3200-2935
Hamadia Sultana http://orcid.org/0000-0002-4851-5308
Robina Begum http://orcid.org/0000-0002-0470-3374
Jan Nisar http://orcid.org/0000-0001-9291-6064
Ahmad Irfan http://orcid.org/0000-0001-6941-6934

References

[1] S. Wu, J. Dzubiella, J. Kaiser, M. Drechsler, X. Guo, M. Ballauff and Y. Lu, Angew. Chem., Int. Ed. **51**, 2229 (2012). doi:10.1002/anie.201106515.
[2] L. Kvítek, A. Panáček, J. Soukupova, M. Kolář, R. Večeřová, R. Prucek, M. Holecova and R. Zbořil, J. Phys. Chem. C **112**, 5825 (2008). doi:10.1021/jp711616v.
[3] Z.D. Pozun, S.E. Rodenbusch, E. Keller, K. Tran, W. Tang, K.J. Stevenson and G. Henkelman, J. Phys. Chem. C **117**, 7598 (2013). doi:10.1021/jp312588u.
[4] S.R. Khan, Z.H. Farooqi, M. Ajmal, M. Siddiq and A. Khan, J. Dispersion Sci. Technol. **34**, 1324 (2013). doi:10.1080/01932691.2012.744690.
[5] H. Naeem, Z.H. Farooqi, L.A. Shah and M. Siddiq, J. Polym. Res. **19**, 9950 (2012). doi:10.1007/s10965-012-9950-1.
[6] Z.H. Farooqi, T. Sakhawat, S.R. Khan, F. Kanwal, M. Usman and R. Begum, Mater. Sci.-Pol. **33**, 185 (2015). doi:10.1515/msp-2015-0025.
[7] J. Rubio-Retama, N.E. Zafeiropoulos, C. Serafinelli, R. Rojas-Reyna, B. Voit, E. Lopez Cabarcos and M. Stamm, Langmuir **23**, 10280 (2007). doi:10.1021/la7009594.
[8] A. Pich, J. Hain, Y. Lu, V. Boyko, Y. Prots and H.-J. Adler, Macromolecules **38**, 6610 (2005). doi:10.1021/ma0505272.
[9] Y. Zhang, H. Liu and Y. Fang, Chin. J. Chem. **29**, 33 (2011). doi:10.1002/cjoc.201190057.
[10] A. Pich, A. Karak, Y. Lu, A.K. Ghosh and H.J.P. Adler, Macromol. Rapid Commun. **27**, 344 (2006). doi:10.1002/marc.200500761.
[11] R. Contreras-Cáceres, A. Sánchez-Iglesias, M. Karg, I. Pastoriza-Santos, J. Pérez-Juste, J. Pacifico, T. Hellweg, A. Fernández-Barbero and L.M. Liz-Marzán, Adv. Mater. **20**, 1666 (2008). doi:10.1002/adma.200800064.

[12] J. Zhang, S. Xu and E. Kumacheva, J. Am. Chem. Soc. **126**, 7908 (2004). doi:10.1021/ja031523k.
[13] Y. Dong, Y. Ma, T. Zhai, F. Shen, Y. Zeng, H. Fu and J. Yao, Macromol. Rapid Commun. **28**, 2339 (2007). doi:10.1002/marc.200700483.
[14] Z.H. Farooqi, H.U. Khan, S.M. Shah and M. Siddiq, Arabian J. Chem. **10**, 329 (2017). doi:10.1016/j.arabjc.2013.07.031.
[15] R. Begum, K. Naseem, E. Ahmed, A. Sharif and Z.H. Farooqi, Colloids Surf., A **511**, 17 (2016). doi:10.1016/j.colsurfa.2016.09.076.
[16] I. Gorelikov, L.M. Field and E. Kumacheva, J. Am. Chem. Soc. **126**, 15938 (2004). doi:10.1021/ja0448869.
[17] M. Das, N. Sanson, D. Fava and E. Kumacheva, Langmuir **23**, 196 (2007). doi:10.1021/la061596s.
[18] Z.H. Farooqi, A. Ijaz, R. Begum, K. Naseem, M. Usman, M. Ajmal and U. Saeed, Polym. Compos. **39**, 645 (2018). doi:10.1002/pc.23980.
[19] C.D. Sorrell, M.C. Carter and M.J. Serpe, Adv. Funct. Mater. **21**, 425 (2011). doi:10.1002/adfm.201001714.
[20] M. Bradley, J. Ramos and B. Vincent, Langmuir **21**, 1209 (2005). doi:10.1021/la047966z.
[21] A. Khan, J. Colloid Interface Sci. **313**, 697 (2007). doi:10.1016/j.jcis.2007.05.027.
[22] G.E. Morris, B. Vincent and M.J. Snowden, J. Colloid Interface Sci. **190**, 198 (1997). doi:10.1006/jcis.1997.4843.
[23] R. Begum, Z.H. Farooqi and S.R. Khan, Int. J. Polym. Mater. Polym. Biomater. **65**, 841 (2016). doi:10.1080/00914037.2016.1180607.
[24] Z.H. Farooqi, K. Naseem, A. Ijaz and R. Begum, J. Polym. Eng. **36**, 87 (2016). doi:10.1515/polyeng-2015-0082.
[25] K. Li, X. Chen, Z. Wang, L. Xu, W. Fu, L. Zhao and L. Chen, Polym. Compos. **38**, 708 (2017). doi:10.1002/pc.23630.
[26] D.-M. Han, Q.M. Zhang and M.J. Serpe, Nanoscale **7**, 2784 (2015). doi:10.1039/C4NR06093H.
[27] S. Srivastava, R. Sinha and D. Roy, Aquat. Toxicol. **66**, 319 (2004). doi:10.1016/j.aquatox.2003.09.008.
[28] S. Khattri and M. Singh, J. Hazard. Mater. **167**, 1089 (2009). doi:10.1016/j.jhazmat.2009.01.101.
[29] M.A. Ahmad and R. Alrozi, Chem. Eng. J. **171**, 510 (2011). doi:10.1016/j.cej.2011.04.018.
[30] S. Thakur and M. Chauhan, Int. Res. J. Eng. Technol **3**, 254 (2016).
[31] C. Chen, C. Lu, Y. Chung and J. Jan, J. Hazard. Mater. **141**, 520 (2007). doi:10.1016/j.jhazmat.2006.07.011.
[32] I.F.H. Al-Jawhari and K.J. AL-Mansor. Int. J. Environ. Agric. Biotech. 2017;**2**: DOI:10.22161/ijeab/2.2.21.
[33] C. Prasad, K. Sreenivasulu, S. Gangadhara and P. Venkateswarlu, J. Alloys Compd. **700**, 252 (2017). doi:10.1016/j.jallcom.2016.12.363.
[34] E. Murugan, J.N. Jebaranjitham, K.J. Raman, A. Mandal, D. Geethalakshmi, M.D. Kumar and A. Saravanakumar, New J. Chem. **41**, 10860 (2017). doi:10.1039/C7NJ01054K.
[35] R. Dobrucka and J. Inorg, Organomet. Polym. Mater. **28**, 1953 (2018). doi:10.1007/s10904-018-0858-z.
[36] M. Ajmal, Z.H. Farooqi and M. Siddiq, Korean J. Chem. Eng. **30**, 2030 (2013). doi:10.1007/s11814-013-0150-4.
[37] Z.H. Farooqi, N. Tariq, R. Begum, S.R. Khan, Z. Iqbal and A. Khan, Turk. J. Chem. **39**, 576 (2015). doi:10.3906/kim-1412-15.
[38] J.-T. Zhang, X.-L. Liu, A. Fahr and K.D. Jandt, Colloid Polym. Sci. **286**, 1209 (2008). doi:10.1007/s00396-008-1890-2.
[39] Y. Zhang, Y. Guan and S. Zhou, Biomacromolecules **7**, 3196 (2006). doi:10.1021/bm060557s.
[40] W. Wu, J. Shen, Y. Li, H. Zhu, P. Banerjee and S. Zhou, Biomaterials **33**, 7115 (2012). doi:10.1016/j.biomaterials.2012.06.031.
[41] W. Wu, T. Zhou and S. Zhou, Chem. Mater. **21**, 2851 (2009). doi:10.1021/cm900635u.
[42] Z.H. Farooqi, S.R. Khan, R. Begum, F. Kanwal, A. Sharif, E. Ahmed, S. Majeed, K. Ejaz and A. Ijaz, Turk. J. Chem. **39**, 96 (2015). doi:10.3906/kim-1406-40.
[43] S. Ma, J. Mu and L. Jiang, J. Dispersion Sci. Technol. **29**, 682 (2008). doi:10.1080/01932690701757832.

[44] R. Begum, Z.H. Farooqi, K. Naseem, F. Ali, M. Batool, J. Xiao and A. Irfan, Crit. Rev. Anal. Chem. **48**, 503 (2018). doi:10.1080/10408347.2018.1451299.
[45] W. Wu, J. Shen, P. Banerjee and S. Zhou, Biomaterials **31**, 7555 (2010). doi:10.1016/j.biomaterials.2010.06.030.
[46] M. Kurečič, M. Sfiligoj-Smole and K. Stana-Kleinschek, Mater. Tehnol. **46**, 87 (2012).
[47] S. Behrens, J. Wu, W. Habicht and E. Unger, Chem. Mater. **16**, 3085 (2004). doi:10.1021/cm049462s.
[48] Y. Lu, Y. Mei, M. Ballauff and M. Drechsler, J. Phys. Chem. B **110**, 3930 (2006). doi:10.1021/jp057149n.
[49] Y.Y. Liu, X.Y. Liu, J.M. Yang, D.L. Lin, X. Chen and L.S. Zha, Colloids Surf., A **393**, 105 (2012). doi:10.1016/j.colsurfa.2011.11.007.
[50] S.R. Khan, Z.H. Farooqi, A. Ali, R. Begum, F. Kanwal and M. Siddiq, Mater. Chem. Phys. **171**, 318 (2016). doi:10.1016/j.matchemphys.2016.01.023.
[51] K. Naseem, R. Begum, W. Wu, A. Irfan, A.G. Al-Sehemi and Z.H. Farooqi, J. Cleaner Prod. **211**, 855 (2019). doi:10.1016/j.jclepro.2018.11.164.
[52] R. Begum, Z.H. Farooqi, Z. Butt, Q. Wu, W. Wu and A. Irfan, J. Environ. Sci. **72** (43) (2018). doi:10.1016/j.jes.2017.12.003.