

Synthesis, characterization and fabrication of copper nanoparticles in N-isopropylacrylamide based co-polymer microgels for degradation of p-nitrophenol

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Poly(N-isopropylacrylamide-co-acrylic acid) [P(NIPAM-co-AAc)] microgels were synthesized by precipitation polymerization. Copper nanoparticles were successfully fabricated inside the microgels by in-situ reduction of copper ions in an aqueous medium. The microgels were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and Dynamic Light Scattering (DLS). Hydrodynamic radius of P(NIPAM-co-AAc) microgel particles increased with an increase in pH in aqueous medium at 25 °C. Copper-poly(N-isopropylacrylamide-co-acrylic acid) [Cu-P(NIPAM-co-AAc)] hybrid microgels were used as a catalyst for the reduction of 4-nitrophenol (4-NP). Effect of temperature, concentration of sodium borohydride (NaBH₄) and catalyst dosage on the value of apparent rate constant (k_{app}) for catalytic reduction of 4-NP in the presence of Cu-P(NIPAM-co-AAc) hybrid microgels were investigated by UV-Vis spectrophotometry. It was found that the value of k_{app} for catalytic reduction of 4-NP in the presence of Cu-P(NIPAM-co-AAc) hybrid microgel catalyst increased with an increase in catalyst dosage, temperature and concentration of NaBH₄ in aqueous medium. The results were discussed in terms of diffusion of reactants towards catalyst surface and swelling-deswelling of hybrid microgels.

Keywords: *microgels; copper; nitrophenol; catalysis; energy of activation*

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1. Introduction

The study of synthesis and stabilization of copper (Cu) nanoparticles is of great importance due to their diverse applications in anti-microbial activity [1], optics [2], lubrication [3], biosensing [4] and catalysis [5, 6]. The study of Cu nanoparticles is always hindered because these nanoparticles do not stabilize easily. They oxidize and coagulate rapidly. Thus, these nanoparticles are not be suitable for applications even after a very short storage time. On the other hand, these coinage metals are very cheap and abundantly available in Earth's crust. Therefore, in this work, we synthesized and stabilized Cu nanoparticles within microgels. Cu nanoparticles have been synthesized by solvothermal [7], metal salt

reduction [8], microwave heating [9], metal vapour [10] and sonochemical reduction methods [11]. Synthesis of Cu nanoparticles by metal salt reduction method is the most advantageous due to its feasibility and fast reaction rate [12]. Commonly microgels [13], surfactants [14] and dendrimers [5] are used for stabilization of Cu nanoparticles. Microgels are good candidates for stabilization of Cu nanoparticles because they can be used as micro-reactors for in-vivo synthesis of monodisperse Cu nanoparticles. Microgels fabricated with Cu nanoparticles can be used for catalytic reduction, oxidation, degradation and synthesis of various organic and inorganic compounds [15–18]. Sahiner et al. synthesized Cu-P(2-acrylamido-2-methyl-1-propanesulfonic acid) hybrid hydrogels and used them for the study of catalytic reduction of 4-NP and o-nitrophenol (2-NP) [19].

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Nemanashi *et al.* prepared Cu nanoparticles fabricated dendrimers for catalysis of 4-NP [20]. Santhanalakshmi *et al.* synthesized three different hybrid systems: copper-poly(ethylene glycol) (Cu-PEG), copper-carboxy methyl cellulose (Cu-CMC) and copper-poly(N-vinyl pyrrolidone) (Cu-PVP), for catalysis of a series of nitroarenes [21]. According to the best of our knowledge, Cu nanoparticles fabricated within multiresponsive poly(N-isopropylacrylamide-co-acrylic acid) microgels [P(NIPAM-co-AAc)] have never been reported for detailed study of catalytic reduction of 4-NP.

In this work, we synthesized P(NIPAM-co-AAc) microgels by precipitation polymerization method. Cu nanoparticles were fabricated within these microgels by metal salt reduction method. Pure microgels were characterized by FT-IR and DLS. Cu-P(NIPAM-co-AAc) hybrid microgels were used as catalyst for reduction of 4-NP. Effect of pH, temperature, catalyst dosage and concentration of NaBH₄ on the value of apparent rate constant (k_{app}) and induction time (t_0) of reduction of 4-NP by Cu-P(NIPAM-co-AAc) catalyst was discussed.

2. Experimental

2.1. Materials

N-isopropylacrylamide (NIPAM) (≥ 97 % pure), acrylic acid (AAc) (≥ 99 % pure), N,N-methylenebis(acrylamide) (BIS) (≥ 99.5 % pure), sodium dodecylsulfate (SDS) (≥ 99 % pure), ammonium persulfate (APS) (≥ 98 % pure) and p-nitrophenol (4-NP) (≥ 99.5 % pure) were purchased from Sigma-Aldrich, Germany. Sodium borohydride (NaBH₄) (synthesis grade) was purchased from Scharlau Company, Australia. Aluminum oxide (Al₂O₃) was used for purification of AAc via filtration under reduced pressure. All other chemicals except AAc were used without any purification. Deionized water was used for all solution preparation, synthesis, dialysis and catalytic reduction.

2.2. Synthesis of P(NIPAM-co-AAc) microgels

P(NIPAM-co-AAc) microgels were prepared by precipitation polymerization of NIPAM and AAc using BIS as a crosslinker and APS as an initiator in aqueous medium, using the method reported by our group previously [22–26]. 13.14×10^{-3} mol NIPAM, 0.73×10^{-3} mol AAc, 0.73×10^{-3} mol BIS and 0.06 g SDS were dissolved in 95 mL deionized water in a 250 mL three-necked round bottom flask fitted with nitrogen gas inlet and condenser. This solution was allowed to heat up to 70 °C for 30 min under continuous purge of N₂ gas. Then, 5 mL of freshly prepared 0.05 M APS solution was added dropwise after 30 min. After the appearance of turbidity, the reaction was further continued for 5 hours under constant supply of N₂ gas at 70 °C. After synthesis the P(NIPAM-co-AAc) microgels were cooled and dialyzed using Spectra/Por® molecular porous membrane tubing containing MWCO 12000-1400. Dialysis was done for 7 days at room temperature along with frequent exchange of water.

2.3. In-situ synthesis of Cu nanoparticles in P(NIPAM-co-AAc) microgels

36 mL deionized water, 9 mL P(NIPAM-co-AAc) microgel dispersion and 37 mL copper chloride solution (1 mM) were poured into a 250 mL three-necked round bottom flask equipped with a condenser and N₂ gas inlet. After 20 min, 8 mL of 0.173 M NaBH₄ aqueous solution was added dropwise into the reaction mixture. The color of the solution changed abruptly from colorless to dirty green. After 2 hour stirring, Cu-P(NIPAM-co-AAc) hybrid microgels were subjected to dialysis against deionized water for 60 min at room temperature.

2.4. Catalytic reduction of p-nitrophenol

Initially 1 mL hybrid gel was diluted upto 10 mL using deionized water. Then 1.8 mL of diluted hybrid gel, 0.6 mL of 0.5 mM 4-NP and 0.6 mL of 50 mM NaBH₄ were added into a cuvette. Then the spectra were scanned in 200 to 500 nm wavelength range with a UVD 3500

spectrophotometer at a constant time intervals till the absorbance at 400 nm became constant.

Catalytic reduction of 4-NP was studied by varying the catalyst dosage, temperature and amount of NaBH_4 as given in Table 1.

2.5. Characterization

FT-IR spectra were scanned in 400 to 4000 cm^{-1} range with RX I FT-IR, Perkin Elmer, USA. DLS studies were conducted on BI-200SM using He-Ne laser at a scattering angle 90° . UV-Vis studies were carried out with UVD-3500 spectrophotometer.

3. Results and discussion

3.1. Fourier transform infrared spectra of P(NIPAM-co-AAc) microgels

The FT-IR spectra of P(NIPAM-co-AAc) microgel is shown in Fig. 1. Appearance of the absorption band at 3358.07 cm^{-1} represents symmetric stretching of N-H bond of NIPAM. Band at 3072.60 cm^{-1} represents the stretching vibration of C-H bonds of AAc, NIPAM and BIS. Absorption band at 2970.38 cm^{-1} indicates anti-symmetric stretching of alkanes. Band at 1558.55 cm^{-1} reflects the bending vibration of alkanes. Carbonyl group (C=O) gives characteristic band at 1654.92 cm^{-1} . Thus, it confirms that all monomers and the crosslinker have incorporated into synthesized P(NIPAM-co-AAc) polymer microgels. In literature the absorption band of carbonyl groups of NIPAM and AAc is found at 1640 cm^{-1} [27]. In FT-IR spectrum of P(NIPAM-co-AAc) microgels, this characteristic band becomes broader because of hydrogen bonding of water with carbonyl oxygen and amino nitrogen. There is no absorption band at 1600 cm^{-1} in FT-IR spectrum of P(NIPAM-co-AAc) copolymer microgels, which indicates that polymerization has occurred at carbon-carbon double bond (C=C) present in both monomers. This is because sulfate radicals transform the double bond into a single bond (C-C). Wang et al. also reported the same results [28]. Ajmal et al. used the same method for structural analysis of poly(*N*-isopropylacrylamide-

co-acrylamide-co-methacrylic acid) copolymer microgels [29].

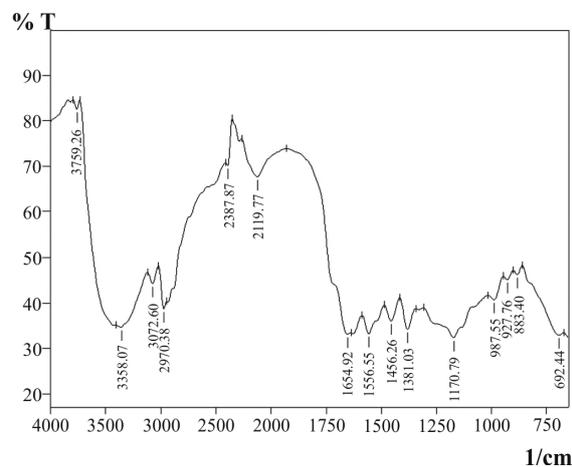


Fig. 1. FT-IR spectra of pure P(NIPAM-co-AAc) microgels.

3.2. pH sensitivity of P(NIPAM-co-AAc) microgels

Fig. 2 shows the change in hydrodynamic radius (R_h) of microgels as a function of pH of medium at 25°C . It is depicted from Fig. 2 that R_h of microgels continuously increases with an increase in pH of the medium. Continuous increase in R_h is due to successive ionization of carboxyl groups of AAc. pK_a of AAc is 4.35 so the carboxyl groups of AAc are in protonated form when pH is less than 4.35 [30]. Therefore, no electrostatic repulsive forces are present and the size of P(NIPAM-co-AAc) microgel particles becomes small. When pH becomes greater than the pK_a of AAc then almost all carboxyl groups get ionized into carboxylate ions [31]. Carboxylate groups are negatively charged, so electrostatic repulsive forces are developed. These forces push away polymer network of microgels, hence R_h of microgel particles increases. Carboxylate groups are more hydrophilic as compared to carboxyl groups [30]. Therefore, large amount of water enters into the microgel particles and osmotic pressure develops; as a result R_h of microgels particles increases [32]. That is why R_h abruptly increases in 4 to 8 pH range. On the other hand, there is no significant increase in R_h in the pH range of 8 to 12 because a very small

Table 1. Summary of composition of various reaction mixtures, values of k_{app} and values of induction time involved in catalysis by Cu-P(NIPAM-co-AAc) hybrid microgels using 0.1 mM 4-NP.

Factors	NaBH ₄ (mM)	Hybrid gel (mg/L)	Temperature (°C)	pH	t ₀ (min)	k _{app} (min ⁻¹)
Hybrid gel	10	0.06	16	10	10	0.104
	10	0.1	16	10	02	0.187
	10	0.2	16	10	01	0.274
NaBH ₄	10	0.06	16	10	10	0.104
	14	0.06	16	10	03	0.239
	16	0.06	16	10	03	0.583
Temperature	10	0.06	16	10	10	0.104
	10	0.06	26	10	01	0.114

number of carboxyl groups are present in the protonated state. In this way, pH of the medium affects the size of responsive P(NIPAM-co-AAc) microgel particles (Fig. 2).

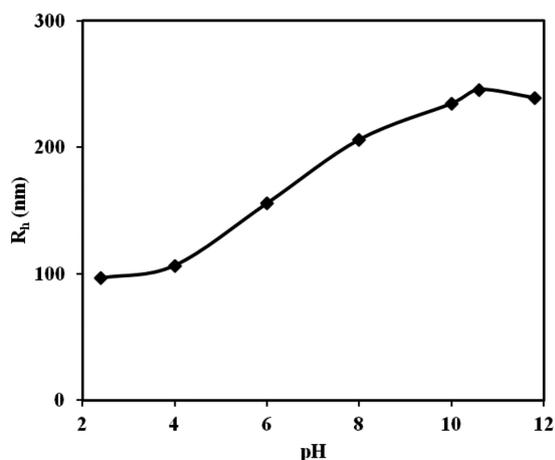


Fig. 2. Plot of hydrodynamic radius of P(NIPAM-co-AAc) microgels as a function of pH in aqueous medium at 25 °C.

In this study catalytic reduction of 4-NP was carried out at high pH. So, the reactants can easily access nanoparticles for catalytic reduction because the polymer network barrier against diffusion of reactants is negligible at high pH.

3.3. Catalytic reduction of p-nitrophenol

The reduction of 4-NP by Cu-P(NIPAM-co-AAc) hybrid microgels was chosen as a model

reaction to study the catalytic activity of Cu nanoparticles. Both reactant 4-NP and product 4-AP are UV-Vis absorbers and have different values of λ_{max} . UV-Vis spectrophotometry was used to monitor the progress of reaction. Initially the peak of 4-NP appears at 400 nm indicating the presence of 4-NP in the medium. Yellow color of 4-NP fades away slowly with the progress of reaction. Thus, the absorbance at 400 nm successively decreases and the absorbance at 300 nm (λ_{max} of 4-AP) successively increases as shown in Fig. 3. The measure of the reaction of 4-NP is the ratio of absorbance of 4-NP at any time t to the absorbance at time $t = 0$ (A_t/A_0) [33]. The reaction follows pseudo first order kinetics because the concentration of NaBH₄ was taken very large as compared to that of 4-NP.

Absorbance at 400 nm was noted at regular time intervals after addition of NaBH₄ only. No change in absorbance at 400 nm was observed, which indicates that reduction of 4-NP has not occurred in the absence of catalyst. Nanoparticles play an important role in transfer of electron from BH₄⁻ to 4-NP [34]. Therefore, this reaction is kinetically restricted in absence of Cu-P(NIPAM-co-AAc) hybrid microgels. Wu et al. have reported that catalytic reaction is kinetically restricted in the absence of hybrid composite microspheres [35]. Wang et al. used gold nanoparticles stabilized in P(N-isopropylacrylamide-co-4-vinylpyridine) colloid for reduction of 4-NP and observed that the reaction was kinetically hindered without addition of hybrid microgel [36].

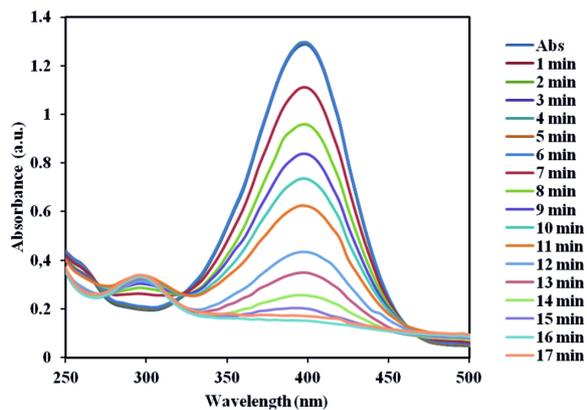


Fig. 3. UV-Vis spectra for reduction of 4-NP catalyzed by Cu-P(NIPAM-co-AAc) hybrid microgels at 16 °C (conditions: $[\text{NaBH}_4] = 10 \text{ mM}$ and $[\text{4-NP}] = 0.1 \text{ mM}$ in the presence of 0.06 mg/L catalyst dosage).

Catalytic reduction of 4-NP was carried out under various conditions of temperature, catalyst dosage and NaBH_4 concentration (Table 1).

3.3.1. Effect of catalyst dosage on the value of k_{app}

Plots of $\ln(A_t/A_0)$ versus time (min) for catalytic reduction of 4-NP at different catalyst dosages is shown in Fig. 4. Initially the value of $\ln(A_t/A_0)$ does not change for some time and then it starts to decrease. The time duration, in which the value of $\ln(A_t/A_0)$ remains constant is called induction period (t_0). The constant value of $\ln(A_t/A_0)$ upto this certain period indicates that reaction is not occurring in this time. Many other important processes, like diffusion of reagents and nanoparticles surface activation, occur in this time. The value of t_0 is different for different catalyst dosages. It decreases with an increase in catalyst dosage as given in Table 1. This shows that diffusion of reactants is the main process which occurs during t_0 . When the dosage of catalyst is low then the access of reactants to the surface of nanoparticles is difficult as compared to their access at high catalyst dosage. Therefore, the value of induction time decreases from 6 to 1 min when catalyst dosage increases from 0.06 to 0.2 mg/mL.

After t_0 the value of $\ln(A_t/A_0)$ starts to decrease with the passage of time (Fig. 5). The decrease in

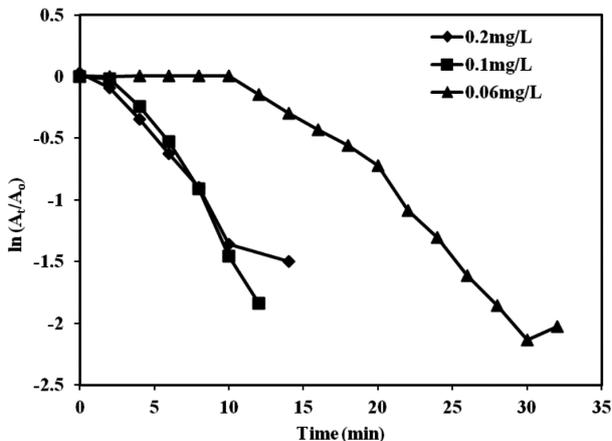


Fig. 4. Plot of $\ln(A_t/A_0)$ as a function of time for various concentrations of Cu-P(NIPAM-co-AAc) hybrid microgels (Conditions: $[\text{4-NP}] = 0.1 \text{ mM}$, $[\text{NaBH}_4] = 10 \text{ mM}$ and temperature 16 °C).

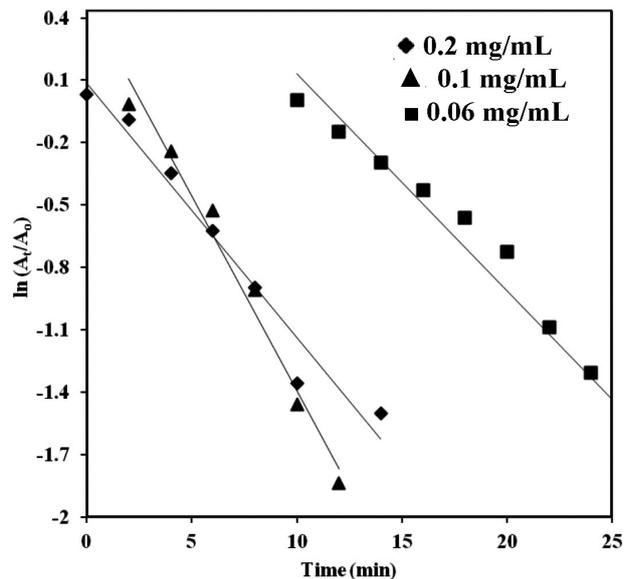


Fig. 5. Plot of $\ln(A_t/A_0)$ as a function of time used to calculate the value of k_{app} for various concentrations of Cu-P(NIPAM-co-AAc) hybrid microgels (conditions: $[\text{4-NP}] = 0.1 \text{ mM}$, $[\text{NaBH}_4] = 10 \text{ mM}$ and temperature 16 °C).

the value of $\ln(A_t/A_0)$ shows that reaction is taking place and concentration of 4-NP decreases with the passage of time [10]. The value of k_{app} for reduction of 4-NP was determined from the slope

of linear regions of the plot of $\ln(A_t/A_0)$ as a function of time. The values of k_{app} are given in Table 1 for different catalyst dosages. The value of k_{app} increases with an increase in the catalyst dosage. The surface for adsorption of reactants increases with an increase of catalyst dosage [37–39]. When catalyst dosage is high then greater number of molecules adsorb on the surface of nanoparticles and are converted into the product as compared to that when the catalyst dosage is low. Therefore, the value of k_{app} increases with an increase in catalyst dosage. Moreover, due to an increase of catalyst particle concentration, reactants take short time to reach the catalyst surface. That is why the value of k_{app} increases with the increase of the amount of catalyst employed. Our results have good agreement with previously reported results by Wu *et al.* [35]. Wu and his coworkers found that the value of k_{app} increases from 0.003 to 0.004 min^{-1} for catalytic reduction of 1.0×10^{-4} 4-NP using 0.1 M NaBH_4 as a reducing agent by varying the amount of silver-cellulose catalyst from 100 to 150 mg/mL, respectively.

3.3.2. Effect of NaBH_4 concentration on the value of k_{app}

The values of k_{app} and t_0 for catalytic reduction of 4-NP in the presence of different concentrations of NaBH_4 were determined from the plot of $\ln(A_t/A_0)$ versus time (Table 1). The value of t_0 decreases from 10 to 3 min when the concentration of NaBH_4 increases from 10 to 16 mM (Table 1). Small value of t_0 under high concentration of NaBH_4 shows that surface activation of nanoparticles occurs rapidly when the concentration of NaBH_4 is high. The surface of catalyst is susceptible to oxidation in oxygen containing environment. So, there is a probability of copper oxide formation on the catalyst surface. Addition of NaBH_4 first reduces the oxides of Cu and restores the surface for further reaction proceeding [40]. Therefore, quick removal of oxide layer occurs under high concentration of NaBH_4 and the value of t_0 decreases. The values of k_{app} for 10, 14 and 16 mM NaBH_4 are mentioned in Table 1. It is clear from Table 1 that the rate of reaction linearly increases with an increase in concentration of NaBH_4 . When

the concentration of NaBH_4 is increased in the reaction mixture, large number of NaBH_4 gets adsorbed on the surface of Cu nanoparticles [41]. It was predicted that the reaction follows the Eley-Rideal mechanism, according to which an increase in the concentration of adsorbed species enhances the overall rate of reaction. Thus, the value of k_{app} increases with an increase in concentration of NaBH_4 as reported previously in literature for metal nanoparticles fabricated in a cellulose system [35].

3.3.3. Effect of temperature on catalytic activity of Cu-P(NIPAM-co-AAc) hybrid microgels

Catalytic reduction of 4-NP was carried out at two different temperatures in an aqueous medium. The values of t_0 and k_{app} at 289 and 299 K are given in Table 2. It is clear from Table 2 that the value of t_0 decreases from 10 to 1 min when temperature increases from 289 to 299 K due to an increase of diffusion rate with temperature as predicted by Stokes-Einstein's equation [42]. The value of k_{app} increases with an increase of temperature as given in Table 2, which is due to well known Arrhenius behavior of reaction. The studied system does not deviate from Arrhenius behavior at temperature below the volume phase transition temperature, so Arrhenius equation was used for determination of activation energy (E_a) and pre-exponential factor (A). The values of E_a and A are given in Table 2. The low value of E_a indicates that Cu-P(NIPAM-co-AAc) is an effective catalyst for reduction of 4-NP in an aqueous medium. Manesh *et al.* studied silver nanoparticles dispersed in a network of polyaniline bridged silica for catalytic reduction of 4-NP and found that the rate of catalytic reduction of 4-NP increased with an increase in temperature [40].

4. Conclusions

P(NIPAM-co-AAc) microgels were synthesized by precipitation copolymerization. FT-IR and DLS techniques were used to characterize the polymer microgels. The synthesized P(NIPAM-co-AAc) microgels were used as microreactors for synthesis of Cu nanoparticles. Synthesized

Cu-P(NIPAM-co-AAc) hybrid microgel were employed as catalyst for reduction of 4-NP in aqueous medium. Pseudo first order kinetic equation was used to investigate the catalytic activity of the hybrid system. Effect of various parameters, such as temperature, catalyst dosage and concentration of NaBH₄ on the induction period as well as on the overall catalytic reduction rate of 4-NP were investigated by UV-Vis spectrophotometry. The values of k_{app} for 0.06 to 0.2 mg/L catalyst dosage were found in the range of 0.104 to 0.274 min⁻¹, whereas for 10 to 16 mM concentration range of NaBH₄, the values of k_{app} were in the range of 0.104 to 0.583 min⁻¹. It was predicted that the synthesized Cu-P(NIPAM-co-AAc) hybrid system follows Eley-Rideal mechanism. Calculated activation energy for catalytic reduction reaction of 4-NP is 0.8 kJ/mol. Therefore, the prepared Cu-P(NIPAM-co-AAc) hybrid microgel is applicable in various fields, in which controlled nanoparticles synthesis and their subsequent application for the removal of 4-NP from industrial sludge is involved.

Table 2. Calculated activation energy and pre-exponential factor of catalytic reduction reaction of 4-NP.

Temperature (K)	k_{app} (min ⁻¹)	Pre-exponential factor (A) (min ⁻¹)	E_a (kJ/mol)
289	0.104	0.145	0.8
299	0.114	0.157	

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