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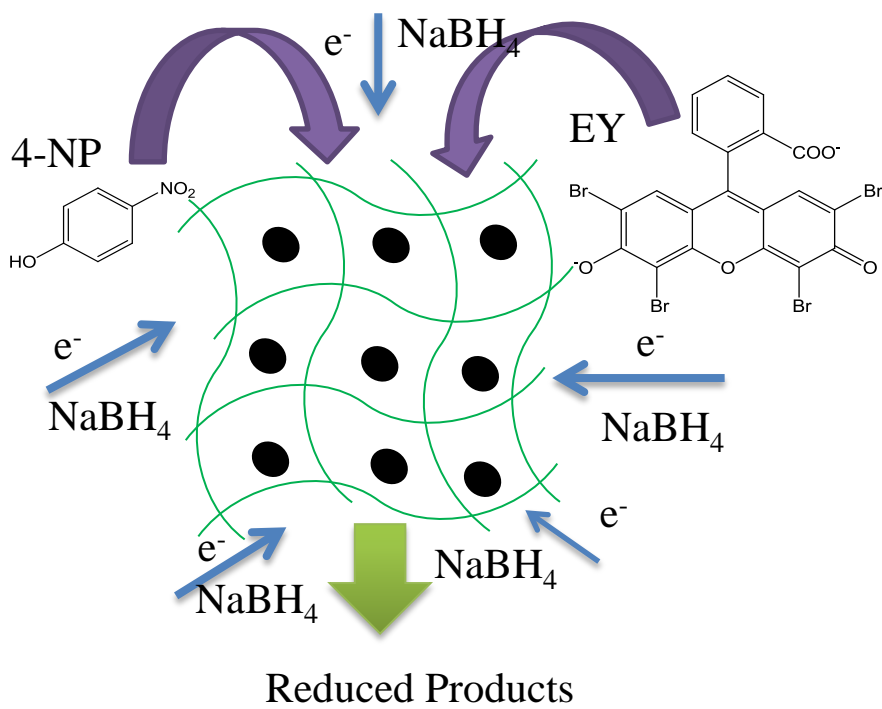
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Graphical Abstract



ARTICLE

Highly versatile p(MAc)-M (M:Cu, Co, Ni) microgels composite catalyst for individual and simultaneous catalytic reduction of nitro compounds and dyes

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Abstract

Poly(methacrylic acid) (P(MAc)) microgels were synthesized by inverse suspension polymerization and used as template for Copper, Nickel, and Cobalt nanoparticles preparation. Upon absorption of Co(II), Ni(II), and Cu(II) by p(MAc) microgels from related aqueous solutions, the metal ion laden microgels were treated with sodium borohydride (NaBH₄) to obtain the corresponding metal nanoparticles within p(MAc) network as p(MAc)-M (M:Co, Ni, Cu). Microgels and metal nanoparticle containing composites were visualized and analyzed by Optical Microscopy, SEM, and TEM analysis. Thermal properties and the metal nanoparticle content of the prepared composites were investigated by TG analysis. However, the exact amounts of metal nanoparticles entrapped within microgels was calculated by AAS measurements after dissolution of metal nanoparticles within p(MAc) microgel composites by concentrated HCl acid treatment. The prepared p(MAc)-M composites were employed as catalyst for the degradation of some organic dyes such as Eosin Y (EY), and Methyl Orange (MO), and reduction of nitro aromatic pollutants such as 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 4-nitroaniline (4-NA) to their corresponding amino phenols. More importantly, we report the simultaneous degradation of EY and 4-NP reduction catalyzed by p(MAc)-Cu microgel composites. Various parameters effecting the degradation of dyes and nitro compound reduction such as metal types, and their amounts, temperature and amount of reducing agent were investigated.

Introduction

From the last few decades, metal nanoparticles have been used for many purposes including catalysis [1], biomedicine [2], bio/imaging [3], sensors [4–6] electronics and so on. The large surface area and high surface energy enable nanoparticles to become excellent catalytic materials and some of them reported as superb catalysts for many chemical reactions such as CO oxidation [7], carbon nanotube nucleation [8], alcohol dehydrogenation [9] and formic acid electro-oxidation [10]. However, because of the high surface energy and the presence of van der Waal forces, the nano-sized particles can aggregate readily leading to decrease in their surface area causing a significant decrease for catalytic activity [11,12]. Nevertheless, metal nanoparticles should be stabilized and prevented from aggregation by using suitable stabilizing systems such as hydrogels

[13–16], dendrimers [17,18], block copolymer micelles [19] and latex particles [20,21]. Among the various types of carrier systems hydrogels are becoming more popular carriers not only for *in situ* metal nanoparticle preparation capability but also because of their ability to swell to a large extent by absorbing huge amount of water and thereby providing an excellent medium for the aquatic catalytic reactions. These carrier systems also facilitate easy recycling of nano catalysts without leaching or loss of metal nanoparticles. The presence of metal-binding functional groups in the hydrogel networks, such as –SO₃H, –OH, –COOH, –SH, and –NH₂ enable them to uptake high amounts of metal ions from aqueous medium, and fix them in the hydrogels matrices due to electrostatic and dipole-ion attractions and then readily reduced *in situ* under mild conditions by using a suitable reducing agent. Therefore, it is pertinent to use hydrogels as effective reactors for *in situ* synthesis

of metal nanoparticles to prevent their aggregation and store them for longer times. Many polymeric hydrogel networks have been reported as soft reactors for *in situ* preparation of metal nanoparticles and their use as catalyst for degradation of aromatic pollutants and dyes [22-25]. Most of research in the literature focused on Au, Ag and Pd nanoparticles preparation and their use in the catalytic reduction of 4-NP to 4-aminophenol [26-28]. Similarly Au, Ag, and Pt nanoparticles fabricated in microgels and their use as catalysts have been reported by different research groups [29-31]. Although these noble metals show high catalytic activity, but their high cost and rather difficult and time consuming recovery from the reaction medium hinders their use at industrial scale. Therefore, there is a great need for cost effective and at least analogous to noble catalysts in terms of catalytic performance with additional advantages such as readily removal ability from the reaction medium, on demand to control the reaction and for their reusability. To overcome the separation, recovery and economical problems, magnetically recyclable catalysts, and nanoparticles of cheap metals embedded in micron or macro size hydrogel particles which can be easily recycled with centrifugation or filtration have been synthesized by our research group [32-34].

However, instead of using magnetic iron oxides, to use inherently magnetic nanoparticles with a good catalytic performance is of great significance to explore the effect of chemical atmosphere on the stability, and the catalytic activity of the metal nanoparticles. In this context, herein p(MAc) microgels were prepared and used as micro reactors for the synthesis of Ni, Co, and Cu nanoparticles by *in situ* reduction of these ions, and then used as catalysts for the degradation of aromatic dyes, EY and MO, and also in the reduction of 2-NP, 4-NP and 4-NA to their amino forms. More interestingly, until now, there have been no reports on simultaneous degradation of pollutants from the same industrial effluent e.g., an organic dye and nitro aromatic reduction can be done simultaneously. Although there are many reports on the individual degradation of organic dyes and nitro aromatic pollutants [12, 25, 32-34], there is no report for the concurrent catalytic elimination of different toxic organic species such as nitro compound and aromatic dyes. Here, the simultaneous degradation of organic dyes and nitro compounds in the same reaction medium is reported. To the best of our knowledge this is the first report that micron sized p(MAc) microgel particles have been employed as micro reactors for the fabrication of common transition metal nanoparticles, and then catalyst for two different reaction reactions taking place concurrently at the same time medium. Since industrial waste may contain different pollutants in the same stream requiring individual treatments necessitating various processes resulting in high cost or economic problems, longer times and tedious treatment procedures with extra burden for chemicals and premises. Therefore, the simultaneous removal and/or degradation toxic species by only one operating system such as p(MAc)-Cu can be very useful to overcome these hurdles. Degradation of more than one pollutant at the same time from industrial waste provide great advantageous in terms of time, energy and labour with great economical benefits.

Experimental

Materials

Methacrylic acid (MAc, 99%, Aldrich) as monomer, *N,N*-methylenebisacrylamide (MBA 99%, Acros) as the crosslinking agent, ammonium persulfate (APS 98%, Aldrich) as initiator, *N,N,N',N'*-tetramethylethylenediamine (TEMED, Merck) as an accelerator and cyclohexane (99.8%, Sigma Aldrich) used as

solvent. All these chemicals were used as received. Sodium hydroxide (NaOH, 98%, Aldrich) was used to neutralize p(MAc) microgels and cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 99% Sigma Aldrich), copper(II) chloride (CuCl_2 , 99% Aldrich) and nickel (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 97%, Riedel-de Haën) were used as metal ion sources while sodium borohydride (NaBH_4 , 98% Aldrich) was used as reducing agent for metal nanoparticle preparation. Organic nitro compounds, 2-nitrophenol (2-NP, 99% Acros), 4-nitrophenol (4-NP, 99% Acros), 4-nitroaniline (4-NA, 99% Sigma) were used in the reduction. Eosin Y (EY, 90%, Sigma Aldrich) and methyl orange (MO containing acid orange 52, Fluka analytical) were used as organic dyes. Double distilled water (DI) was used throughout the experiments.

Synthesis of P(MAc) Microgels

P(MAc) microgels were prepared by inverse suspension polymerization with some modifications in earlier reported method [35]. Briefly, in a 100 mL round bottom flask, 50 mL cyclohexane containing 160 μL span 80 was added. This mixture was homogenized by stirring and purged with N_2 for 15 minutes to remove oxygen. The initiator, 0.054g of APS (2 mol% of MAC, dissolved in 1 ml distilled water (DI)), and 0.0091g MBA (0.5 mol% of MAC) and 1 mL MAC were mixed in a vial, and added into reaction flask containing cyclohexane and span 80 mixture. This new reaction mixture was stirred continuously and purged with N_2 for further 10 minutes. Then the reaction was initiated by the addition of 250 μL TEMED and allowed to proceed for 5 hours at 40 °C in an oil bath. Then, the prepared microgel particles were collected by decantation of cyclohexane. The microgel particles were washed with ethanol and then with DI by centrifugation at 10 000 rpm at 20 °C for 10 minutes followed by removal of the supernatant solution and re-dispersing in distilled water and re-centrifugation at least five times for cleaning purpose. After cleaning microgels were neutralized by treating with equivalent amount of NaOH and washed again with DI two times, and then precipitated in water-ethanol mixture. Finally P(MAc) microgels particles were dried in freeze dryer (Christ Alpha 1-2 LD plus). These microgel were used for characterization and as microreactor for the synthesis of metal nanoparticles, and then catalysis for reduction of nitro compound and dyes.

In Situ Synthesis of Metal Nanoparticles in P(MAc) Microgels

For *in situ* synthesis of metal nanoparticles within p(MAc) micronetwork, first metal ions were loaded into microgel network by dispersing 0.1g of the dried neutralized dried p(MAc) microgel in 50 mL, 500 ppm aqueous solution of metal chlorides (M (II): Co (II), Cu (II), Ni (II)) for overnight at room temperature under continuous stirring (500 rpm). M (II) ions loaded microgels were separated from this mixture by centrifugation (2000 rpm), and washed with DI to remove unbound metal ions. Then, metal ions laden microgels were treated with 50 mL, 0.1M NaBH_4 to reduced metal ions within microgel network. The reduction was allowed to proceed until no more H_2 gas was evolved. Finally, the prepared p(MAc)-M microgel composites were filtered (with plankton cloth filter paper having pore size 2 μm), washed with DI and used for characterization and as catalysts. The amounts of metal nanoparticles entrapped in microgels were calculated by atomic absorption spectroscopic (AAS) measurements after dissolution of metal nanoparticles entrapped within p(MAc) microgel by treating with 5M HCl aqueous solution.

Catalytic Tests

Catalytic activity of the synthesized microgel nanoparticle composites (p(MAc)-M) were investigated by using them as catalyst for the reduction of 2-NP, 4-NP and 4-NA, as well as some dyes. Nitro compound solutions of 0.01 M 2-NP, 0.01 M 4-NP and 0.0025 M 4-NA in 50 mL were prepared and to this solution 0.756 g NaBH₄ was added and stirred in a temperature control oil bath at 750 rpm at 30 °C. To this mixture, certain amount of composite microgel containing specific amount of metal nanoparticles (e.g., 0.092 mmoles of M(II) as determined by AAS) was added as a catalyst to initiate the reduction. During the reduction, about 0.1 mL samples were withdrawn from the reaction mixture at certain time intervals, and diluted to certain ratios with DI i.e., 80 times dilution for 4-NP, 30 times for 2-NP and 20 times for 4-NA. Then, their absorption spectra were recorded by UV-Visible spectrophotometer (UV-Vis, T80+, PG Instruments). Reduction rate constants for nitro compounds were calculated by measuring the decrease in intensities of their absorption peaks at 400 nm, 414 nm, and 380 nm for 4-NP, 2-NP and 4-NA respectively. For each nitro compounds, a calibration curve is formed at the mentioned wavelengths for determination of the concentration of the reactants. The effect of temperature on reduction rates was studied by conducting the reactions at four different temperatures, 30 °C, 40 °C, 50 °C and 60 °C. In this manuscript, every measurement was carried out at least three times, and average values are given as the mean value with standard deviations.

Catalytic properties of prepared composites were also studied by using them as catalyst in the degradation of EY and MO dyes. In a typical experiment, 0.075 g of NaBH₄ was added in 100 mL aqueous solution of dye (EY 4x10⁻⁵ M and MO 4x10⁻⁴ M). P(MAc)-M composite (M: 0.092 mmoles) was added as a catalyst to initiate this reaction. From the reaction mixtures, 0.5 mL samples were withdrawn at specific interval of times, and diluted 10 times for EY, and 8 times for MO with DI, and their absorption spectra were recorded by UV-Visible spectrophotometer. P(MAc)-Cu composites were also employed as catalysts for the simultaneous degradation of EY and 4-NP. For this reaction, 50 mL of 0.002 M solution of 4-NP and 50 mL of 16x10⁻⁵ M solution of EY were mixed to prepare a 100 mL solution containing both 4-NP and EY. And, 0.15 g of NaBH₄ was added as reducing agent, and progress of reaction was monitored in the presence p(MAc)-Cu composite catalyst containing 0.092 mmoles Cu. During reaction, 0.5 mL of samples were withdrawn from reaction mixture, diluted 11 fold by addition of DI, and their absorption spectra were recorded by UV-Visible spectrophotometer. The reusability of catalyst was demonstrated by using the same catalysts for four times consecutively in the reduction of 4-NP. After every usage, the catalyst was separated from reaction mixture by filtration, washed with DI and reused in the same reaction conditions again.

Results and Discussion

Synthesis of p(MAc) microgels, and their use for *in situ* metal nanoparticles preparation

P(MAc) microgels were synthesized by inverse suspension polymerization as described in experimental part. Monomer, initiator and cross-linking agent react to form spherical micron size microgel particles. Initiator starts the polymerization by reacting with monomers and form oligomers as unstable colloidal precursors, these colloidal precursor particles may tend to aggregate or grow to form a longer chain until they become stable particle. Figure 1(a) illustrates the schema of *in situ* metal nanoparticle preparation within p(MAc) microgels, whereas in (b) the SEM images of p(MAc)

microgel where the particle sizes are about 200 μm, and the digital camera images of the different metal ion absorbed microgels e.g., blue for p(MAc)-Cu, pink for p(MAc)-Co, and light green for p(MAc)-Ni is clearly seen, and their reduction to corresponding metal nanoparticle, black colored as p(MAc) is also given in Figure 1(b). As p(MAc) microgels contain many carboxyl groups (-COOH) that readily deprotonate to form negatively charged groups (COO⁻) and these groups can be utilized to load positively charged metal ions into microgel network from aqueous solution of Cu, Co, and Ni salts due to electrostatic attraction. By applying this approach, metal nanoparticles were synthesized by *in situ* reduction of metal ions within microgels matrices. Digital camera images of metal ion absorbed p(MAc) microgels and p(MAc)-M composites were illustrated in Figure 1(b). As illustrated each metal ions give its unique color to the p(MAc) microgels and turn in black color upon reduction with NaBH₄ as an indication of the formation of nanoparticles.

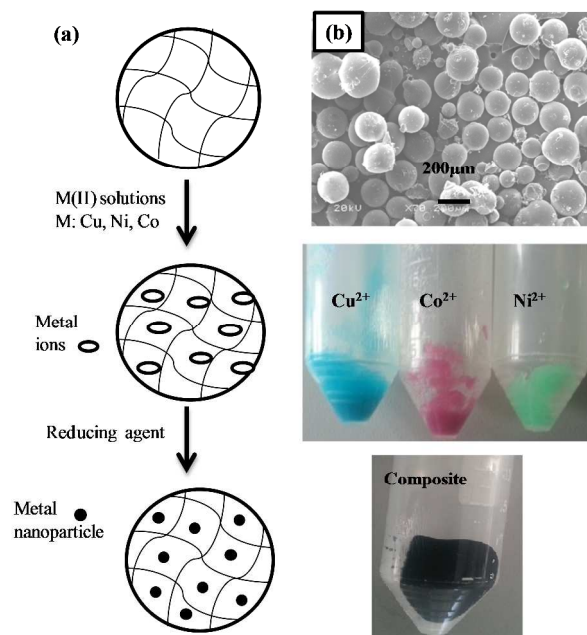


Figure 1. (a) The schematic representation of *in situ* metal nanoparticle preparation within p(MAc) microgel as p(MAc)-M, and (b) SEM images of P(MAc) Microgel particles, and the digital camera visualization of different metal absorption with p(MAc) microgel and their reduction to the corresponding metal nanoparticles as p(MAc)-M (M: Co, Ni, Cu).

Metal nanoparticles prepared inside the microgels network were visualized by TEM. The TEM images of the metal nanoparticles prepared within p(MAc) microgel are given in Figure 2. It is obvious from the images that depending upon the nature of metal sources the prepared metal nanoparticles are spherical in shape and almost homogeneously distributed within the polymeric matrices as there is no aggregation.

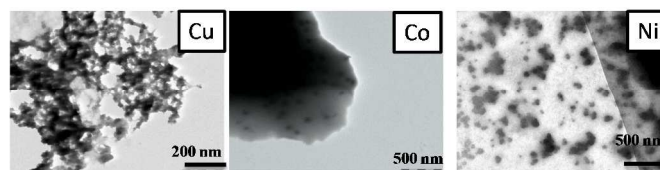


Figure 2. TEM Images of p(MAc)-M (M:Cu, Co, Ni) microgels composites.

To determine the thermal properties and the amount of metal nanoparticles entrapped inside the microgels network, thermal gravimetric analysis (TGA) were performed. Thermograms of pure and composite microgels are given in **Supporting Figure S1**, which shows the bare and composite microgels degradation heating up to 700 °C. It is noteworthy mentioning here, that bare p(MAc) have two distinct degradation temperature at about 241 and 442 °C with 24 and 94 wt% lost, respectively. On the other hand, p(MAc)-M composites depending on the metal nanoparticles have higher degradation temperature and lesser amount of weight losses even up to heating 800 °C, e.g., p(MAc)-Cu with 39 wt% loss, p(MAc)-Ni with 48 wt% loss, and p(MAc)-Co with 56 wt% loss was observed. However, it is obvious that an increase in thermal stability was observed in case of all composites due to entrapment and entanglements of complexed nanoparticles with the polymer chains. Although, the TGA result give some information about the thermal stability of the particle, the exact amount of metal nanoparticles present in the microgels network can not be estimated by TGA measurements due to formation of some metal oxides as abundant existence of -COO groups within microgels network that cause the oxidation of metal nano particles as well as the formation boronic metal nanoparticles during reduction period since NaBH₄ was used as reducing agents. To calculate the exact amounts metal ion absorption capacity p(MAc) microgels and the amounts of metal nanoparticles present in p(MAc)-M composites atomic absorption spectroscopy (AAS) was used. The amount of metal ions absorbed by the microgels was calculated by measuring concentration of metal ions from their corresponding aqueous solution before and after their interaction with microgels. It was observed that 195 mg of Co²⁺, 190 mg of Cu²⁺ and 140 mg of Ni²⁺ was absorbed per gram of dry microgel. Since these metal ions were absorbed from their 50 ml, 500 ppm solutions, it was calculated that 76 weight % of Cu²⁺, 66 weight % of Ni²⁺ and 78 weight % of Co²⁺ was absorbed by p(MAc) microgels from 50 ml, 500 ppm aqueous solutions of these metal salts. Therefore, the ability the same functional group to absorb different metal ions is different even though the metal ions have the same charges on them. Therefore, the absorption capacity of a functional group not only depends on the charge of metal ion but also depends on their nature such as size and the ability to complex with ligand as well. In order to calculate the percent conversion of absorbed metal ions to metal nanoparticles, the prepared p(MAc)-M composites were washed with DI and treated with 5 M HCl solution (30 ml) to dissolve metal nanoparticles into their ionic forms as M²⁺ to determine their amounts by AAS. And it was found that p(MAc)-M composite microgels contain 181.2 mg Co, 173.5 mg of Cu and 125.7 mg of Ni per gram of composite microgel. So, these results show that 93% of Co²⁺, 91% of Cu²⁺ and 90% of Ni²⁺ out of total loaded amounts were converted to their metal nanoparticle forms. The decrease in the conversion to metal nanoparticles from the absorbed metals ions within p(MAc) may be attributed due to loss of metal ions or metal nanoparticles during washing of metal ion loaded or composite microgels. It is worth mentioning that the amount of metal ions absorbed by p(MAc) microgels is very high as compared to previous reports [36, 37]. The high metal ion absorption capacity of these microgels is due to presence of large number of -COO groups generated by neutralization by NaOH treatment of p(MAc) microgel before loading with M(II) ions, which interact with the large amount of metal ions in comparison to its non ionized forms (-COOH). And thus, the amounts of metal nanoparticles generated within these microgels are higher than the earlier studies [36, 37]. This also demonstrates an important advantage of this microgel system that by using small amount of microgels greater number of

metal nanoparticles can be generated within polymeric matrix proving the economical feasibility and more favorable nature of charges in polymeric micronetworks. Moreover p(MAc)-Co nano composites were found to show inherently magnetic behavior as shown in Figure 3.

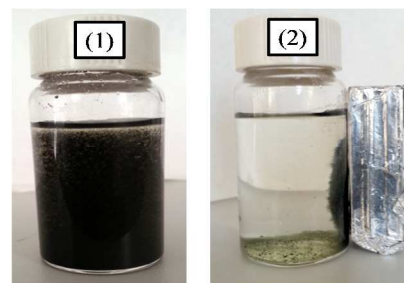


Figure 3. P(MAc)-Co composites (1) in the absence and (2) presence of externally applied magnetic field.

Upon applying an external magnetic field on p(MAc)-Co composite suspended in water as illustrated in Figure 3 as (1), the microgel composites were attracted to the direction of magnet as shown in Figure 3 as (2). This inherently **magnetic responsive behaviour for catalysts** make them unique and offer great opportunity in recovery of catalysts from the reaction medium upon performing their task, e.g., completion of catalytic reactions.

Catalytic activity of P(MAc)-M composites

Catalytic activity of the prepared p(MAc)-M composites was investigated by employing these microgel composites as catalysts for degradation of organic dyes such as EY and MO, and in the reduction of 2-NP, 4-NP and 4-NA and then most importantly for simultaneous reduction of nitrophenol and dye in the same reaction medium. Nitro compound reactions were selected due to their importance in the environments, and in the number of manufacturing of various pharmacology products and various aromatic products in dye and pigment industries [38, 39]. For example in pharmaceutical industries some important antipyretic and analgesic medicines such as paracetamol, acetanilide and phenacetin are prepared from 4-aminophenol which can be obtained by catalytic reduction of 4-NP [40, 41]. While the products obtained by reduction of 2-NP and 4-NA are extensively used in industries for the synthesis of various dyes and pigments. However, these nitro compounds are considered as very toxic pollutants and as they are discharged from many industries as waste materials. Therefore, their elimination by any means i.e., reduction is also important to convert these toxic pollutants into useful compounds. The reduction of each of 2-NP, 4-NP and 4-NA produce only their corresponding amines and the progress of reaction can be readily monitored by UV-Visible spectroscopy by measuring absorption maxima at suitable wavelengths. Although thermodynamic studies suggest that the reduction of these nitro compounds are feasible in the presence of aqueous solution of NaBH₄, the presence of large potential difference between electron donor and acceptor creates a large kinetic barrier that suppresses the feasibility of these reduction even in the presence of excess amounts of reducing agent [42, 43]. Fortunately, the presence of a catalyst helps to overcome this energy barrier and makes these reactions feasible under mild conditions such as room temperature. Herein, initially the reduction of 4-NP in

the presence of only NaBH_4 was studied, and it was observed that very small amounts of nitro compounds were converted to corresponding amino compounds even after long times as shown in Figure 4 (a). The UV-Vis spectra for 2-NP reduction in the absence, and presence of p(MAc)-Cu was given in Supporting Figure S2 (a) and (b), respectively and for the reduction of 4-NA, the spectra are also given in Figure S2 as (c), (d) in the absence and presence of p(MAc)-Cu composites at 30 °C.

In all the catalytic reduction of nitro aromatic compounds 0.092 mmoles of metal ions containing p(MAc)-M composites were used as catalyst. Also, all the reduction of nitro compound reactions were carried out in the presence of large excess of NaBH_4 (40 fold as compared to nitro compound in moles). The catalysts facilitate electron transfer from electron donor BH_4^- to acceptor nitro compounds and thus accelerating the reaction to proceeds [43, 44]. Reduction of nitro compounds was tracked by measuring the decrease in their absorbance peak in UV-Vis spectra taken at various intervals of times as shown in Figure 4(b). The difference in reduction of aromatic nitro compounds in the presence of p(MAc)-Cu is tremendous as seen in the corresponding figures.

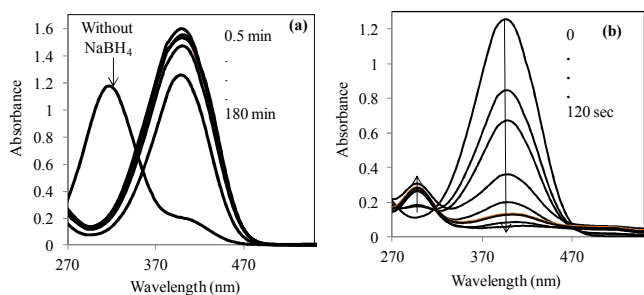


Figure 4. UV-Visible spectra for the reduction of 4-NP (a) in the absence, and (b) in the presence of P(MAc)-Cu composites at 30 °C.

As the reduction were carried out in the excess of NaBH_4 , the reaction supposed to be pseudo first order reactions. Therefore, pseudo-first-order kinetics with respect to the nitro compound concentration was used for evaluation of apparent rate constants (k_{app}). The values of k_{app} were calculated from the slope of straight line regions of plots of $\ln(C_t/C_0)$ against time and were shown in Figure 5 (a), and the change in k_{app} with temperatures were shown in Figure 5(b) for 4-NP reduction. The reduction by p(MAc)-M composite versus time for the determination of k_{app} values for 2-NP, and 4-NA were given in Supporting Figure S3.

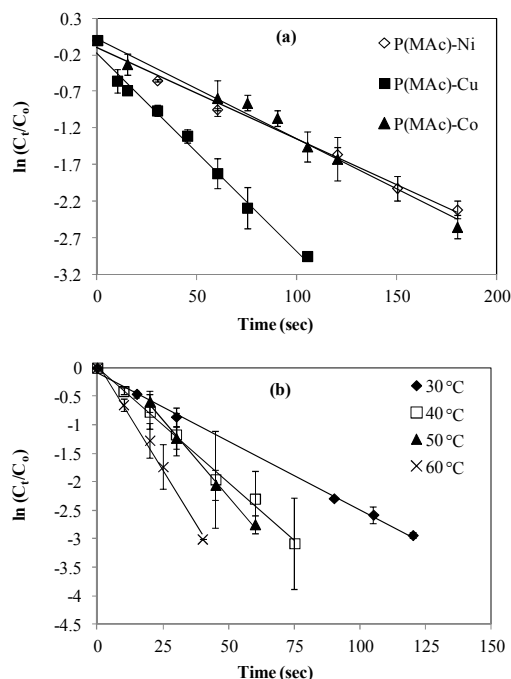


Figure 5. The determination of apparent rate constants (k_{app}) for the reduction 4-NP catalyzed by p(MAc)-M (Cu, Co, Ni) composites 30 °C (a) with time, and (b) with temperature by p(MAc)-Cu.

The values of k_{app} calculated at 30 °C for different metal composites and different nitro aromatic compounds are given in Table 1. As can be seen from Table, the k_{app} values for the reduction of 2-NP, 4-NP and 4-NA are rather small for all p(MAc)-M, and there is no trend between or amongst them. As 4-NP is considered comparatively more toxic than the others [45], and also its reduction to 4-AP is an intermediate step in the synthesis of some important antipyretic and analgesic medicines such as paracetamol, acetanilide and phenacetin, the kinetics of the reduction of this compound was studied in detail.

Table 1. Values of k_{app} for the reduction of nitro compounds and dyes.

Nitro compound	Catalyst	k_{app} (sec ⁻¹)	R^2
2-NP	P(MAc)-Cu	0.0071 ± 0.0009	0.9761
	P(MAc)-Co	0.0095 ± 0.002	0.9857
	P(MAc)-Ni	0.0197 ± 0.008	0.9972
4-NP	P(MAc)-Cu	0.027 ± 0.0020	0.989
	P(MAc)-Co	0.014 ± 0.0016	0.982
	P(MAc)-Ni	0.0125 ± 0.0002	0.992
4-NA	P(MAc)-Cu	0.052 ± 0.01	0.9986
	P(MAc)-Co	0.0037 ± 0.0018	0.9891
	P(MAc)-Ni	0.035 ± 0.001	0.9912
MO	P(MAc)-Cu	0.025 ± 0.01	0.9919
	P(MAc)-Co	0.004 ± 0.00003	0.9928
	P(MAc)-Ni	0.002 ± 0.0002	0.9894
EY	P(MAc)-Cu	0.004 ± 0.00007	0.9276

k_{app} = apparent rate constant R^2 = coefficient of determination

Reaction conditions = 50ml solution [0.01M 4-NP, 0.01M 2-NP, 0.0025M], 100ml solution [EY 4×10^{-5} M and MO 4×10^{-4} M]. P(MAc)-M composite (M: 0.092 mmoles). $\text{NaBH}_4 = 0.756\text{g}$, 750rpm, 30°C.

The effect of metal types on the reduction rate of 4-NP catalyzed by p(MAc)-M composites that contains the same amounts of Cu, Co, and Ni nanoparticle as catalysts were shown in Figure 5 (a), and as can be seen that p(MAc)-Cu composites reduce 4-NP faster than Ni and Co containing composites, therefore p(MAc)-Cu composite was chosen as catalyst for the detailed kinetic study. Catalytic performances of p(MAc)-Cu composites for the reduction of different nitro compound was demonstrated in Supporting Figure S3, shows that 4-NP was reduced faster as compared to 2-NP. As p(MAc)-Co microgel composites are inherently magnetic, they can be very useful in the reduction of 4-NP, and as shown in Table 1, the reduction rate constant of 0.013 sec⁻¹ was estimated which is almost very close to previously reported 0.015 sec⁻¹ by Goong and Lin when they employed highly expensive magnetic Au-Fe₂O₃ composite nanoparticles for the reduction of 4-NP [46]. Additionally, Ni/graphene nano composites were developed by Wu et al. in order to get increased catalytic activity as compared to bare Ni nanoparticles due to presence of graphene which adsorb hydrogen thus provides hydrogenation atmosphere which leads to a 2 fold increase in the catalytic activity [47]. The authors reported catalytic activity of Ni/graphene composite for the reduction of 4-NP to 4-AP as 0.0117 sec⁻¹ by using 3 mg Ni/graphene catalysts, 10 mg NaBH_4 for the reduction of 2 mL 0.1 mM 4-NP. Herein, the Ni nanoparticles prepared within p(MAc) microgels, and used for the same reaction employing comparatively higher concentration of reactants and lower amount of catalyst (33.4 mg of P(MAc)-Ni for 50 ml 0.01M 4-NP solution). And the reduction rate of 0.0125 sec⁻¹ was attained that is greater than reported by Wu et al. Furthermore, as compared to reports by Wu and Goong where they used Au-Fe₂O₃ composite particles and Ni/graphene nano composites [46,47], here very high reduction rate, 0.027 sec⁻¹, for the same reaction by using relatively cheaper Cu nanoparticles fabricated within p(MAc)

microgels demonstrates the significant advantages and the versatility of the p(MAc)-M catalyst systems.

Catalytic activity of p(MAc)-Cu composites for the reduction of 4-NP was studied as a function of temperature by carrying out the reduction at four different temperatures; 30 °C, 40 °C, 50 °C and 60 °C keeping the amount of reactant and catalyst constant. Dependence of rate of reaction on temperature is shown in Figure 5(b) in terms of change in $\ln(C_t/C_o)$ as function of time at different temperatures. With the increase in temperature, the reduction rates were also increased linearly as shown in Supporting Figure S4 (a). The increase in rate of reduction with temperature can be explained by the reason that at higher temperature, the average kinetic energy of molecules is increased which in turn increases the rate of diffusion of reactant molecules into microgel particles. Hence, an increase in the collision frequency of reactant and catalyst occurs. This increase in diffusion rate and collision number increases the rate of conversion of reactants into products. Using well known Arrhenius and Eyring equations, activation parameters can be calculated for reduction carried out at different temperatures catalyzed by p(MAc)-Cu. The activation energy (E_a) belonging to 4-NP reduction catalyzed by p(MAc)-Cu was calculated by plotting $\ln k_{app}$ vs. $1/T$ as shown in Supporting Figure S4 (b), and it was found as 31.3 kJ mol⁻¹. The activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) were calculated by plotting $\ln(k_{app}/T)$ vs $1/T$ as shown in Supporting Figure S4 (c), and their values were found as $\Delta H^\ddagger = 28.63$ kJmol⁻¹ and $\Delta S^\ddagger = -181.18$ kJmol⁻¹. To assess the effect of catalyst amount on the reduction rate of 4-NP reduction catalyzed by p(MAc)-Cu microgel composite, different amounts of catalysts were used for the same reduction under the same conditions. As illustrated in Figure 6(a), the increase in rate of reduction was observed with the increase in amount of catalyst. By increasing the amount of catalyst the total numbers of active sites to carry out the reaction in the reaction mixture are increased which increase the rate of formation of activated complex and effective collisions and thus the rate of reaction is also increased.

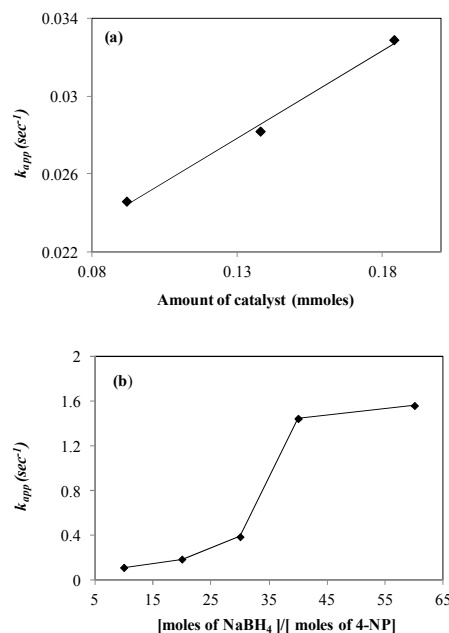


Figure 6. The dependence of k_{app} on (a) the amount of catalyst, and (b) amount of reducing agent normalized to NaBH_4 concentration catalyzed by p(MAc)-Cu microgel for the reduction of 4-NP to 4-AP.

In order to investigate the effect of amount of reducing agent on the reduction rate, different amounts of NaBH_4 were used by keeping all other parameters constants. It was observed that reduction rate was increased by increasing the amount of NaBH_4 as it can be seen from the increase in slope of linear regions of plots of $\ln(C_t/C_0)$ vs time drawn for different amounts of NaBH_4 and shown in Supporting Figure S5. By increasing the concentration of NaBH_4 from 10 folds to 40 folds (as compared to that of nitro compound), it was found that the apparent rate constant increases in such a way that it follows polynomial of order of third degree as shown in Figure 6(b). However, the further increase after 40 fold in the amounts of NaBH_4 makes the reduction rates independent of its concentration that is the reason in this investigation 40 fold excess amounts of NaBH_4 than nitro compounds were used. This relationship between amount of reducing agent and rate of reaction is similar to the previously reported studies where it was observed that initially by increasing the amount of NaBH_4 , reduction rate increased linearly but after specific amount of NaBH_4 reduction rate become almost independent on the amount of NaBH_4 [36, 48].

Catalytic activity of the prepared p(MAc)-M composites was also investigated for degradation of organic dyes such as EY and MO. As these dyes degradations in the absence of catalyst, and in the presence of NaBH_4 takes longer times as shown in Figure 7 (a) and (b), e.g., 45 min for EY and 45 min for MO, respectively, the existence of p(MAc)-Cu catalysts tremendously reduced their catalytic reduction time as illustrated for EY and MO from Figure 7(c), and (d), respectively. For example the degradation of both dyes; EY and MO in the presence of excess NaBH_4 and p(MAc)-Cu took in very shorter times 12 min, and 45 sec, respectively.

To investigate the effect of different metal nanoparticles on MO degradation, p(MAc)-M (M: Cu, Co, Ni) was used in MO degradation at the same conditions, and the corresponding UV-Vis spectra was shown in Supporting Figure S6.

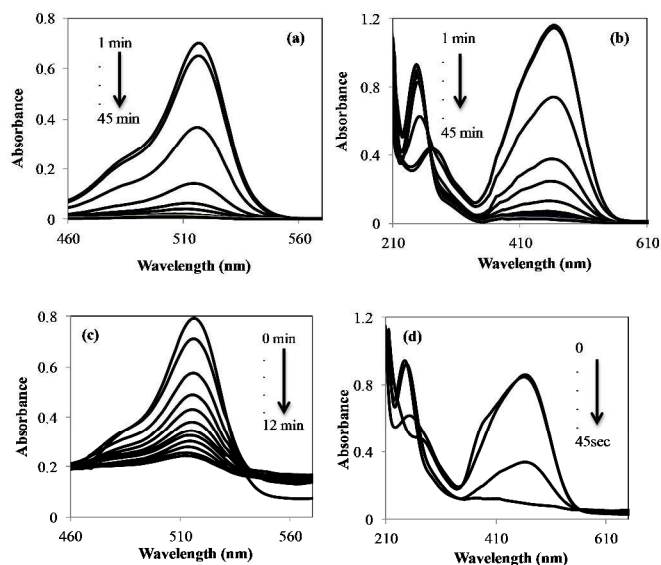


Figure 7. UV-Visible spectra of reduction of (a) Eosin Y, and (b) Methyl Orange in the absence of p(MAc)-Cu microgel composites, and the reduction of (c) Eosin Y, and (d) Methyl Orange in the presence of p(MAc)-Cu composites catalyst at 30°C reaction temperature.

As expected p(MAc)-M composites containing different metal nanoparticles showed different catalytic efficiency, and amongst them p(MAc)-Cu catalyst were found to have higher catalytic efficiency as compared to Ni and Co nanoparticle containing composites. The k_{app} values for the degradation of MO and EY in the presence of different composites were calculated from the linear portion of plots of $\ln(C_t/C_0)$ vs time and their values are given in Table 1. It is clear that k_{app} values of p(MAc)-Cu are much bigger than p(MAc)-Co, and p(MAc)-Ni for MO degradations, and EY degradation cannot be catalyzed by containing p(MAc)-Co, and p(MAc)-Ni composite, and only be catalyzed by p(MAc)-Cu microgel composites.

Most importantly, the catalytic performances of the prepared p(MAc)-Cu composites was also tested for the simultaneous degradation of nitro compounds and dyes. A solution that contains 4-NP and EY at the same time were subjected to concurrent degradation in the presence of NaBH_4 using p(MAc)-Cu microgel composite as catalysts. As demonstrated in UV-Vis absorption spectra given in Figure 8, both of these pollutants were simultaneously degraded. As illustrated in Figure 8(a), in the presence of NaBH_4 and in absence of catalyst there is no degradation up to 10 min for 4-NP, whereas EY is completely degraded in 10 minutes. However, upon the addition of p(MAc)-Cu microgel composites, both compound degraded simultaneously, e.g., it took 3 min for 4-NP and 20 sec for EY as given in Figure 8(b). It is also evident from separate and simultaneous degradation studies that p(MAc)-Cu microgel composite catalyst are more effective in the nitro compound reduction as compared to dyes as they can reduce larger amounts of nitro compound in comparison to dyes within same time interval.

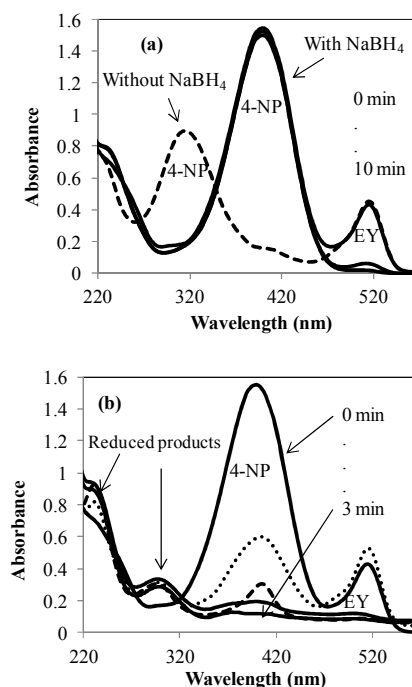


Figure 8. UV-Visible absorption spectra for simultaneous degradation of 4-NP and EY in the absence (a) and (b) presence of p(MAc)-Cu catalyst.

Therefore, the reported p(MAc)-M (M:Cu, Ni, Cu and so on) microgel composite system here enable to design advanced catalytic system for multi task catalysts that can perform more than two or more reactions simultaneously. Since industrial effluents may contain both the nitro compounds and dyes or some other contaminants. These pollutants can be concurrently degraded by using a single catalyst system revealing the versatility of the reported p(MAc)-M catalysts system here. The reusability of p(MAc)-Cu and Co catalyst systems were studied by using the same catalyst in 4-NP reduction repeatedly up to four times. After every use, the catalysts were filtered and washed with DI, and used again for the same reaction under the same reaction conditions. The percent activity and conversion for 4-NP reduction by p(MAc)-Cu and p(MAc)-Co are illustrated in Figure 9 as (a) and (b), respectively.

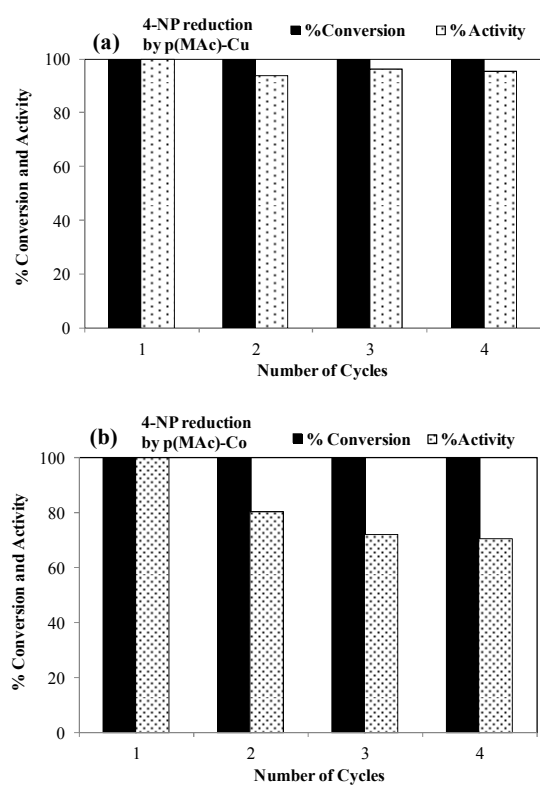


Figure 9. The change in conversion and activity of (a) p(MAc)-Cu, and (b) p(MAc)-Co catalyst systems with repetitive usage in 4-NP reduction. [30 °C, 0.01 M 4-NP=100 ml for p(MAc)-Cu, and 50 ml for p(MAc)-Co , [NaBH₄]=0.4 M, Catalyst= 0.092 mmoles of Cu or Co, under 500 rpm].

Activity was calculated by taking ratio of reduction rate of every successive reaction to the initial reduction rate, and as illustrated from Figure 9 (a) and (b), 100% conversion of 4-NP was observed after 4th use of both Cu and Co nano catalyst systems. However, 4.5% loss in the activity of p(MAc)-Cu and 30% loss in the activity of p(MAc)-Co catalysts was observed at the end of four consecutive use. The higher reduction in the catalytic activity of p(MAc)-Co can be attributed to the negative reduction potential of Co²⁺ (-0.29 V) in comparison to positive reduction potential of Cu²⁺ (+0.34 V) meaning that the particles of Co can be readily oxides in comparison

to Cu particles. Therefore, the decrease in catalytic activity for 4-NP reduction may be attributed to the formation of metaloxides layers on the surface of metal nano catalysts that can hinder the interaction between the catalyst and the substrate (phenolate ions). This impediment between the catalyst and substrate decreases the rate of formation of the activate species, and hence rate of reaction or catalytic activity is also decreased. The decrease in reduction rate after every successive reaction may also occur due to loss of p(MAc)-M catalysts during filtration or washing process.

Conclusion

Herein, it was demonstrated the synthesis of micron sized p(MAc) microgel particles by micro emulsion polymerization, and their successfully use for *in situ* metal nanoparticle preparation such as Cu, Co, and Ni by loading their metal ions into microgels from their aqueous solutions. The prepared p(MAc)-M microgel composites were demonstrated excellent catalytic activity for the degradation of organic dyes and reduction of nitro compounds. The TEM images of metal nanoparticle within hydrogel network and high catalytic performance of the prepared composites also demonstrated that p(MAc) polymeric microgel networks prevent the aggregation of metal nanoparticles. It was also illustrated here that p(MAc)-M microgel composites can also be employed as effective catalysts for reduction of aromatic nitro compounds, and organic aromatic dyes in aqueous solutions, as well as for the simultaneous degradation of organic dyes and nitro compounds if they are present together in same waste.

The main outcome of this report is the followings;

- P(MAc)-Co microgel composite is inherently magnetic provide a catalytically control of the reaction by an externally applied magnetic field.

- Amongst the p(MAc)-M (M:Cu, Co, Ni) microgel composite, p(MAc)-Cu microgel composite shown superior catalytic performances in the reduction of nitro aromatic compounds such as 2-NP, 4-NP and 4-NA and organic aromatic dye degradations such as MO, and EY.

- More importantly, it was shown that p(MAc)-Cu microgel composite system can be used for simultaneous reduction of 4-NP and EY opening new avenues for multitask advanced catalyst systems.

Overall, the ability to eliminate multiple organic pollutants such as nitro compound, and dyes and absorption of some inorganic pollutants such as metal ions from the same industrial effluents in a single step with one versatile absorbent and/or catalyst system demonstrates the superiority of present investigation to the similar researches in the literature. Therefore, the demands for multi tasks catalyst systems now can be met by designing and using polymeric hydrogel system with various functionality and dimensions, and our research is focused on the simultaneous use of microgel-M catalyst system for different catalytic application in organic reaction and waste water treatments.

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Electronic Supplementary Information (ESI) available: [UV-Vis spectra of 2-NP, 4NA and MO; Plots of $\ln(C_0/C_t)$ vs. time for the calculation of reduction rates of 2-NP and 4-NA in the presence of different catalysts; Plots of $\ln(C_0/C_t)$ vs. time for reduction of 4-NP, 2-NP and 4-NA in the presence of P(MAc)-Cu composite; Plots of k_{app} vs T, $\ln k_{app}$ vs (1/T), $\ln(k_{app}/T)$ vs (1/T) for the calculation of activation parameters and Plots of $\ln(C_0/C_t)$ vs. time for the calculation of k_{app} in the presence of different amounts of NaBH_4]. See DOI: 10.1039/b000000x/

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