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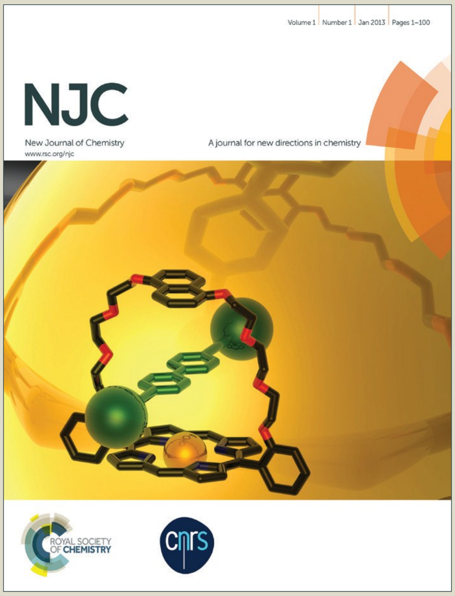

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Simultaneously catalytic degradation/reduction of multiple organic compounds by modifiable p(Methacrylic acid-co-Acrylonitrile)-M (M:Cu, Co) microgel catalyst composites

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We prepared poly(methacrylic acid-co-acrylonitrile) (p(MAc-co-AN)) microgels by inverse suspension polymerization, and converted the nitrile groups into amidoxime groups to obtain more hydrophilic amidoximated poly(methacrylic acid-co-acrylonitile) (amid-p(MAc-co-AN)) microgels. Amid-microgels were used as microreactors for *in situ* synthesis of copper and cobalt nanoparticles by loading Cu(II) and Co(II) ions into microgels from their aqueous metal salt solutions and then converted to corresponding metal nanoparticle (MNP) by treating the loaded metal ions with sodium borohydride ($NaBH_4$). The characterization of the prepared microgels and microgel metal nanoparticle composites was carried out by SEM, TEM and TG analysis. The amounts of metal nanoparticles within microgels were estimated by AAS measurements by dissolving the MNP entrapped within microgels by concentrated HCl acid treatment. Catalytic performances of the prepared amid-p(MAc-co-AN)-M (M: Cu, Co) microgel composites were investigated by using them as catalyst for the degradation of cationic and anionic organic dyes such as eosin Y (EY), methylene blue (MB) and methyl Orange (MO), and for the reduction of nitro aromatic pollutants like 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) to their corresponding amino phenols. Here, we also report for the first time, the simultaneous degradation/reduction of MB, EY and 4-NP by amid-p(MAc-co-AN)-Cu microgel composites. Different parameters affecting the reduction rates such as metal types, amount of catalysts, temperature and the amount of reducing agent were investigated.

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Simultaneously catalytic degradation/reduction of multiple organic compounds by modifiable p(Methacrylic-acid-Acrylonitrile)-M (M:Cu, Co) microgel catalyst composites

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[FT-IR spectra of p(MAc-co-AN) microgels before and after amidoximation. Amid-p(MAc-co-AN)-Co composites (a) in the absence of external magnetic field and (b) movement of magnetic nanoparticles towards externally applied magnetic field (c) attraction of all nanoparticles towards externally applied magnetic field. Plots of $\ln(C_t/C_o)$ as a function of time for the reduction of 4-NP catalyzed by amid-p(MAc-co-AN)-Cu composites with different amounts of $NaBH_4$. Plots of ln (C_t/C_o) vs. time for the reduction of 4-NP catalyzed by amid-p(MAc-co-AN)-Cu composites at different temperatures. Plots of $\ln(C_t/C_o)$ as a function of time for the reduction of 4-NP catalyzed by amid-p(MAc-co-AN)-Co composites at different temperatures. UV-Vis spectra for the absorption of MB by amid-p(MAc-co-AN)-Cu composites. Digital camera images of MB solution (a) original solution (b) after absorption by amid-p(MA-co-AN)-Cu composites and (c) after reduction in the presence of $NaBH_4$ and amid-p(MAc-co-AN)-Cu composites. UV-Vis spectra recorded for the degradation of MB by $NaBH_4$ without any aid of catalyst. Plots of $\ln(C_t/C_o)$ as a function of time for the reduction of EY and MO catalyzed by amid-p(MAc-co-AN)-Cu composites.]. See DOI: 10.1039/x0xx00000x

Introduction

Hydrogels are three dimensional cross linked polymeric networks that can swell in aqueous medium to large extent in comparison to their original mass and volume. These soft and flexible materials have rapidly gained importance in the field of material science due to their potential applications in many areas such as controlled drug delivery [1], tissue engineering [2], biomedical implants [3], water purification [4], enhanced oil recovery [5], template-based synthesis of inorganic nanoparticles [6] and bionanotechnology [7]. Such a wide range of applications of hydrogels arises due to their environmental friendly nature and tunable physical and chemical characteristics [8]. The applications of hydrogels can be further increased by combining hydrogels with metal nanoparticles. Due to the large surface area and high surface energy of metal nanoparticles, they act as efficient catalysts for different reactions such as CO oxidation [9], carbon nanotube nucleation [10], alcohol dehydrogenation [11], and formic acid electro-oxidation [12]. The catalytic properties of metal nanoparticles embedded in various polymeric carriers have been investigated. The catalytic properties of metal nanoparticles embedded in polyelectrolyte brushes have been reported by Wunder et al. [13]. The authors found that the nanoparticles embedded in polymer brushes were able to catalyse the reduction of 4-NP after and induction period that was observed due to slow surface reconstruction of nanoparticles. The catalytic activity of metal nanoparticles can be modulated by changing the physical and chemical composition of the carrier system. For example, Lu et al. have embedded silver (Ag) nanoparticles in thermoresponsive carriers and modulated the catalytic activity of Ag nanoparticles through thermodynamic transition in carrier system [14, 15]. Metal nanoparticles can also be immobilized in polymer membranes and the resulting membranes can be utilized as catalysts. For example, Dhar and Patil designed layer-by-layer self-assembled thin films of Ag and gold (Au) nanoparticles embedded in polymer membranes [16]. It was found that catalytic activity of such systems can be controlled by changing the porosity and number of layers of membranes. The Synthesis of Au nanoparticles in nanoporous polymer membrane have also been reported by Tripathi and co-workers [17]. The catalytic properties of these membranes fabricated with Au nanoparticles were studied for the reduction of 4-NP and degradation of Congo red. Tripathi et al. also used hollow microgels based ultrathin thermoresponsive membranes for the preparation of Au nanoparticles [18]. This system was found to act as an excellent catalyst for the reduction of 4-NP in terms of accommodating greater number of Au nanoparticles and greater diffusion of reactants due to hollow structure of microgels. For the catalytic applications of metal nanoparticles the soft and flexible hydrogels gaining much attention as compared to other carrier systems. Three dimensional crosslinked networks of the hydrogels effectively prevent the aggregation of nanoparticles and the swelling ability allows an easy and fast diffusion of reactants into the hydrogels.

Recently, the development of hydrogels containing modifiable functional groups has become of increasing interest in the field of materials science. Motivation behind the designing of modifiable hydrogels is the formation of new diverse structures with tunable properties which makes these materials applicable under a wide range of conditions and hence their application range is increased [19, 20]. Modification of nitrile groups to the corresponding amidoxime groups was carried out by Sahiner and his coworkers in poly(acrylonitrile-co-N-isopropylacrylamide) (p(AN-co-NIPAM)) core-shell hydrogel nanoparticles which were used as drug delivery systems [20]. It was observed that after amidoximation the active agent loading/release capacity of nanoparticles is increased almost two-fold emphasizing the post modification methods as useful tool to design a tunable drug delivery system to release drug according to desired rate. Therefore, in biomedicinal applications of hydrogels, an appropriate functional group generation on the hydrogel matrices by post modification can make these hydrogels as resourceful materials. Apart from biomedical field, modifiable hydrogels have also become very popular in environmental application. For example Luo et al. [21] have synthesized poly(N-isopropylacrylamide-co-acrylic acid) (p(NIPAM-AA)) hydrogels that are temperature, pH and ionic strength responsive materials. After modification with 40-aminobenzo-18-crown-6 ((ABC) 6) via EDC coupling, crown ether groups were introduced in these hydrogels. The hydrogels became sensitive towards lead ions due to the ability of crown ether groups to form host-guest complex with lead ions and this system was used as lead ions sensor. Synthesis of acrylonitrile based hydrogels and conversion of nitrile group to amidoxime has gained much attention due to the very high tendency of amidoxime groups to absorb heavy metal and uranium ions from aqueous mediums [22-25]. Efficient removal of uranium ions from sea water by using polymeric resins containing amidoxime groups have been reported in many investigations [25-27]. Absorption of heavy metal ions from water by applying polymeric resins bearing amidoxime groups was studied by Maria et al. [28]. They prepared polymeric resin by copolymerization of acrylonitrile (AN) and divinylbenzene (DVB). Nitrile groups were modified to amidoximes by treating with hydroxylamine hydrochloride and the resin was used for the removal of heavy metal ions from water. In this study a large increase in the absorption of metal ions was observed after modification of nitriles to amidoximes. Lutfor and coworkers have also reported removal of heavy metal ions from water by using poly(amidoxime) chelating resin and they found that amidoxime groups can absorb larger amount of Cu^{2+} as compared to other metal ions [29]. The higher absorption capacity of polymeric materials bearing amidoxime groups for Cu^{2+} as compared to other metal ions have also been reported by some other researchers as well [30-32]. Until now, most of the applications of amidoxime based resin have been focused on their use as sorbents for the removal of heavy metal and uranium ions from aqueous medium. Here, we have used amidoxime group containing spherical hydrogel particles with micrometer dimensions that are called as “microgels” for the *in situ* synthesis of Cu and Co MNP. The ability of amidoxime group containing microgels to stabilize metal nanoparticles and their applications to individual and simultaneous catalytic degradation of industrial pollutants like 4-nitrophenol (4-NP), 2-nitrphenol (2-NP) and cationic/anionic dyes such as eosin y (EY), methyl orange (MO) and methylene blue (MB) was investigate. Although there are many reports for the individual degradation of these pollutants by metal nanoparticles stabilized in cationic or anionic hydrogels [33], there is no report for the amidoximated polymeric structures for *in situ* metal nanoparticle preparation and their use simultaneous reduction of dyes and nitro compound [34]. Due to the existence of a variety of pollutants in industrial effluent together, their one by one removal or degradation is not only time consuming but also very costly. Therefore, the industrial applications demand to design of versatile catalysts systems that is be able to catalyze the degradation of different types of pollutants such as dyes and nitro compounds simultaneously. In this regard previously we have reported simultaneous degradation of 4-NP and a cationic dye EY by metal nanoparticles fabricated in anionic microgels [24]. Here, we report simultaneous degradation of nitrophenols, cationic and anionic dyes by Cu NP stabilized within amid-p(MAc-co-AN) microgels. Due to amidoxime groups present in microgel network the metal ions absorption capacity of microgels for the *in situ* formation of metal nanoparticles is increased. Also, hydrophilic nature of amidoxime groups causes greater swelling of microgels. The highly swollen microgels facilitate the diffusion of nitrophenols and cationic and anionic dyes to metal nano catalysts surfaces irrespective of the charges on these pollutants. The micron size of the amid-p(MAc-co-AN) microgel particles allow their easy recovery by filtration. Therefore, these types of catalysts can also be used repeatedly after recovering from the reaction medium by simple filtration process.

Experimental

Materials

Methacrylic acid (MAc, 99%, Aldrich) and Acrylonitrile (AN) as monomers, *N,N*–methylenebisacrylamide (MBA 99%, Acros) as the crosslinking agent, ammonium persulfate (APS, Aldrich) as initiator, N,N,N′,N′-tetramethylethylenediamine (TEMED, Merck) as an accelerator, sorbitane monooleate (SPAN®80, Fluka) as a surfactant and cyclohexane (99.8%) used as solvent were purchased from Aldrich and used as received. Hydroxylamine hydrochloride (NH_2OH. HCl, 98% Sigma Aldrich) and sodium hydroxide (NaOH, 98-100.5% Sigma Aldrich) were used in amidoximation reaction. Cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$, 99% Sigma Aldrich) and copper(II) chloride ($CuCl_2$, 99% Aldrich) were used as metal ion sources while sodium borohydride ($NaBH_4$, 98% Aldrich) was used as reducing agent for metal nanoparticle preparation. 2-nitrophenol (2-NP 99% Acros) and 4-nitrophenol (4-NP 99% Acros) were used as nitro compounds for reduction reactions. Eosin Y (EY, 90%, Sigma Aldrich), methyl orange (MO, containing acid orange 52, Fluka analytical) and methylene blue (MB) were used as organic dyes. Double distilled water (DDW) was used throughout the experiments.

Synthesis of p(MAc-co-AN) Microgels

p(MAc-co-AN) microgels were prepared by micro-emulsion polymerization. Briefly, in a 250 mL round bottom flask, 320 µL span 80 was mixed in 100 mL cyclohexane. This mixture was homogenized by rapid stirring and purged with N_2 for 15 minutes to remove dissolved oxygen. MBA, 0.0364g (0.5 mol% of monomers), and 0.2154 g of APS (2 mol% of monomers) were dissolved in 2mL DDW in a vial by vortex mixer; and then 2 mL MAc and 1.548 mL of AN were also added in the same vial and the mixture was vortexed again to homogenize. The mixture of monomers, cross-linker and initiator was transferred to reaction flask already containing cyclohexane-span 80 mixture. This new reaction mixture was stirred for 10 minutes at 600 rpm continuously under N_2 purging. Then the reaction was initiated by the addition of 0.5 mL TEMED and allowed to proceed in N_2 atmosphere for 4 hours at 40 °C in an oil bath. The prepared microgel particles were collected by decantation of cyclohexane. In order to clean, the microgel particles were washed with ethanol and then with DDW by centrifugation at 10,000 rpm and 20 °C for 10 minutes followed by removal of the supernatant solution and redispersing in distilled water and re-centrifugation at least five times. Finally, p(MAc-co-AN) microgel particles were dried in oven at 60 ˚C for further use.

Amidoximation Reaction

In order to increase the hydrophilcity and metal ion absorption capacity of the prepared microgels, the hydrophobic nitrile (AN) groups were converted into hydrophilic amidoxime groups. This conversion was carried out by treating p(MAc-co-AN) microgels with hydroxylamine hydrochloride (NH_2OH. HCl). In a typical reaction, in a reaction flask at least three fold excess (with respect to number of moles of AN in microgel) $NH_2OH.HCl$ was first neutralized by treating with equivalent amount of NaOH in 100 mL DDW. Then, certain amount of p(MAc-co-AN) microgel was added in reaction flask and reaction was allowed to proceed for 24 hours at 80 °C in an oil bath. At the end of this reaction time, the obtained amidoximated-poly(methacrylic acid-co-acrylonitrile) (amid-p(MAc-co-AN)) microgels were washed with DDW several times and dried at 60 °C in oven. These dried microgels were further used for characterization and as microreactors for the synthesis of metal nanoparticles.

***In situ* synthesis of metal nanoparticles**

Metal nanoparticles were synthesized by *in situ* reduction of metal ions within the microgel particles. Metal ions were loaded by suspending 0.1 g of dried amid-microgels in 50 mL, 500 ppm aqueous solution of metal chlorides ($CoCl_2.6H_2O$ and $CuCl_2$) for 5 hours under continuous stirring (400 rpm). In our previous work [35], it was shown that amid-p(MAc-co-AN) microgels can absorb various heavy metal ions, organic dyes and herbicide up to maximum capacity in the first 40 minutes and no more increase in the absorbed amounts was observed upon increasing the contact time. However, in the present study in order to ensure the establishment of stable equilibrium between metal ions inside the microgels and those in aqueous solution surrounding the microgels, the contact time was increased to 5 hours. At the end of the loading time, metal ion loaded microgels were allowed to settle down and then separated by decantation from the metal ions in aqueous solution, and microgels loaded with metal ions were washed with DDW to remove loosely bound or unbound metal ions. The reduction of metal ions was carried out in 50 mL 0.1M solution of $NaBH_4$ at room temperature under continuous stirring at 400 rpm for 3 h. The prepared microgel-metal nanoparticle composites were filtered with plankton cloth filter having pore size of 2 μm, and washed with DDW and used for characterization and as catalysts. The amounts of metal nanoparticles entrapped in microgels were calculated by Atomic Absorption Spectroscopic (Thermo Scientific, ICE 3000 series, AAS) measurements after dissolution of entrapped metal nanoparticles within amid-p(MAc-co-AN) microgel by treating with 5M HCl aqueous solution.

Catalytic Tests

Catalytic performances of MNP containing microgel composites were studied by employing them as catalysts for the individual reductions of 4-NP, 2-NP, EY, MO and MB as well as for the simultaneous reduction of 4-NP, EY and MB. For the reduction of nitro compounds, in a typical run, certain amount of amid-p(MAc-co-AN)-M composite (containing 0.045 mmoles of M(II) as determined by AAS) was dispersed in 100 mL 0.01 M solution of 4-NP or 2-NP, and the reaction was initiated by the addition of 1.89 g $NaBH_4$. During the reaction, 0.1 mL sample was withdrawn from the reaction mixture at specific time intervals and diluted to certain ratio (150 times dilution for 4-NP, and 50 times for 2-NP) with DDW. After dilution, absorption spectra were recorded by UV-Vis spectrophotometer (UV-Vis, T80+, PG Instruments). The reduction rate constants were calculated by measuring the decrease in absorption peak at 400 nm and 414 nm for 4-NP and 2-NP respectively. The effect of temperature on the reaction rate was evaluated by conducting the reaction at four different temperatures; 30 °C, 40 °C, 50 °C and 60 °C.

The catalytic performances of amid-p(MAc-co-AN)-Cu composites for the degradation of organic dyes was studied by adding certain amount of amid-p(MAc-co-AN)-Cu composite (containing 0.045 mmoles of Cu^{2+}) in 100 mL solution of dye with MO = 4 x 10^{-5} M , EY = 4 x 10^{-4} M and MB = 1.6 x 10^{-4} M concentrations. The Degradation of dyes was initiated by the addition of 0.075 g $NaBH_{4.}$ From the medium, 0.5 mL of aliquots were withdrawn at specific time intervals diluted: 4 times dilution for EY and 10 times for each of MO and MB with DDW and their absorption spectra were recorded by UV-Vis spectrophotometer. Reduction or degradation of these compounds was monitored by measuring the decrease in their corresponding absorption maxima at 414 nm, 400 nm, 464 nm, 516 nm and 664 nm for 2-NP, 4-NP, MO, EY and MB respectively. For simultaneous catalytic reduction of 4-NP, EY and MB, a 100 mL solution containing 0.001 M 4-NP, 16 x 10^{-4} M EY and 2.4 x 10^{-4} M MB was subjected to degradation in the presence of 0.38 g $NaBH_4$ and certain amount of amid-p(MAc-co-AN)-Cu (containing 0.045 mmoles of Cu^{2+}). During the reaction, 0.5 mL sample was withdrawn from the reaction mixture, diluted 15 folds by the addition of DDW, and their absorption spectra were recorded by UV-Vis spectrophotometer. In order to demonstrate the reusability of catalyst systems, these catalysts were separated from the reaction mixture by filtration, washed with DDW and were reused under the same experimental conditions for seven successive runs in the reduction of 4-NP. All the experiments were repeated at least three times and there average values are given with standard deviations.

Results and discussion

Synthesis of p(MAc-co-AN) microgels and amidoximation of nitrile groups

The synthesis of p(MAc-co-AN) microgels were accomplished by inverse suspension polymerization, and a schematic representation of the synthesis of p(MAc-co-AN) microgels and amidoximation of nitrile groups is given in Figure 1 (a). As demonstrated in Figure 1 (b) by the SEM image of p(MAc-co-AN) microgels particles have well defined spherical shapes, and size of most of the particles is around 200 µm.

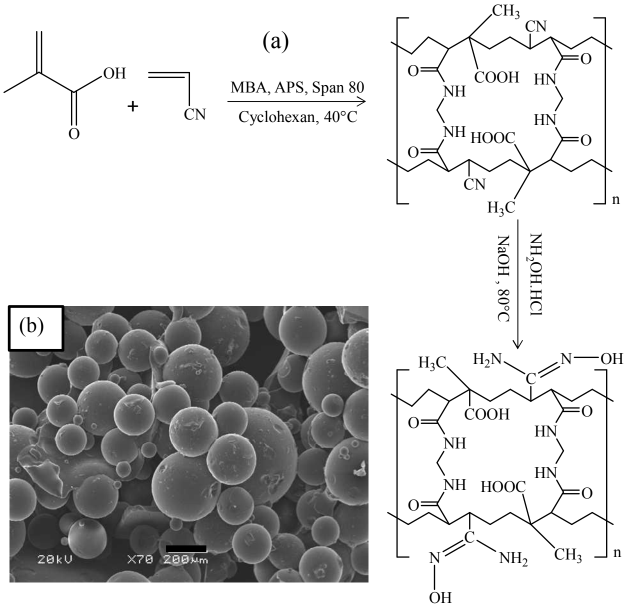

Fig. 1. (a) Schematic representation for the synthesis of p(MAc-co-AN) microgels, amidoximation reaction and (b) SEM images of p(MAc-co-AN) microparticles. Scale bar = 200µm.

The introduction of amidoxime groups on microgels network was achieved by converting nitrile groups into amidoxime groups, this amidoximation reaction was confirmed by Fourier Transformation Infrared Spectroscopy (FT-IR). The FT-IR spectra of microgels before and after amiodoximation are given in Supporting Figure S1. It is obvious that a broad peak about 3000 cm^{-1} for –OH and another peak at about 1700 cm^{-1} for –C=O group before and after amidoximation represent the presence of carboxylic groups from the methacrylic acid moieties. However, after treatment of p(MAc-co-AN) with NH_2OH, the disappearance of nitrile peak at 2241 cm^{-1} confirms the conversion of nitrile groups to amidoxime groups [22-24]. Moreover, the complete disappearance of nitrile peak indicates that almost all the nitrile groups were converted to amidoxime groups as reported earlier [36, 37].

***In situ* synthesis of metal nanoparticles**

In situ synthesis of Cu and Co nanoparticles was carried according to previously reported work [24], and Figure 2 demonstrates the schematic representation for the absorption of metal ions by microgels and subsequent reduction of the absorbed metal ions to generate metal nanoparticles within amid-p(MAc-co-AN) microgel network.

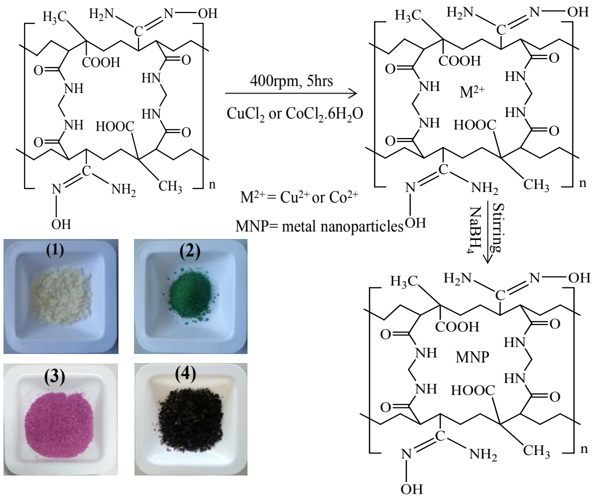

Fig. 2. Schematic representation for the synthesis of metal nanoparticles, and digital camera images of (1) bare amid-p(MAc-co-AN) microgels and microgels loaded with (2) Cu^{2+} (3) Co^{2+} and (4) metal nanoparticles.

As it has been reported by many researchers that amidoxime groups have very good tendency to absorb heavy metals ions such as Cu^{2+} and Co^{2+} ions [28-31], therefore, in this study we have also utilized amidoxime groups to absorb Cu^{2+} and Co^{2+} ions. Due to the metal ion absorption ability these types of microgels or other polymer resins containing the functional groups similar to those present in these microgels can be used as adsorbents for the removal of various pollutants from water. So, the applications of these microgels are not limited only to the field of catalysis but they can also be extended to adsorption of toxic pollutants from water. The physical appearance of reaction system at every step is illustrated by digital camera images as shown in Figure 2 which shows that amid-p(MAc-co-AN) microgels are colorless as shown in digital camera image (1). The absorption of metal ions can be clearly seen in Figure 2 from their corresponding green and pink colors of copper and cobalt ions loaded amid-microgels, respectively as given in images (2) and (3). After reduction, metal ions were converted into MNP, and the reactor, microgel system was turned black as shown by digital camera image (4) in Figure 2. TEM images of the prepared amid-p(MAc-co-AN)-M composites are given in Figure 3 (a) and 3 (b) that show that metal nanoparticles were homogeneously distributed in microgels.

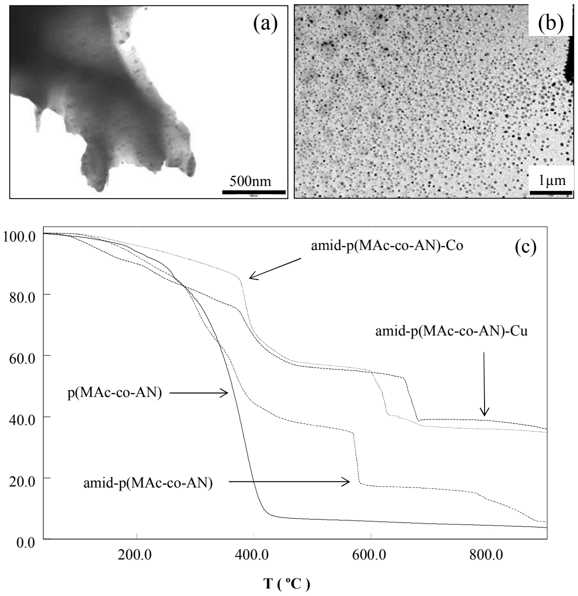

Fig. 3. TEM images of (a) amid-p(MAc-co-AN)-Cu and (b) amid-p(MAc-co-AN)-Co composites. (c) TGA thermograms of p(MAc-co-AN) before and after amidoximation and of amid-p(MAc-co-AN)-M composites.

However, depending upon the nature of metals different size of nanoparticles that can be assumed about 10-50 nm obtained for Cu and Co. Thermal properties of the prepared microgels and microgel metal nanoparticle composites were investigated by performing thermo gravimetric (TG) analysis. Thermograms of bare microgels before and after amidoximation and of composite microgels are given in Figure 3 (c). As can be seen bare p(MAc-co-AN) microgels degradation was started around 100 °C, initially degradation rate was slow and 21% weight loss was occurred as the temperature was raised to 300 °C. However, with further increase in temperature, the degradation rate was increased and another 71% weight loss was occurred in the temperature range of 300 °C to 428 °C. After amidoximation of microgels, degradation was also started around 100 °C and 15% weight loss was observed when temperature was reached to 267 °C. Another 46% weight loss was observed with rapid degradation rate as the temperature was increased from 267 to 457 °C. Two more distinct degradation temperatures were also observed in the temperature ranges from 568 to 581 °C and 783 to 900 °C with 21 and 10% weight losses respectively. The different thermal behavior of microgels before and after amidoximation represents some structural changes that are achieved by amidoximation. Overall, higher degradation temperature and lesser weight loss was shown by amid-p(MAc-co-AN)-M composites implying the better thermal resistance behavior of amidoximated hydrogel. For amid-p(MAc-co-AN)-Co, 45% weight loss was observed when it was heated to 600 °C and a total 66% weight loss occurred even by increasing the temperature to 900 °C. In case of amid-p(MAc-co-AN)-Cu composites 47% weight loss up to 656 °C and 64% weight loss was observed by heating up to 900 °C. The higher thermal stability of amid-p(MAc-co-AN)-M composites may be the results of strong coordination interaction between metal nanoparticle and amidoxime groups that can be developed due to the presence of small amount of charge on the surface of metal nanoparticles [38]. However, strength of this coordination interaction may be different for Co and Cu nanoparticles as it can be seen from initial regions of thermogrames of amid-p(MAc-co-AN)-M composites. Up to 370 °C only 15% weight loss with relatively slow degradation rate in amid-p(MAc-co-AN)-Co composites was observed while 25% weight loss was occurred for amid-p(MAc-co-AN)-Cu composites that shows that Co nanoparticles may have strong coordination with amidoxime groups as compared to Cu nanoparticles. Thermal treatment of hydrogels-metal nanoparticles composites may also results in the formation of oxides or oxonitrides, however; as the TGA experiments were performed under N_2 atmosphere, there is no possibility of presence of oxygen. Therefore, the reaction with oxygen, or the formation of oxide compounds after calcination in the TGA experiment can be negligible. Therefore, the greater contribution towards the increased in thermal stability can be the coordination of nanoparticle with functional groups of microgels. The amount of metal ions absorbed by the microgels, and the amounts of the formed metal nanoparticles within microgels was calculated by AAS measurements. The amount of metal ions absorbed by the microgels was calculated by measuring the concentration of metal ions from their corresponding aqueous solutions before and after the sorption by microgels. It was observed that 55.05 mg of Cu^{2+} and 37 mg of Co^{2+} were absorbed by per gram of dried p(MAc-co-AN) microgels. However, after amidoximation reaction, the absorption capacity of microgels was increased to 128.675 mg of Cu^{2+} and 120 mg of Co^{2+} per gram of dried amid-p(MAc-co-AN) microgels. Such an increase in the metal ions absorption tendency is in the accordance of the previous reports in literature [28-32]. As, the metal ion loaded microgels were washed to remove loosely bound metal ions and then metal ions entrapped within microgels were reduced to metal nanoparticles, so some amount of metal ions may be lost in washing process. Therefore; in order to calculate exact amount of metal nanoparticles and percent conversion of the absorbed metal ions into corresponding metal nanoparticles, the prepared amid-p(MAc-co-AN)-M composites were washed with DDW and then metal nanoparticles were dissolved into their corresponding metal ions by treating with 5M HCl (30 mL) solution. The amount of metal ions was again recorded with AAS and it was found that 108.26 mg of Cu^{2+} and 104.56 mg of Co^{2+} were present in per gram of amid-p(MAc-co-AN) microgels. These results show that 84.14% of Cu^{2+} and 95.05 % of the absorbed Co^{2+} were obtained as metal nanoparticles. This loss of metal ions may be attributed due to loss of loosely bound metal ions during washing process and some uncompleted conversion of the metal ions to MNPs. Another important feature of the prepared composites is the magnetic behavior of amid-p(MAc-co-AN)-Co composites that is illustrated in Supporting Figure S1 In the absence of an external magnetic field, the amid-p(MAc-co-AN)-Co composites remain suspend in water as shown in Supporting Figure S2 (a). As shown, upon an external magnetic field was applied to amid-p(MAc-co-AN)-Co composites suspension, the microgel compsoites started to move towards the magnet and a few seconds later, all of the composite particles were collected and stick to the surface of the vial where the magnet is situated as illustrated in Supporting Figure S2 (b) and (c) respectively. This inherently magnetic behavior of the catalysts offers great advantage in terms of their recovery and reusability [33, 39].

Catalytic activity of amid-p(MAc-co-AN)-M composites

Catalytic activity of the prepared amid-p(MAc-co-AN)-M composites was evaluated by using them as catalysts for the reduction of 2-NP and 4-NP as well as for the degradation of cationic and anionic dyes such as MB, MO and EY. It is important that the simultaneous degradation of nitrophenole, cationic and anionic organic dyes was also accomplished by use of p(MAc-co-AN)-Cu composite catalyst system. The values of apparent rate constants (k_{app}) calculated by applying pseudo first kinetics for the degradation of these pollutants are given in Table 1.

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

Pollutant	Catalyst	k_{app} (min^{-1})	R^2
2-NP	amid-p(MAc-co-AN)-Cu	0.3299 ± 0.007	0.966
	amid-p(MAc-co-AN)-Co	0.1468 ± 0.003	0.998
4-NP	amid-p(MAc-co-AN)-Cu	0.4251 ± 0.021	0.987
	amid-p(MAc-co-AN)-Co	0.0745 ± 0.002	0.989
MO	amid-p(MAc-co-AN)-Cu	1.2001 ± 0.166	0.996
EY	amid-p(MAc-co-AN)-Cu	0.2143 ± 0.012	0.974

k_{app} = apparent rate constant, R^2 = coefficient of determination
Reaction conditions = 100 ml solution [0.01 M 4-NP, 0.01 M 2-NP, 4 x 10^{-5} M EY, and 4 x 10^{-4} M MO], amid-p(MAc-co-AN)-M composite (M: 0.045 mmoles). $NaBH_4$ = 01.89 g for nitrophenoles and 0.0756 g for dyes, 600 rpm mixing rate, and 30 °C.

Although $NaBH_4$ is a strong reducing agent, it cannot reduce nitrophenoles without any support of MNP catalyst. Actually, there is a large kinetic barrier between electron donor BH_4^- and acceptor of nitro compounds, and $NaBH_4$ do not have so much potential to overcome this potential barrier. Therefore, it could not reduce the nitro compounds without any external aid that is provided by a metal nano catalyst. Metal nanoparticles are known as excellent catalysts for the reduction of nitro compounds by $NaBH_4$ due to having potential to relay electron from BH_4^- to nitro compounds by overcoming the large kinetic barrier [40, 41]. Therefore, we have used amid-p(MAc-co-AN)-M composites containing metal nanoparticles as catalysts. UV-Vis spectra for the reduction of 4-NP and 2-NP catalyzed by amid-p(MAc-co-AN)-Cu are given in Supporting Figure S3 (a) and 4 (b) respectively.

The reduction of nitrophenoles is evident from the successive decrease in their absorption peaks with the passage of time. Different parameters that can affect the reduction rate of these nitro compounds were investigated. First of all, the effect of the amounts of $NaBH_4$ on the reduction of 4-NP was evaluated by using 20, 30 40, 50 and 60 fold excess amount of $NaBH_4$ as compared to moles of 4-NP. Initially, an increase in the reduction rate was observed by increasing the relative concentration of $NaBH_4$ up to 50 folds. However, by further increase in amount of $NaBH_4$ no change in reduction rate was observed as shown in Figure 4 (a). Since the concentration of $NaBH_4$ in reaction mixture was in large excess as compared to that of 4-NP so reaction was supposed as pseudo first order. Therefore, reduction rates were calculated by plotting $\ln(C_t/C_o)$ vs. time, where C_t is the concentration of reactants at different time intervals during the progress of reaction and C_o is the initial concentration of reactants as given in Supporting Figure S4.

As the reduction rate of 4-NP was found to be independent on the concentration of $NaBH_4$ when it was increased above 5 folds; therefore, the catalytic reductions of 4-NP and 2-NP were carried in the presence of 5 folds excess of amount of $NaBH_4$ throughout this research. In order to evaluate the effect of metal types on the catalytic efficiency of the prepared composites, certain amounts of composites containing MNPs composed of equal number of moles of Co and Cu ions were employed in the reduction of 2-NP and 4-NP while keeping all other reaction parameters constant. Composites containing Cu nanoparticles were found as more effective catalysts for the reduction of nitrophenoles which can be seen from greater values of k_{app} calculated for amid-p(MAc-co-AN)-Cu as compared to those for amid-p(MAc-co-AN)-Co that are given in Table 1.

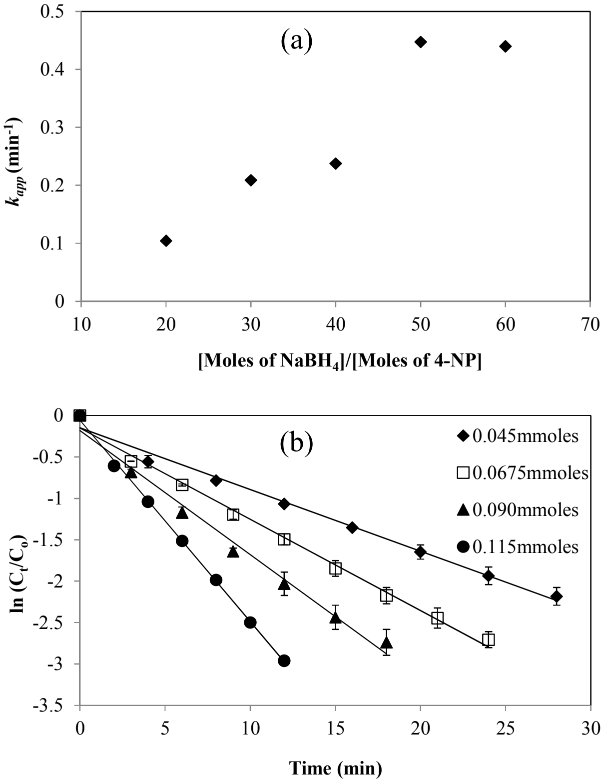

Fig. 4. Dependence of k_{app} on (a) amount of $NaBH_4$ and (b) amount of catalyst for the reduction of 4-NP catalyzed by amid-p(MAc-co-

AN)-Cu. Reaction conditions; 0.01 M 4-NP = 100 mL, $NaBH_4$ = 1.89g, 30 °C, 600 rpm.

The effect of the amounts of catalyst was studied by using different amounts of prepared composites as catalysts in the same reduction reactions catalyzed by amid-p(MAc-co-AN)-Cu. The plots of $\ln(C_t/C_o)$ vs time shown in Figure 4 (b) for the reduction of 4-NP catalyzed by different amounts of catalysts. The reduction rate was increased by increasing the amount of catalysts as it can be seen from the increase in slope of the plots of $\ln(C_t/C_o)$ vs. time in Figure 4 (b). As with the increase in amount of catalysts, the available catalytic sites are also increased. The presence of larger catalytic sites in the reaction mixture increases the effective collision frequency, and hence the rate of reaction is also increased. The effect of temperature on the catalytic activity of both of the Cu and Co nanoparticle containing composites was also investigated by carrying out the reduction of 4-NP at four different temperatures i.e. 30, 40, 50, and 60 ^{o}C keeping all other parameters constant. As presented in Supporting Figure S5, a good linear pattern of plots of $\ln(C_t/C_o)$ vs time for the reduction of 4-NP catalyzed by amid-p(MAc-co-AN)-Cu composites was observed. Such a linear correlation not only confirms that these reactions follow pseudo first order kinetics but also demonstrates the homogeneous distribution of Cu MNP within amid-p(MAc-co-AN) microgels. A similar linear pattern of plots of $\ln(C_t/C_o)$ vs time for the reduction of 4-NP catalyzed by amid-p(MAc-co-AN)-Co composites was also obtained at different temperatures as given in Supporting Figure S6. As illustrated in Figure 5, the variations in k_{app} values were increased with the increase in temperature of the reaction medium. By increasing the temperature of reaction medium, the average kinetic energy of reactants was increased and this increases the rate of collision of reacting species, and as a result the rate of reaction was also increased. Although rate of reaction was increased by increasing the temperature in case of both composites, a different trend in the variations was observed.

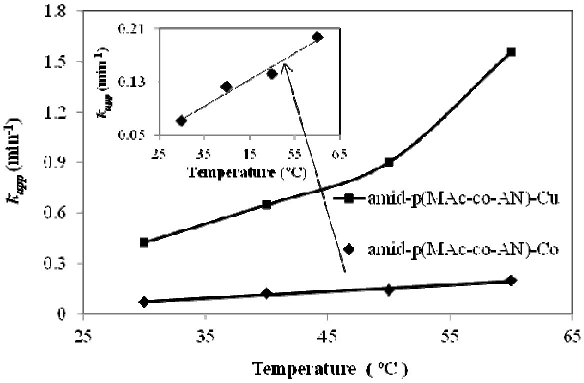

Fig. 5. Change in k_{app} as a function of temperature. Reaction conditions; 0.01 M 4-NP = 100 mL, $NaBH_4$ = 1.89 g, catalyst = 0.045 mmoles of Cu or Co, 30 °C, 600 rpm.

For amid-p(MAc-co-AN)-Co composites comparatively small but almost linear increase in reduction rate was observed by increasing temperature from 30 to 60 ^{o}C. On the hand, in case of amid-p(MAc-co-AN)-Cu composites, k_{app} was increased linearly by increasing temperature from 30 to 50 ^{o}C and then a rapid increase by increasing from 50 to 60 ^{o}C was observed. The coordination interaction of metal nanoparticle with any functional group depends upon the charge density on the surface of MNP [25]. So the nanoparticle of different metals may have different coordination interaction due to having different charge density, surface properties, and their sizes and the number of electrons in their valance shells. Here, as the nanoparticles are prepared from two different elements which were stabilized by same functional groups present in the microgels, it is possible that these MNPs may show different coordination interaction resulting in different stability and thermal response of the prepared composites. Catalytic performance of the amid-p(MAc-co-AN)-M composites was also investigated for the degradation of some organic dyes: EY, MO and MB that are generally discharged from industrial waste and cause water pollution [42]. Both of Cu and Co containing microgel composites were used as catalysts but it was found that amid-p(MAc-co-AN)-Co composites were not able to catalyze the degradation of these dyes. UV–Vis spectra obtained for amid-p(MAc-co-AN)-Cu catalyzed degradation of MO, EY and MB are given in Supporting Figure S7 (a), (b) and (c) respectively.

It can be seen that MB was completely degraded within 10 seconds while the degradation of MO was completed in 2.5 minutes, and the degradation of EY took more than 16 minutes. The greater catalytic efficiency of amid-p(MAc-co-AN)-Cu composites for MB was attributed due to the fact that amid-p(MAc-co-AN)-Cu composites have tendency to absorb MB because of the charge-charge interaction between negatively charged microgel and positively charged MB. This absorption tendency of the composites increases the rate of diffusion of MB molecules which results in an increase in the rate of reaction. The absorption of MB was also observed by UV-Vis spectroscopy and the corresponding absorption spectrum of MB is given in Supporting Figure S8 (a). The absorption of MB by amid-p(MAc-co-AN)-Cu composites and then reduction upon the addition of $NaBH_4$ is also illustrated by digital camera images of reaction mixtures in Supporting Figure S6 (b). In Supporting Figure S8 (b), the image of original solution of MB has dark blue color seen in (1), and upon the addition of amid-p(MAc-co-AN)-Cu composites in to the medium, the intensity of blue color was decreased due to absorption of MB molecules by microgel composites which can be seen from blue color of composites as shown in (2). By the addition of $NaBH_4$ to the solution, the solution color became transparent and amid-p(MAc-co-AN)-Cu composites were also turned back to their original black color as shown in (3). The disappearance of blue color of reaction mixture illustrates the degradation of all the MB molecules. It was also observed that MB can be degraded by $NaBH_4$ without using any catalyst but with very slow reduction rate. UV–Vis spectrum for the reduction of MB is given in Supporting Figure S9 that shows that even after 40 minutes the existence of $NaBH_4$ can only reduce 50% of MB. The degradation of MO and EY by $NaBH_4$ without any aid of catalyst was demonstrated in our previous report [34]. As degradation of these dyes was carried out in large excess of $NaBH_4$ so these reactions were supposed as pseudo first order and values of k_{app} were calculated by plotting $\ln(C_t/C_o)$ vs. time as shown in Supporting Figure S10, and the values of k_{app} are given in Table 1. “The values of k_{app} calculated from the present work was compared with the similar works that are reported in literature, and presented in Table 2. This comparison represents that the results obtained here are much better than the previously reported results of similar studies. The better performance of our catalysts can be attributed to the soft, flexible and hydrophilic nature of the microgels that are used as reactors for the preparation metal nanoparticles and as well as carriers and stabilizers for the prepared metal nanoparticles and the polymeric network contribution to the overall catalytic reaction such hydrophilicity and functional groups.”

Table 2. Comparison of the rate constants calculated in the present work with reported literature.

Catalysts	Reducing Compound	k_{app} (min^{-1})	Reference
Cu nanoparticles	4-NP	0.09529	43
Microgel-Ag Composites	4-NP	0.248	44
PS-NIPA-Ag composite	4-NP	0.00216	15
Thin Film-Au Nanocomposite	4-NP	0.0083	16
p(AMPS)-Cu Hydrogel Composite	4-NP	0.1032	45
Amid-p(MAc-co-AN)-Cu	**4-NP**	**0.4251**	**Present Work**
p(AMPS)–Co composites	2-NP	0.06	46
poly(sulfobetain methacrylate)-Ni	2-NP	0.1258	47
Amid-p(MAc-co-AN)-Cu	**2-NP**	**0.3299**	**Present Work**
TiO_2 nanoparticles	**MO**	0.114	48
Al doped ZnO	**MO**	0.1073	49
Amid-p(MAc-co-AN)-Cu	**MO**	1.2	**Present Work**
CuO nanoleaves	**EY**	0.089	50
Ag–TiO_2coated	**EY**	0.029	51
Amid-p(MAc-co-AN)-Cu	**EY**	0.214	**Present Work**

There are multiple sources of contaminations and different pollutant can exist in the same polluted aquatic environments. Therefore, the ability of amid-p(MAc-co-AN)-Cu composites to catalyze two reactions taking place in same reaction medium at the same time was also investigated by employing them as catalysts for the concurrent reduction of 4-NP and EY, 4-NP and MB and EY and MB. UV-Vis spectra obtained for these simultaneous catalytic reactions are given in Figure 6 (a), (b) and (c) for 4-NP and EY, 4-NP and MB and EY and MB, respectively. From these reactions, it was observed that the nature of organic dye present in the reaction mixture effects the reduction rate of 4-NP. Figure 6 (a) represents the reduction of 4-NP together with an anionic dye EY and it can be seen from this Figure, 4-NP was completely reduced in 4 minutes as can be seen from decrease in absorption peak at 400 nm, while reduction of EY continued up to 17 minutes as can be visualized in UV-Vis absorption peak of 514 nm. However, interestingly the reduction rate of 4-NP was decreased to a large extent when it was reduced together with MB.

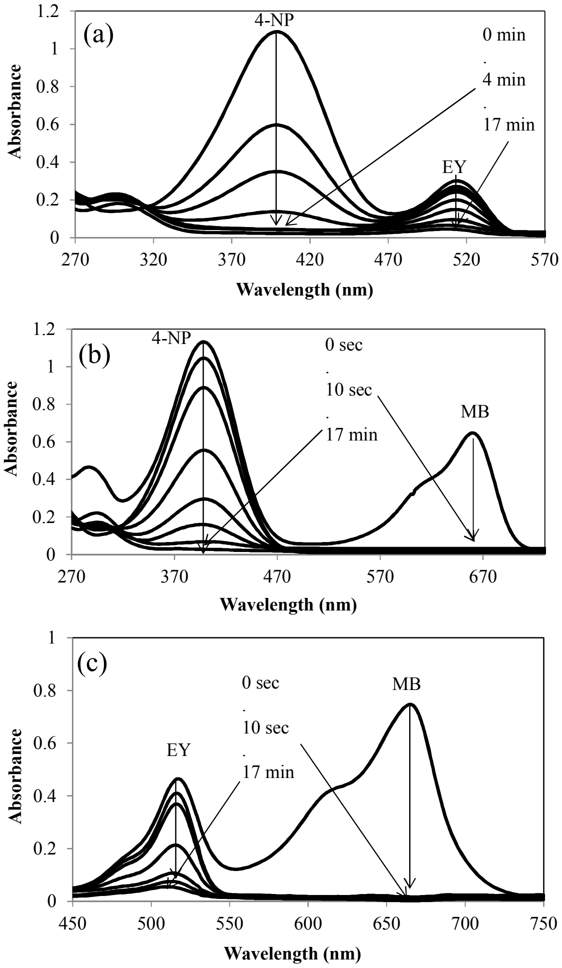

Fig. 6. UV-Vis spectra representing simultaneous reduction of (a) 4-NP and EY (b) 4-NP and MB and (c) EY and MB from aqueous medium in the presence of amid-p(MAc-co-AN)-Cu catalyst. Reaction conditions; solution = 100 mL (8 x 10^{-5} M and EY, 2.4 x 10^{-4} M and MB and 1 x 10^{-3} M and 4-NP), $NaBH_4$ = 0.38g, catalyst = 0.045 mmoles, 30 °C, 600 rpm.

This decrease in reduction rate of 4-NP can be seen from Figure 6 (b) that shows that when MB and 4-NP were subjected to degrade simultaneously by amid-p(MAc-co-AN)-Cu from the same reaction mixture. As can be seen from the Figure, MB was completely degraded in 10 sec while reduction of 4-NP was completed in 17 minutes. This result shows that in the simultaneous reduction of 4-NP and an organic dye, there is a decrease the reduction rate of 4-

NP due to the presence of cationic organic dye, MB. On the other hand, when the degradation of MB and MO was carried out simultaneously as shown in Figure 6(c), the reduction rates of MB and EY were found to be independent from each other. As MB was completely degraded within 10 sec in the presence of both the 4-NP and EY and similarly EY was degraded in 17 minutes in the presence of 4-NP as well as MB. Consequently, the existence of a nitro compound together with an organic dye or the existence of two organic dyes in a contaminated water can be readily eliminated by amid-p(MAc-co-AN)-M catalyst composite systems. Moreover, the catalytic activity of amid-p(MAc-co-AN)-Cu composites was also studied for the concurrent degradation of three different types of pollutant i.e., MB as a cationic dye, MO as an anionic dye and 4-NP as organic toxic compounds. This reaction was conducted by preparing a solution containing MB, MO and 4-NP, and the determined amounts of $NaBH_4$ and amid-p(MAc-co-AN)-Cu were added in the reaction mixture as reducing agent and catalysts respectively. Samples were taken from the reaction mixture after certain intervals of time and UV-Vis spectra were recorded by spectrophotometer. The corresponding UV-Vis spectra for the simultaneous degradation of all the three pollutants present in reaction mixture was given in Figure 7 (a). The degradation of MB was completed within 10 sec while 4-NP and EY were degraded completely in 18 minutes as demonstrated in Figure 7 (b). Therefore, it is obvious that amid-p(MAc-co-AN)-Cu composites can do multiple dye degradations and 4-NP reduction that may be present in the contaminated real waters.

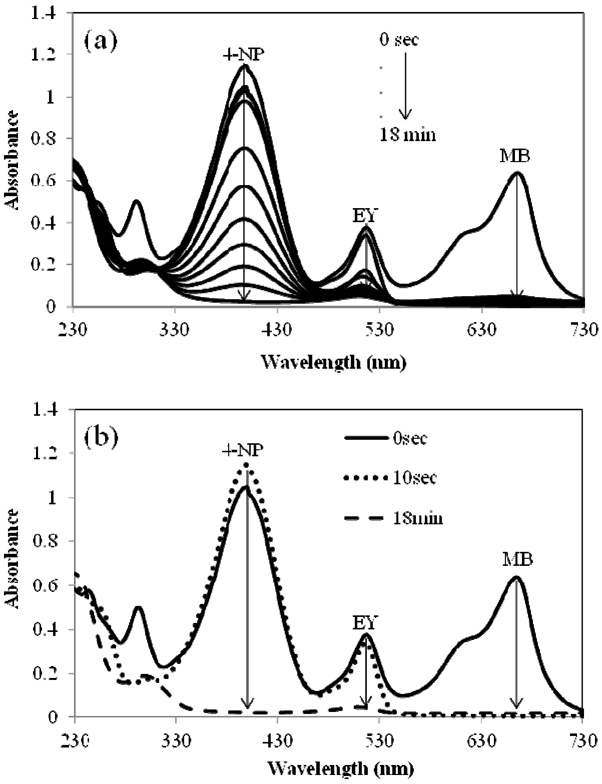

Fig. 7. UV-Vis spectra representing (a) concurrent reduction of MB, EY and 4-NP from aqueous medium in the presence of amid-p(MAc-co-AN)-Cu composites, (b) initial and final spectral lines for each pollutant. Reaction conditions; Solution = 100 mL (8×10^{-5} M EY, 2.4×10^{-4} M MB, and 1×10^{-3} M 4-NP), $NaBH_4$ = 0.38 g, catalyst = 0.045 mmoles, 30 °C, 600 rpm.

We furthermore investigated the reusability of the prepared catalyst systems by using the same amount of catalysts in the reduction of 4-NP repeatedly up to four cycles for amid-p(MAc-co-AN)-Cu and up to seven cycles for amid-p(MAc-co-AN)-Co composites. After every use, the catalysts were separated from reaction mixture by filtration, washed with DDW and used again for the same reactions under the same conditions. The percent activity of the catalysts and percent conversion of 4-NP is illustrated in Figure 8 (a) and (b), respectively. The activity is calculated by dividing each reduction rates to the initial reduction rate, and the conversion is determined in terms of the change in the concentration of reactant. As illustrated in Figure 10 (a), 100%

conversion of 4-NP was achieved after every cycle by using both the composite systems catalysts system, amid-p(MAc-co-AN)-Co/Cu. As it can be seen from Figure 8 (a) in third cycle, the catalytic activity of amid-p(MAc-co-AN)-Cu was decreased by 10% and the time required for the 100 % conversion was increased from 8 to 12 minutes; interestingly, after that a rapid increase was observed in fourth cycle and 100 % conversion was achieved in 6 minutes. At the end of fourth cycle amid-p(MAc-co-AN)-Cu composites were almost completely degraded and they could not be separated from reaction mixture. The increase in catalytic activity after third cycle and then structural break down after fourth cycle indicates that amid-p(MAc-co-AN)-Cu composites were not very stable. Therefore, after third cycle, cross-linked polymeric network of microgel was partially broken and converted into polymer brushes like structure which offers no resistance against diffusion of molecules as due to cross-linked network of polymer chains. Consequently, it can be suggested that amid-p(MAc-co-AN)-Cu composites can be used up to four times as sacrificial catalysts systems in cleaning contaminated waste waters. Greater catalytic activity of nanoparticles attached with polymer brushes as compared to that of nanoparticles entrapped in polymer microgels has also been reported earlier by Mei et al. for palladium nanoparticles [52]. On the other hand, as shown in Figure 10 (b) in case of amid-p(MAc-co-AN)-Co composites, surprisingly, a 20% increase in the catalytic activity was observed after first time use, and then no loss in catalytic activity was observed until seven cycles. The increase in catalytic efficiency was accompanied by a decrease from 50 to 44 minutes in the total time of conversion 4-NP to 4-AP.

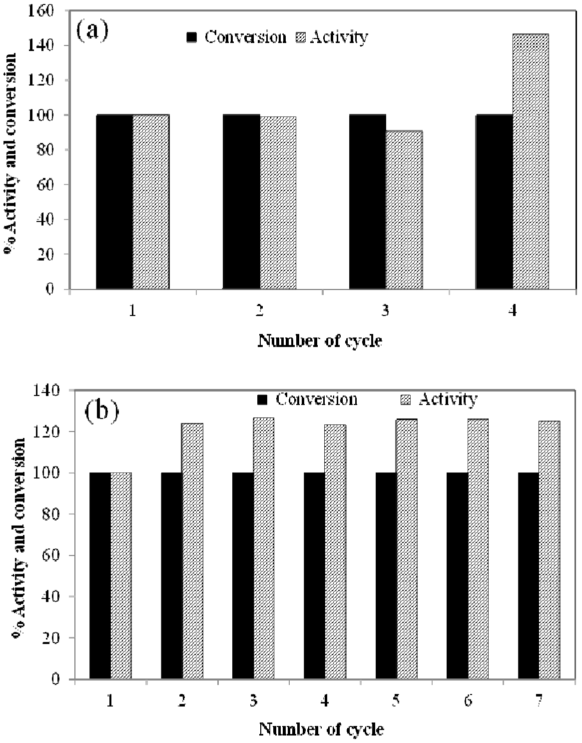

Fig. 8. The change in % conversion of 4-NP and activity of (a) amid-p(MAc-co-AN)–Cu, and (b) amid-p(MAc-co-AN)-Co catalyst systems with repetitive usage in 4-NP reduction. [0.01 M 4-NP = 100 mL, [$NaBH_4$] = 1.89g, catalyst = 0.045 mmoles of Cu or Co, 600 rpm and 30 °C].

The reusability till seven cycles without any loss in catalytic activity shows that amid-p(MAc-co-AN)-Co composites were more stable as compared to amid-p(MAc-co-AN)-Cu composites in similar aquatic environments. The higher stability of amid-p(MAc-co-AN)-Co can be achieved due to strong coordinating interaction of Co nanoparticles with amidoxime groups. Generally, lower activity of catalysts leads to higher stability so another reason for the higher stability of amid-p(MAc-co-AN)-Co composite catalysts can be its lower catalytic activity than that of amid-p(MAc-co-AN)-Cu catalyst. And, the increase in catalytic activity of amid-p(MAc-co-AN)-Co composites after first use can be attributed to the removal of contaminants from the surface of MNP that can be deposited during synthesis process and detached upon their utilization as catalysts [53]. Catalytic activity was also increased after first cycle due to elimination of impurities which might be formed on the surface of nanoparticles after their synthesis and/or re-structuring, and causes an increase in their activity after they are used for the first time. Such an increase in catalytic activity after first cycle due to activation of nanocatalysts was also observed by Böhmer et al [54] as they employed Pt/zeolite catalysts for the enantioselective hydrogenation of ethyl pyruvate. Another reason for this increase in catalytic activity may be a structural re-arrangements in microgel network due to the swelling and/or replacement of some metal nanoparticle at the interior part of microgels to the surface or appropriate surfaces. Such kinds of changes can occur due to continuous diffusion and elimination of reactants and products into the microgels network. These type of structural changes results in an increase in rate of diffusion and elimination of reactants and products through the microgels network and hence rate of reaction is increased. Therefore, the prepared amid-p(MAc-co-AN)-M catalysts system are resurface and have promising results for nitro compound reduction and aromatic dye reductions.

Conclusions

It was demonstrated here that a facile preparation of p(MAc-co-AN) microgels by inverse suspension polymerization was accomplished. Additionally, via amidoximation reaction, the nitrile groups were converted into hydrophilic amidoxime groups within microgels that provided higher metal ion absorption capabilities. The amidoximated microgels were then used as templates for *in situ* synthesis of Cu and Co nanoparticles to prepare amid-p(MAc-co-AN)-M composites. It was demonstrated that the prepared composites were found very effective catalysts for the individual and simultaneous degradation of nitrophenoles and cationic and anionic organic dyes such as MB, MO, and EY. Furthermore, the triple contaminants can also be simultaneously catalyzed by amid-p(MAc-co-AN) particles showing the great advantages of the this amid-p(MAc-co-AN)-M catalytic systems. Furthermore, Cu nanoparticle containing system was shown faster catalytic performances than that of Co nanoparticle containing microgel composites in 4-NP reduction and MB, MO, and EY degradations. Also amid-p(MAc-co-AN)-Cu composites have shown more efficient catalytic behavior for the degradation of cationic dye MB as compared to that for anionic dyes, MO and EY. On the other hand, Co nanoparticle containing microgel composites were found to be inherently magnetic and highly stable as no loss in their catalytic activity was observed even up to seven successive usages in the catalytic reactions. To sum up, the microgels containing amidoxime groups can be employed for the synthesis of inherently magnetic, highly stable and reusable Co nano catalysts or very effective Cu nano catalysts to be used in nitro compound reductions and dye degradations. The most important outcome from this work is that the prepared amid-p(MAc-co-AN)-M (M= Cu, Co) microgel composite catalysts can be used for individual and simultaneous degradation of nitrophenoles and cationic/anionic dyes pairs or in the triple combinations that may exist in the contaminated aquatic environments.

Acknowledgements

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References

1 N. Sahiner and P. Ilgin, *J. Appl. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5239.
2 F. Brandl, F. Sommer and A. Goepferich, *Biomaterials* **2006**, *28*, 134.
3 D. Seliktar, *Science*. **2012**, *336*, 1124.
4 G. Jing, L. Wang, H. Yu, W. A. Amer and L. Zhang, *Colloid. Surface. A* **2013**, *416*, 86.
5 H. Q. Sun, L. Zhang, Z. Q. Li, L. Zhang, L. Luo and S. Zhao, *Soft Matter* **2011**, *7*, 7601.
6 J. Zhang, S. Xu, and E. Kumacheva, *J. Am. Chem. Soc.* **2004**, *126*, 7908.
7 N. A. Peppas, J. Z. Hilt, A. Khademhosseini and R. Langer, *Adv Mater.* **2006**, *18*, 1345.
8 S. Ekici, p. Ilgin, S. Butun and N. Sahiner, *Carbohyd Polym*. **2011,** *84*, 1306.
9 H. Lang, S. Maldonado, K. J. Stevenson and B. D. Chandler, *J. Am. Chem. Soc.,* **2004**, *126*, 12949.
10 H. Ago, K. Murata, M. Yumura, J. Yotani and S. Uemura, *Appl.Phys. Lett.,* **2003***, 82*, 811.
11 T. Mitsudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem.,* **2008**, *120,* 144.
12 P. Waszczuk, T. M. Barnard, C. Rice, R. I. Masel and A. Wieckowski, *Electrochem. Commun.,* **2002,** *4*, 599.
13 S. Wunder, F. Polzer, Y. Lu, Y. Mei, and M. Ballauff *J. Phys. Chem. C* **2010**, *114,* 8814.
14 Y. Lu, Y. Mei, and M. Ballauff, *J. Phys. Chem. B* **2006,** *110,* 3930.
15 Y. Lu, Y. Mei, M. Drechsler, and M. Ballauff, *Angew. Chem. Int. Ed.* 2006, 45, 813.
16 J. Dhar and S. Patil, *ACS Appl. Mater. Interfaces* **2012**, 4, 1803.
17 B. P. Tripathi, N. C. Dubey, and M. Stamm, *ACS Appl. Mater. Interfaces* **2014**, 6, 17702.
18 B. P.Tripathi, N. C. Dubey, S.Choudhury, P. Formanek and M. Stamm, *Adv. Mater. Interfaces*, **2015**, *2*, 1500097.
19 Z. H. Farooqi, W. Wu, S. Zhou and M. Siddiq, *Macromol. Chem. Phys.* **2011**, *212*, 1510.
20 N. Sahiner, A. M. Alb, R. Graves, T. Mandal, G. L. McPherson, W. F. Reed, and V. T. John, *Polymer* **2007**, *48*, 704.
21 Q. Luo, Y. Guan, Y. Zhanga and M. Siddiq, *J. Polym. Sci. Pol. Chem.* **2010**, *48,* 4120.
22 N. Pekel, N. Sahiner, P. Akkasa and O. Guven, *Polym Bull*. **2000**, *44*, 593.
23 N. Sahiner, N. Pekel and O. Guven, *Radiat. Phys. Chem.* **1998**, *52*, 271.
24 N. Sahiner, H. Yu, G. Tan, J. He, V. T. John and D. A. Blake, *ACS Appl. Mater. Interfaces* **2012**, *4*, 163.
25 D. Alpaslan, N. Aktas, S. Yilmaz, N. Sahiner, and O. Guven, *Hacettepe J. Biol. & Chem.* **2014**, *42*, 89.
26 D. James G. Venkateswaran and T. R. Rao, *Micropor. Mesopor. Mat.* **2009**, *119*, 165.
27 M. F. Hamza, I. E. EL Aassy, *Deslin. Water Treat.* **2014**, *52*, 331.
28 L. C. de Santa Maria, M. C. V. Amorim, M. R. M. P. Aguiar, P. I. C. Guimaraes, M. A. S. Costa, A. P. de Aguiar, P. R. Rezende, M. S. de Carvalho, F. G. Barbosa, J. M. Andrade and R. C. C. Ribeiro, *React. Funct. Polym.* **2001**, *49*, 133.
29 M. R. Lutfor, S. Silong, S.; W. M. Zin, M. Z. A. Rahman, M. Ahmad and J. Haron, *Eur. Polym. J.* **2000**, *36*, 2105.
30 A. S. El-khouly, Y. Takahashi, A. A. Saafan, E. Kenawy and Y. A. Hafiz, *J. Appl. Polym. Sci.* **2011**, *120*, 866.
31 A. S. Singh, A. Guleri, and R. K. Rana, *Int. J. Polym. Anal. Ch.* **2013**, *18*, 451.
32 T. Sahan, H. Ceylan, N. Sahiner and N. Aktas, *Bioresource Technol*. **2010**, *101*, 4520.
33 N. Sahiner, *Prog. Polym. Sci*. **2013**, *38*, 1329.
34 M. Ajmal, M. Siddiq, H. Al-Lohedan and N. Sahiner, *RCS Adv*.**2014**, *4*, 59562.
35 M. Ajmal, M. Siddiq, N. Aktas and N. Sahiner RSC Adv., 2015, 5, 43873.
36 N. Pekel, N. Sahiner and O. Guven, *Radiat. Phys. Chem.* **2000**, *59*, 485.
37 K. Saeed, S. Haider, T. J. Oh and S. Y. Park, *J. Membr.* Sci. **2008**, *322*, 400.
38 H. H. Patterson, R. S. Gomez, H. Lu and R. L. Yson, *Catal. Today* **2007**, *120*, 168.
39 N. Sahiner and P. Ilgin, *Polymer*, **2010**, *51*, 3156.
40 S. Jana, S. K. Ghosh, S. Nath, S. Pande, S. Praharaj, S. Panigrahi, S. Basu, T. Endo and T. T. Pal, *Appl. Catal. A.* **2006**, *313*, 41.
41 Y. Deng, Y. Cai, Z. Sun, J. Liu, C. liu, J. Wei, W. Li, C. Liu, Y. Wang and D. Zhao, *J. Am. Chem. Soc.* **2010**, *132*, 8466.
42 V. K. Gupta and Suhas. *J. Environ. Manage.* **2009**, *90*, 2313.
43 P. Deka, R. C. Deka, and P. Bharali, *New J. Chem.* **2014**, *38*, 1789.
44 Z. H. Farooqi, N. Tariq, R. Begum, S. R. Khan, Z. Iqbal, A. Khan, *Turk. J. Chem.* **2015,** *39*, 576.
45 N. Sahiner and O. Ozay, C*urr. Nanosci.* **2012**, 8, 367.
46 N. Sahiner, H. Ozay, O. Ozay, N. Aktas, *Appl. Catal. B- Environ* **2010**, *101*, 137.
47 M. Ajmal, S. Demirci, M. Siddiq, N. Aktas, N. Sahiner, *Colloid Surface A* **2015,** *486*, 29.
48 D. Ljuba, G. Smoljani, H. Juretic, *J. Environ. Manage.* **2015**, *161*, 83.
49 H. j. Lee, J. H. Kim, S. S. Park, S. S. Hong, and G. D. Lee. *J. Ind. Eng. Chem.* **2015**, *25*, 199.
50 A. Bhattacharjee, and M. Ahmaruzzaman, "Mater. *Lett.* **2015**, *161*, 20.
51 S. O. Alfaro, V. Rodríguez-González, A. A. Zaldívar-Cadena, and S. W. Lee, *Catal. Today* **2011**, *166*, 166.
52 Y. Mei, Y. Lu, F. Polzer, and M. Ballauff, *Chem. Mater.* **2007,** *19,* 1062.
53 D. Wang, H. L. Xin, Y. Yu, H. Wang, E. Rus, D. A. Muller, H. D. Abrun, *J. Am. Chem. Soc.* **2010**, *132*, 17664.
54 U. Böhmer, F. Franke, K. Morgenschweis, T. Bieber and W. Reschetilowski, *Catal. Today* **2000**, *60*, 167.

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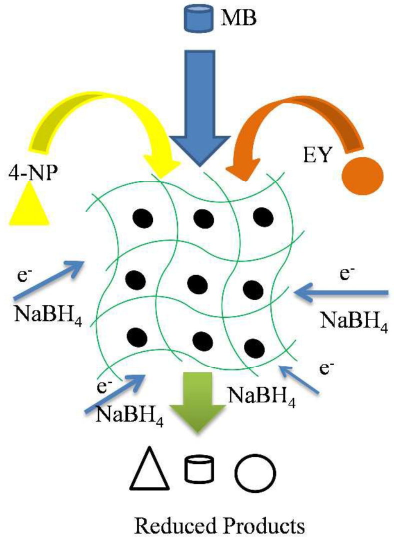

The reactants easily diffuse into microgels network, adsorb at the surface of catalyst nanoparticles and reduced in the presence reducing agent.