

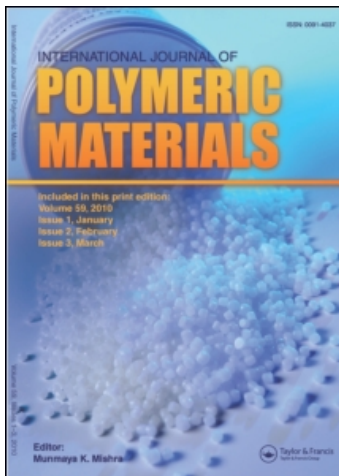
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### Utilization of Environmentally Benign Hydrogels and Their Networks as Reactor Media in the Catalytic Reduction of Nitrophenols

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# Utilization of Environmentally Benign Hydrogels and Their Networks as Reactor Media in the Catalytic Reduction of Nitrophenols

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Iron particles were synthesized inside poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (p(AMPS)) and used as a catalyst in the reduction of nitro benzene and 4-nitrophenol to aniline and 4-aminophenol, respectively, in acidic medium. It was demonstrated that hydrogel networks can be used effectively as catalysis media in the reduction of some organic toxic materials. The results verified that iron particles containing p(AMPS) hydrogel networks yield faster conversion rates. Additionally, iron nanoparticles containing p(AMPS) hydrogel networks could catalyze the reaction, giving 32% yield without any added cocatalyst, providing self cocatalyst mission.

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**Keywords** catalysis, hydrogel, nanocomposite, nanoreactor, remediation, treatment

## INTRODUCTION

Nitroaromatic compounds are toxic materials used in many industries such as the production of anilines, aniline-based dyes, paper, explosives, pesticides, drugs and others [1–3]. Among the nitrocompounds, nitrobenzene poses a major threat to human health as toxic and suspected carcinogenic material even at low concentrations [2–4]. As a potent pollutant, it was reported that the limit for nitrobenzene is 1 ppm in wastewater as it accounts for many health problems such as irritation of the eyes and skin, and weariness, headache, and vertigo, as well as affecting the central nervous system [4–10]. Recently, many researches have been directed towards the degradation of nitrobenzene and its derivatives utilizing many technologies. Due to the strong electron withdrawing ability of the nitro group in nitrobenzenes, oxidation is very difficult with conventional chemical and biological processes [2]. Therefore, a great number of studies for the elimination of these compounds have been performed over the past few decades. Methods such as electrochemical reduction [2], photochemical degradation [4,10–12], biodegradation [5,13], radiolytic degradation [4], autocatalytic oxidation [6], photooxidation [7], Fenton oxidation [1,9], reductive degradation by zero-valent iron [3,8,14,15], sonochemical degradation [16], and ozonation [17–20] are some of the widely employed techniques for the removal of nitrobenzene and its derivatives. However, many of these methods are reasonably expensive. The method of chemical reduction by zero-valent iron is preferred in the treatment of nitroaromatic compounds due to its low cost [3].

Hydrogels as three-dimensional crosslinked polymeric networks are versatile materials and offer extraordinary properties to operate in aqueous environments. Due to the crosslinking of the polymer chains and the hydrophilic groups in their structure, they are not soluble but swollen in water. In addition to neutral functional groups such as  $-\text{OH}$ ,  $-\text{NH}_2$  and carbonyl, the hydrophilic groups can also develop charges in the polymeric hydrogel network to  $-\text{COO}^-$  and  $-\text{SO}_3^-$  to interact with positively charged metal ions. This ability renders hydrogels a superior absorption ability to remove toxic metal ions and some chemical species in the aquatic environments. As generally biocompatible materials, hydrogels have many applications in various areas, ranging from environmental applications to biomedical applications such as drug delivery systems and tissue engineering [21–24].

In this study, we have shown for the first time that hydrogels can offer dual advantages for environmental applications: (i) absorption of heavy metal ions (iron in this case) from aqueous environments followed by the in situ reduction to fabricate iron nanoparticles in hydrogel networks, and (ii) utilization of these iron particles in hydrogel networks for the chemical reduction

of nitrocompounds. To this end, primarily in situ iron particles were prepared in crosslinked poly(2-acrylamido-2-methyl-1-propansulfonic acid) hydrogel networks. Then, reduction of nitrobenzene and 4-nitrophenol were investigated using these iron nanoparticles containing the hydrogel network. The results showed improved and faster conversion in comparison with commercially available iron particles.

## EXPERIMENTAL

### Materials and Methods

Nitrobenzene, 4-nitrophenol, and ethanol were purchased from Aldrich and used without further purification. Hydrogel was prepared using 2-acrylamido-2-methyl-1-propansulfonic acid (AMPS) as monomer, N,N'-methylenebisacrylamide as crosslinker (X-er), N,N,N',N'-tetramethylenediamine (TEMED) as an accelerator, and ammoniumpersulfate (APS) as redox initiator. All products were of analytical grade and purchased from Acros and Fluka Chemical Companies. Iron powder was purchased from Schering A. G. Berlin Company (particle size >10  $\mu\text{m}$ ).

UV-vis spectrometer is employed for the observation of the conversion of nitro compounds to the corresponding reduced forms using a Shimadzu UV-1208 model spectrophotometer. FTIR (Perkin Elmer BX II) spectra were recorded in KBr powder for the visualization of newly formed functional group band frequencies.

Transmission electron microscopy (TEM) measurements were acquired employing JEOL 2010 TEM to visualize iron particle sizes inside hydrogel matrices. Vacuum oven-dried iron nanoparticles containing hydrogels were finely ground with mortar and pestle and placed on formwar-coated copper TEM grids. The micrographs were obtained with an operating voltage of 200 kV.

Scanning electron microscopy (SEM) images were obtained after lyophilizing water swollen hydrogel on SEM stubs at ambient temperature and gold sputtering to a few nm (2–5 nm) thicknesses with an operating voltage of 10–15 kV.

### *Hydrogel Syntheses*

p(AMPS) hydrogels were prepared via radical polymerization in the presence of a redox initiator. Various degrees of crosslinkers (0.5, 0.75 and 1 mole % based on total monomer amount) were used for the syntheses of different pore sizes of hydrogels. In a typical hydrogel synthesis procedure, 4.5 g AMPS (0.0217 mol), 0.0167 g Bis (0.5 mole % with respect to monomer) and 100  $\mu\text{l}$  TEMED were dissolved in 3.5 ml water. To this solution, initiator solution (APS), 0.05 g (1 mol % with respect to monomer) in 1 mL water was added. After mixing thoroughly, the solution was poured into plastic straws with

4 mm diameter and kept at least 24 h to complete polymerization and crosslinking reaction at ambient temperature. The bulk hydrogels were removed from the plastic straws and cut to 2–3 cm long cylinders and cleaned by placing in distilled water for 3 days, replenishing the water every 12 h to remove unreacted species (monomer, polymer, crosslinker, and initiator). After the cleaning procedure, hydrogels were dried in an oven to a constant weight and kept in sealed containers for further use.

#### *In Situ Iron Particle Synthesis in Hydrogel Network*

The preparation of iron particles inside hydrogel matrices was reported previously [25]. Briefly, cleaned and weighed amounts of dried hydrogels were placed in 0.5 M  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (250 mL) solution to load the hydrogels with iron ions. The absorption studies were performed in a water bath shaker at room temperature for 2 days. After the end of the iron ion absorption period, hydrogels were kept in distilled water for another 2 days to remove unbound iron ions. Cleaned iron ion-loaded hydrogels were transferred into 0.5 M  $\text{NaBH}_4$  aqueous solution (100 mL), and the reduction reaction proceeded for 12 h in a water-bath shaker at ambient temperature. After reduction of iron ions in situ, hydrogels were cleaned by washing with distilled water and stored for reduction reactions of nitro compounds as catalysis medium.

#### *Reduction of Nitrobenzene and 4-Nitrophenol*

To reduce nitrobenzene and its derivative, 4-nitrophenol with iron particle-containing hydrogels, the experiments were performed in a water-ethanol mixture. Nitrobenzene (74  $\mu\text{L}$ ) solution in 50 ml water-ethanol mixture (1:1) was heated to 75°C at pH 3. Then, to this solution, iron particle-containing (0.403 g iron particles) p(AMPS) hydrogel (1.493 g) was added, and the reaction proceeded at 75°C. 0.2 ml samples were directly withdrawn from the reaction medium at certain time intervals, and diluted twenty-fold with water-ethanol mixture (1:1). UV-vis spectra of these solutions were taken to monitor the decrease in the intensity of absorption peak at 299 nm in UV-vis spectrophotometer without filtration. After reaction was completed (ca.1 h) the reduction form of nitrobenzene (that is, aniline) was purified and its structure was identified by FTIR spectra.

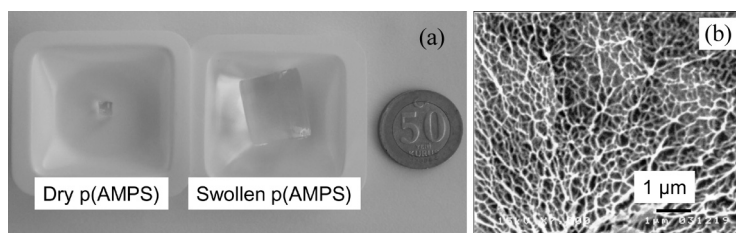
In the reduction of 4-nitrophenol, a process, similar to nitrobenzene reduction, was followed: 0.1 g 4-nitrophenol in 50 ml water-ethanol (2:1 by volume) mixture was heated to 75°C at pH 3 in a sealed beaker. To this solution, iron particle-containing (0.403 g iron particles) p(AMPS) hydrogel (1.493 g) was added, and reaction was followed by TLC. At predetermined time intervals, 0.1 mL samples were directly withdrawn from the reaction medium and diluted 150-fold with water-ethanol mixture (2:1). The reduction in the

intensity of the 317 nm of UV-vis absorption band of the solutions was monitored by UV-vis spectrophotometer. The reduction products of 4-nitrophenol and 4-aminophenol were purified and their structure was confirmed by FTIR spectra.

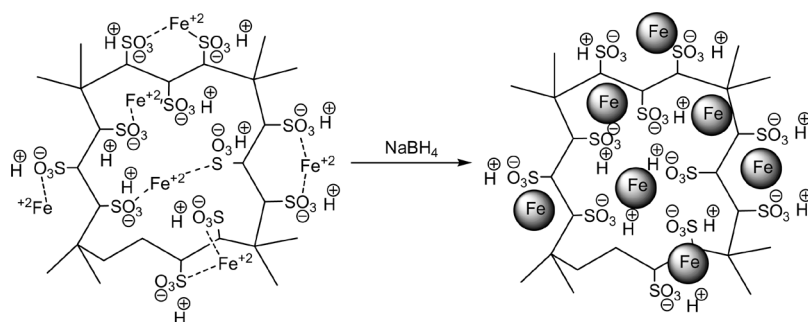
The reduction of nitrobenzene and 4-nitrophenol with commercially available iron particles (size  $> 10 \mu\text{m}$ ) were carried out for comparison, and the experiments were conducted utilizing the same setup. For these experiments, the reaction mixture was filtered through a  $0.22 \mu\text{m}$  millipore filter as it required for removing the catalyst from the reaction media.

## RESULTS AND DISCUSSION

In situ iron particle syntheses were carried out according to the previously reported literature [25]. Figure 1 shows p(AMPS) hydrogel (a) in dry state and swollen state and (b) the SEM images of the freeze-dried 1% X-ed p(AMPS) hydrogel. As can be seen from the SEM images, even 1% X-ed hydrogel is very porous and the porosity can be controlled by the amount of X-er used during hydrogel synthesis. As reported, the crosslinking degree can significantly affect the swelling degree and mechanical strength of the hydrogels while having very little or no effect on the iron ion-loading capacity, as it is used in relatively low concentrations (0.5, 0.75 and 1%) [25]. Therefore, in this study only 1% X-ed hydrogels were used as the most suitable crosslinker amount. A schematic representation of iron particle synthesis in p(AMPS) hydrogel network is depicted in Figure 2 with the suggested mechanism. As shown in Figure 2, due to the electrostatic interactions between iron ions and  $-\text{SO}_3\text{H}$  groups in the p(AMPS) network, the iron ion can be loaded to the hydrogel network. With the suitable reducing agent such as  $\text{NaBH}_4$ , iron ions are reduced to their metallic nanoparticle forms. Figure 3 (a) shows the digital camera images of iron particles containing p(AMPS) hydrogel, and Figure 3 (b) shows the TEM images of iron particles containing 1% X-ed p(AMPS) hydrogel. TEM images illustrate that iron nanoparticle size distribution inside hydrogels is broad and is in the order of 50–250 nm or even

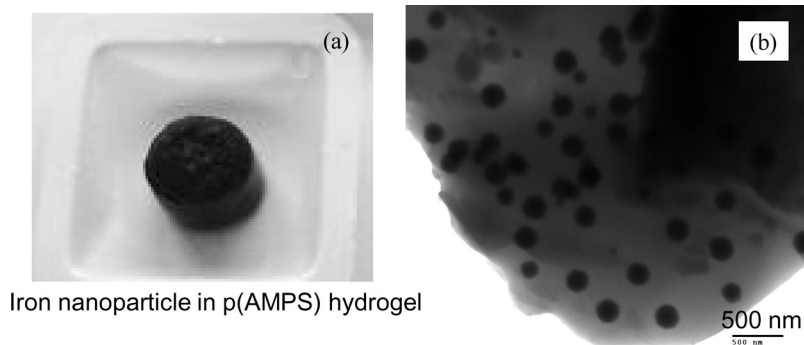


**Figure 1:** (a) Digital camera images of dry and water-swollen 0.5 mole % crosslinked p(AMPS) hydrogel, and (b) SEM images of freeze-dried p(AMPS) hydrogels.

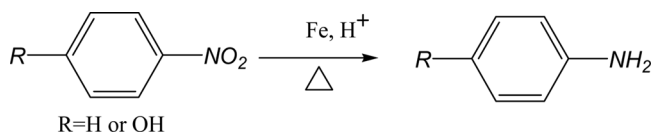


**Figure 2:** A schematic representation of iron particle synthesis inside p(AMPS) hydrogels.

smaller in the form of metal nanoclusters. The magnetic, thermal and morphological properties of these hydrogel-metal nanocomposites were elaborated elsewhere [25]. Hydrogels with various functional groups have been reported for the removal of various toxic and valuable metal ions [26–28]. It was stated that the absorption capacity of p(AMPS) hydrogel is 270 mg iron per gram dry gel [25]. This establishes that these kinds of materials are very effective absorbents for the removal of toxic metal species from the aqueous environments. Here, to the best of our knowledge, we are the first to report the utilization of a hydrogel network that contains in situ synthesized metal particles for the catalytic usage. The exploitation of hydrogel networks as reaction media provide many advantages; for example, the reaction will take place inside the network which eliminates the needs for the catalyst to be removed from the media after the reaction is complete, and hydrogel functional groups can provide micro and/or nano environments acting as cocatalyst, as in the case of nitrobenzene and 4-nitrophenol reduction (the presence of acid groups). The reduction of both reagents required acidic media and the corresponding reaction scheme is shown in Figure 4.



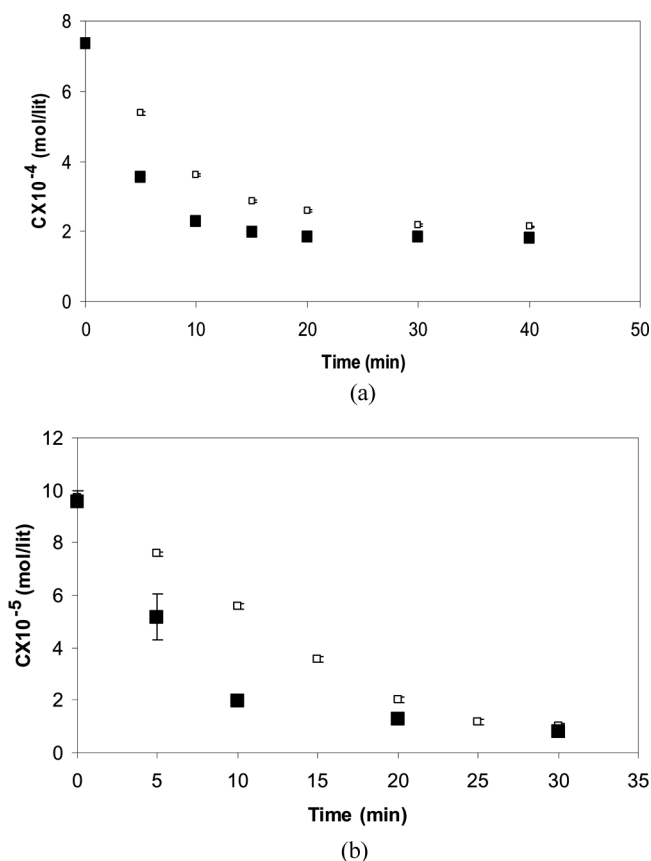
**Figure 3:** Iron particle containing hydrogels (a) digital camera (b) TEM images.



**Figure 4:** Reduction reaction schema of nitrobenzene and 4-nitrophenol in acidic medium in the presence of iron particles.

The reduction reactions of nitrobenzene and 4-nitrophenol were monitored by a UV-vis spectrophotometer with a decrease in the intensity of absorption bands at 299 nm and 317 nm, respectively. Nitrobenzene has an absorption maximum at 299 nm and the reduction of this reagent was followed with time by calculating the decrease in the concentration of nitrobenzene from a calibration curve constructed for the reaction media. The decrease in the concentration of nitrobenzene at 75°C in the presence of iron particles (open square) and hydrogel composites (filled square) is shown in Figure 5 (a). Each experiment was performed in triplicate and good consistent results were obtained and depicted as the standard errors in the graph. Additionally, as can be seen from the graph, the iron particle-containing hydrogels can reduce nitrobenzene faster than the bare iron particles even though both catalysts were the same amount (bare iron particles and the amount of iron particle inside hydrogels were equal, 0.403 g). These could be due to two important factors. One factor is the smaller size of the iron particles inside hydrogels, which as shown in the TEM image of Figure 3 are approximately 50–250 nm. The commercially available iron particles have diameter >10 μm (provided by the supplier). It is well known that smaller particles have higher surface area, and therefore, the overall reduction rate of nitrobenzene is faster. The other factor could be the existence of  $-\text{SO}_3\text{H}$  functional groups (provide acidic behavior) in the network which is closer proximity to the iron catalyst than the free acid in solution. Because the reaction is acid catalyzed, the existence of acid functionality in the hydrogel network can increase the reaction rate. It is known that pH plays a significant role in the reduction of nitrobenzene by zero-valent iron. Mu et al. reported that the optimum pH value is 3 for the reduction of nitrobenzene in the presence of zero-valent iron [3]. Therefore, in this work, the reduction reactions were carried out at pH 3. To test our hypothesis, we carried out experiments in the absence of acid (pH 7) with both hydrogel composite and bare iron particles. It was found that hydrogel composite materials provided 32% conversion in the reduction of nitrobenzene, while commercially available bare iron particles yielded only 7% conversion in the absence of any added acid. An empty hydrogel matrix (no iron particles) resulted in zero conversion. This is a major finding, that a 25% increase in the conversion reaction of nitrobenzene to aniline in the absence of acid verifies our hypothesis and opens new avenues for the application of metal-containing hydrogels in many important organic reactions.





**Figure 5:** (a) The decrease in the concentration of nitrobenzene with time at 75°C in acidic media (pH 3) in the presence of iron particle (open square) and hydrogel composites (filled square) in water-ethanol (1:1 by volume) mixture. (b) The decrease in the concentration of 4-nitrophenol with time, same conditions as in (a) except the mixture is water-ethanol (2:1 by volume).

Similar experiments were performed for 4-nitrophenol reduction to 4-hydroxyaniline (4-aminophenol) following the reduction of the absorption band at 317 nm in water-ethanol (2:1 by volume) at 75°C at pH 3. The corresponding conversion reaction with time is shown in Figure 5 (b), which is the conversion graph of 4-nitrophenol to 4-aminophenol with time. As expected, iron nanoparticles containing hydrogel gave a much faster reduction rate. The same hypothesis is valid for the reduction of 4-nitrophenol to 4-aminophenol. These two experiments pointed out an additional important result, which is the removal of catalyst from the reaction media. In bare iron particle reactions, which use a relatively bigger particle size than hydrogels containing iron particles inside p(AMPS) the reaction necessitates an additional cost, i.e., the filtration (syringe filter, 0.20  $\mu\text{m}$ ), whereas with the iron particle-containing

**Table 1:** FTIR data of the nitrobenzene, 4-nitrophenol and their reduced forms aniline and 4-aminophenol, respectively, with their corresponding functional group frequencies as  $\text{cm}^{-1}$ .

<b>Compounds</b>	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\nu(\text{ArC-H})$	$\nu(\text{N-H})$	$\nu(\text{C=C})$	$\nu(\text{C-N})$	$\nu(\text{NO}_2, \text{asym})$	$\nu(\text{NO}_2, \text{sym})$
Nitrobenzene			3078				1525	1349
Aniline		3345-3208	3034	1619	1498	1276		
4-Nitrophenol	3324		3084		1495			
4-Aminophenol		3341-3283	3024	1615	1510-1475	1387-1256		

hydrogel reaction there is no need for filtration. One can simply remove hydrogel pieces which are on the order of cm in swollen states and separate them from the reaction media, leaving just the product. This is cost saving and can be very crucial in some other organic reactions.

To confirm the reduction reaction of nitrobenzene and 4-hydroxynitrobenzene the reaction mixture was purified and FTIR spectra of the reagent and their corresponding reduction products were taken. Nitrobenzene has characteristic  $\text{NO}_2$  asymmetric and symmetric stretching frequencies at about  $1525$  and  $1349\text{ cm}^{-1}$ . After the reduction, the aniline product, has characteristic peaks in the order for N–H stretching frequencies, and N–H bending vibration and C–N stretching peaks at about  $3345$  and  $3356\text{ cm}^{-1}$ , and  $1619\text{ cm}^{-1}$  and  $1276\text{ cm}^{-1}$ , respectively. The absence of peaks belonging to nitrobenzene in an aniline FTIR spectrum confirms the conversion of nitrobenzene to aniline. Again, similar results were obtained for the reduction of 4-nitrophenol to 4-aminophenol and the results were summarized in Table 1 with all the stretching frequencies of both corresponding compounds. All the observed frequencies are in agreement with the FTIR atlas of the corresponding materials.

## CONCLUSIONS

This investigation has established several important conclusions. (1) Various organic reactions can take place inside the hydrogel network. (2) Hydrogels can be used for metal nanoparticle syntheses in addition to use for the removal of various hazardous and toxic metals from aqueous environments. (3) The porous structure of hydrogel networks can be utilized for the reduction of toxic organic compounds such as nitrobenzene and 4-nitrophenol. (4) The use of hydrogel as a reactor for catalysis media offers additional advantages: (i) networks of hydrogel can have the required functional groups such as acid and base (acid groups in this investigation provide 25% conversion without any cocatalyst), and (ii) they can get rid of the filtration problems such as the separation of catalyst from the product, which is economically advantageous in comparison to conventional catalysis reactions. Therefore, the use of hydrogels and their catalysts containing networks as reactor has much potential in industries as well as for specific reactions. In fact, our current research is focused on such investigations.

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