

Preparation of Metal-Containing Zwitterionic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ - β PDMA Composite Systems and Catalytic Activity Studies

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In response to the current challenges in the field, this study will contribute to the development of a highly versatile magnetic core/shell nanocomposite by addressing issues in the synthesis and functionalization of Fe_3O_4 nanoparticles through the presentation of innovative solutions. Firstly, Fe_3O_4 nanoparticles were synthesized. Tetraethyl orthosilicate was used as a silicon source and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ magnetic nanoparticles were synthesized. The outer surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles were modified and converted into $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ structure. These modified particles were then functionalized with alkyl bromide to be used as an ATRP initiator and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Br}$ structure was obtained. The polymerization of 2-(dimethylamino)ethyl methacrylate (DMA) monomer on the particle surface was

achieved by the SI-ATRP method. In the last step, betainization of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PDMA}$ composite was worked, and the salts of gold and silver were added to composite systems. The dispersions of the metal loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta$ PDMA composite was obtained and used as catalysts in the reduction reaction of p-nitrophenol to p-aminophenol. Consequently, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta$ PDMA composite system with magnetic properties in the range of 145–160 nm was prepared. The structure of synthesized magnetic nanoparticle was characterized by PXRD, TEM, TG-DTA and the catalyst activity in the reduction reaction of p-nitrophenol to p-aminophenol was examined by UV-vis spectrophotometer.

Introduction

Nanometer-scale magnetic entities exhibit substantial surface dimensions, allowing facile alignment under the influence of an external magnetic field.^[1–5] Exploiting their magnetic attributes, these nanoparticulate structures find utility in diverse research applications, including catalytic processes and adsorption studies. Furthermore, their recyclability and ability to be precisely guided within drug delivery systems enhance their appeal for environmental remediation and therapeutic interventions. The integration of magnetic nanoparticles into diverse polymeric matrices yields polymers endowed with magnetic characteristics, broadening the scope of materials engineering. Magnetic particles have a great role in biological applications and human health. Magnetic particles are widely used in subjects such as drug and gene transport, cancer treatment, and cell separation.^[6]

Iron oxides can be found in different molecular forms in nature. These are $\alpha\text{-Fe}_2\text{O}_3$ hematite form, $\gamma\text{-Fe}_2\text{O}_3$ maghemite form and Fe_3O_4 magnetite form.^[7,8]

Silicon dioxide (SiO_2) is a compound of silicon and oxygen, often called silica. SiO_2 elements are bonded by covalent bonds. It is one of the components of sand and can be found naturally in nature. They are usually white or colorless and insoluble in water or ethanol. SiO_2 is an additive in the food industry and has various industrial applications. Its function in the industry is

as a binder, antifoam agent, viscosity controller, dryer, beverage cleaner and pharmaceutical-vitamin excipient.

The ease of synthesis of SiO_2 and their widespread use are among the reasons why silica-polymer composites are widely reported in the literature among organic-inorganic composite materials. Silica nanoparticles are used as fillers in the production of paints, plastic binders and rubber products.^[9] Synthesis of colloidal silicas is widely used due to their stability in size and distribution. A simple synthesis of monodisperse spherical silica particles has been reported in the literature.^[10] The synthesis was initiated by the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in a mixture of water and ammonia added as a catalyst to the alcohol solution. The ionic structures of the nanoparticles obtained as a result of hydrolysis become stable in ammonia solution as a result of electrostatic repulsion. In recent years, brush polymers obtained on the surfaces of silica nanoparticles after polymerization on the surfaces of silica nanoparticles are frequently used in the literature.^[11]

Polymer layers can be directly attached to the surface of magnetic particles.^[12] In this way, biocompatible magnetic polymers can be obtained by using suitable monomers.^[13] However, magnetic particles may lose their stability when surrounded by a polymer layer. This negativity can be prevented by creating a $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell structure as a result of bonding the magnetic particle with a biocompatible material such as silica.^[14] By making various modifications, $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell structures can be coated with a polymer layer using the SI-ARTP method.^[15] The coated polymer layer protects the magnetic core in the reaction environment and

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increases the stability of the magnetic core, increasing its potential for longer use.

The $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core/shell particles were subjected to modification with sodium polyacrylate through SI-ATRP. Osmolality measurements and recovery tests were conducted to investigate the influence of the grafted sodium polyacrylate amount and particle size on draw solute performance. The particles, after synthesis, exhibited the ability to maintain a stable dispersion even after undergoing ten cycles of assembling/dispersing operations.^[16] Liu, G. and colleagues innovated a new material, magnetic core-shell-corona composite nanoparticles with charged polymer brushes grafted onto them ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PSPMA}$), aiming to extract water through the hydration effect and facilitate oil–water separation under the influence of an external magnetic field. The poly(3-sulfopropyl methacrylate potassium salt) (PSPMA) brushes, as charged polymer brushes, possess robust hydration capability and excellent swelling performance, imparting super hydrophilicity and efficient water-absorbing properties to the resulting composite nanoparticles, akin to a sponge.^[15] A two-step procedure was employed for the preparation of superparamagnetic poly(sodium 4-styrenesulfonate) (poly(SSNa)) grafted $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite particles. In the first step, core-shell structured $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles were synthesized through the modified Stöber method. Subsequently, in the second step, poly(SSNa) grafted $\text{Fe}_3\text{O}_4/\text{SiO}_2$ particles were obtained using ATRP of sodium 4-styrenesulfonate (SSNa) with modified magnetic silica. The resulting anionic polyelectrolyte-grafted magnetic silica composite particles exhibit superparamagnetic characteristics, predominantly covering the core-shell structure within the size range of tens of nanometers.^[17] In another study, a lysozyme-imprinted polymer was synthesized via surface-initiated atom transfer radical polymerization on the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ surface. Specific adsorption of lysozyme was performed and it was shown that 86% of the adsorbed lysozyme could be released by changing the temperature.^[18] At the same time, many more core-shell structured $\text{Fe}_3\text{O}_4/\text{SiO}_2$ particles such as $\text{Fe}_3\text{O}_4/\text{DySiO}_2\text{--MPS}$, $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{--}g\text{--PSStNa}$, $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{chitosan-grafted-poly(N-vinylcaprolactam)}$, $\text{Fe}_3\text{O}_4\text{--SiO}_2\text{--P4VP}$, zinc–tetracarboxyl–phthalocyanine- $g\text{--Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2\text{--}g\text{--poly(N-isopropyl acrylamide)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG--Maltose}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--Rho}$, $\text{Fe}_3\text{O}_4/\text{SiO}_2$ decorated trimesic acid–melamine, $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{MXene}$ 3D interlayer structure and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Polydopamine@Ag}$ core-shell nanoparticles have been synthesized in the literature and used in different applications.^[19–28]

Inhere, $\text{Fe}_3\text{O}_4@\text{SiO}_2$ magnetite nanoparticles with core/shell structure were synthesized by coating the Fe_3O_4 surface with silica after Fe_3O_4 nanoparticles were synthesized. By modifying the surfaces of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles, first the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--NH}_2$ structure was obtained, and then, with appropriate reactions, the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--Br}$ structure, which was used as the initiator in ATRP, was obtained. As a result of the polymerization of DMA monomer on the particle surface with the ATRP method, the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--PDMA}$ structure was synthesized, and as a result of the betainization of this structure with betainization chemistry, the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--}\beta\text{PDMA}$ structure was

synthesized. Composite systems were created by adding Au and Ag salts to the system. The resulting dispersions of metal-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--}\beta\text{PDMA}$ composites were used as catalysts in the reduction of p-nitrophenol to p-aminophenol and the effects of metals on the reduction reaction were compared. In addition, since the systems have magnetic properties, the particles were removed from the reduction environment by applying an external magnetic field and their reusability was tested.

Experimental

Material

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich. Iron (III) chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, 97%), iron (II) chloride tetrahydrate ($\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, 98%), sodium hydroxide (NaOH, $\geq 97.0\%$, pellets) and hydrochloric acid (HCl, 37%) were used in synthesis of Fe_3O_4 nanoparticles. Ammonia (NH_3 , $\geq 99.95\%$), tetraethyl orthosilicate (TEOS, 98%) were used in preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles. (3-aminopropyl)triethoxysilane (APTES, $\geq 98\%$) were used in preparation $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--NH}_2$ nanoparticle synthesis. Triethylamine (TEA, $\geq 99\%$), α -bromoisobutyl bromide (BIBB, 98%) were used in preparation $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--Br}$ nanoparticle synthesis. Copper (I) bromide (CuBr, 98%), copper (II) bromide (CuBr_2 , 99%), methanol (MeOH , $\geq 99.8\%$), N, N, N', N'-pentamethyl diethylene triamine (PMDETA, 99%), 2-(dimethylamino) ethyl methacrylate (DMA, 99%) were used in preparation $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--DMA}$ nanoparticle synthesis. 1,3-propanesultone (1,3-PS, $\geq 99\%$), tetrahydrofuran (THF, $\geq 99.0\%$) were used in betainization process of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--DMA}$ nanoparticle. Potassium tetrachloroaurate (III) [$\text{K}(\text{AuCl}_4)$, 98%], silver nitrate (AgNO_3 , $\geq 99.0\%$), sodium borohydride (NaBH_4 , $\geq 98.0\%$) were used in preparation of metal nanoparticle on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--DMA}$ surface. Double distilled water (H_2O), acetone ($\geq 99.5\%$), ethanol (EtOH , $\geq 99.8\%$), toluene (99.8%) were used as solvents throughout the syntheses and to wash the particles in the centrifuge stage.

Method

Hitachi HT 7800 electron microscope was used as a 1200 cryogenic transmission electron microscope (Cryo-TEM) to determine the sizes of the synthesized nanoparticles. All TEM samples were prepared on carbon-coated copper TEM grids. It is based on determining the mass changes that occur in the examined sample as a function of temperature or time while applying a temperature program to the sample. Seiko SII EXSTAR600 model thermogravimetric analyzer (TGA) device was used in thermogravimetric analyzes of the synthesized nanoparticles. Analyzes were performed at heating rates of 10°C in the range of $50\text{--}850^\circ\text{C}$ in a N_2 atmosphere with a flow of 200 mL/min. The catalytic activity study of the synthesized nanoparticles in the reduction reaction of para-nitrophenol (p-NP) to para-aminophenol (p-AP) was performed by looking at the changes in absorbance intensities at wavelengths of 400 and 300 nm using a Perkin Elmer Lambda 35 UV-vis spectrophotometer (UV-Vis). Powder X-ray diffraction method (PXRD) is based on the principle that each crystal phase refracts X-rays in a characteristic pattern depending on its unique atomic arrangements. These diffraction profiles identify that crystal like a fingerprint, for each crystalline phase. The mineralogical structures of the synthesized nanoparticles were analyzed with the Rigaku D/Max 2200 device. Since nanoparticles (NPs) are sensitive to the magnetic field, they

were synthesized using a Heidolph RZR2020 model mechanical stirrer instead of a magnetic stirrer.

Experimental Studies

Preparation of Fe_3O_4 Nanoparticles

Fe_3O_4 nanoparticles were synthesized as described in the literature.^[29] Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (8.1 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3 g) were dissolved in 300 mL 1.2 mmol/L HCl using an ultrasonic bath. 450 mL 1.25 mol/L NaOH solution was prepared and the first solution was mixed in a 3-necked flask using a mechanical stirrer under N_2 atmosphere. NaOH solution was added slowly and it was observed that black precipitates were formed. The mixture was stirred at 80°C for 120 minutes under N_2 atmosphere. The reaction was terminated by taking the N_2 atmosphere to room conditions after stirring for 120 minutes and the mixture was centrifuged three times with water and then ethanol for at 15 minutes at 10000 rpm. The product was dried in a vacuum oven at 50°C and finally, Fe_3O_4 nanoparticles were obtained as black and fine powder (Figure 1).

It is known that NPs aggregate rapidly when an external magnetic field is applied. Since the rapid aggregation of NPs will cause problems in the formation of the core/shell structure, a mechanical stirrer was preferred instead of a magnetic stirrer in the synthesis of Fe_3O_4 nanoparticle and the subsequent synthesis of core/shell structures. In general, an ultrasonic bath was used in the preparation of solutions to ensure that the solution quickly became monodisperse.

Preparation of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ Nanoparticles

$\text{Fe}_3\text{O}_4@/\text{SiO}_2$ core-shell nanoparticles were prepared by the sol-gel process.^[30–32] 1.0 g of the Fe_3O_4 nanoparticle was taken and a solution was prepared in an ultrasonic bath using 0.500 L ethanol, 0.125 L H_2O and 0.032 L NH_3 . 13.5 mL TEOS was added dropwise to the solution and stirred at room temperature for 3 hours in N_2 atmosphere. The reaction mixture was transferred from N_2 atmosphere to room conditions and the reaction was terminated after

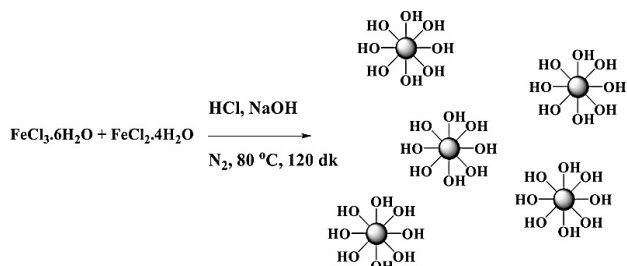


Figure 1. Fe_3O_4 nanoparticle synthesis.

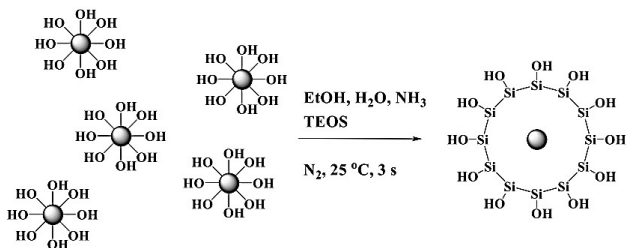


Figure 2. $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ nanoparticle synthesis.

3 hours. Since nanoparticles are sensitive to magnetic fields, a mechanical stirrer was used in all studies. The nanoparticles were centrifuged 3 times at 10000 rpm and washed, first with water and then with ethanol. After washing process, the product was dried in a vacuum oven at 50°C and gray-brown $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ core-shell nanoparticles were obtained (Figure 2).

$\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--NH}_2$ Nanoparticle Synthesis

2.0 g of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ nanoparticle was taken and homogenized in 50 mL toluene in an ultrasonic bath for 15 minutes.^[33] 4 mL of APTES was added to this mixture and the mixture was transferred to a 3-necked flask. A reflux system was set up and mixed in a mechanical stirrer in N_2 atmosphere at 110°C for 12 hours. The reaction mixture was centrifuged 3 times at 10000 rpm and washed, first with ethanol and then with acetone. After washing process, the product was dried in a vacuum oven at 50°C and as a result, $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--NH}_2$ was synthesized (Figure 3).

$\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--Br}$ Nanoparticle Synthesis

1.5 g of $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--NH}_2$ nanoparticle was taken and dissolved in 30 mL of toluene. 2.25 mL of TEA was added and mixed in a mechanical stirrer at 0°C . While the mixing process continued, 0.75 mL BIBB was slowly added to the medium. After the addition of BIBB, it was mixed at 0°C for 90 minutes. It was then stirred at room temperature for 24 hours. The reaction mixture was centrifuged 4 times at 10000 rpm and washed with ethanol. Finally, it was dried in a vacuum oven at 50°C and $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--Br}$ was obtained (Figure 4).

Synthesis of $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--PDMA}$ Composite System

$\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--Br}$ nanoparticle was used as ATRP macroinitiator for the $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--PDMA}$ composite system, which will be synthesized using the surface-initiated atom transfer radical polymerization (SI-ATRP) method.^[34]

0.5 g of $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--Br}$ nanoparticle was taken and dissolved in a mixture of 7.5 mL water and 15 mL acetone. The solution was mixed in a N_2 atmosphere in a mechanical stirrer at 300 rpm. A mixture of 0.0125 g CuBr, 0.0015 g CuBr_2 and 0.15 mL PMDETA was prepared in another bottle and kept in N_2 atmosphere. In a second bottle, 1 mL DMA was kept in N_2 atmosphere. The second solution was transferred to the magnetic nanoparticle solution at the mechanical stirrer. While the solution was mixing in N_2 atmosphere,

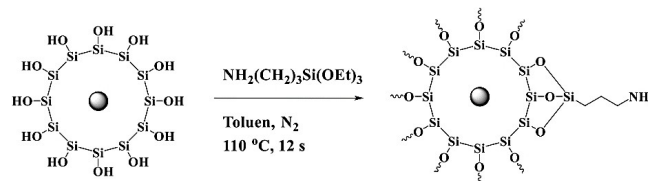


Figure 3. $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--NH}_2$ nanoparticle synthesis.

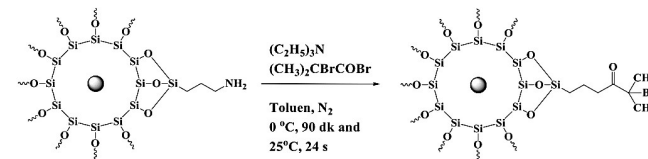


Figure 4. $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--Br}$ nanoparticle synthesis.

DMA monomer was transferred onto it. The solution was stirred at room temperature for 20 hours and the lid was opened at the end of 20 hours to terminate the reaction. The solution was centrifuged 3 times at 10000 rpm, washed with methanol and dried in a vacuum oven at 50 °C. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PDMA}$ composite system was obtained at the end of the process (Figure 5).

Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ Composite System

0.3318 g of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PDMA}$ structure was taken and dissolved in 20 mL THF for the betainization of the PDMA block on the structure.^[35–40] Then, 0.312 mL of 1,3-PS was added and stirred for 24 hours. At the end of 24 hours, the solvent was evaporated and particle was washed 3 times with THF. After the last washing process, THF was removed with a rotary evaporator and the particles were dried with freeze dryer (Figure 6). Finally, the betainized particle was obtained and used in the synthesis of metal-containing catalyst systems.

Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Metal) Composite Systems

It was homogeneously deposited on the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ surface by adsorption based on the interaction of Au and Ag precursor salts, which have opposite charges, with the negative sulfonate ($-\text{SO}_3^-$) group and positive quaternary amine ($-\text{NR}_3^+$) group in the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ composite system (Figure 7). These metal-loaded composite systems [$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Au), $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Ag), and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Ag-Au)] were used as catalysts in the reduction reaction of p-NP to p-AP.



Figure 5. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PDMA}$ composite system.

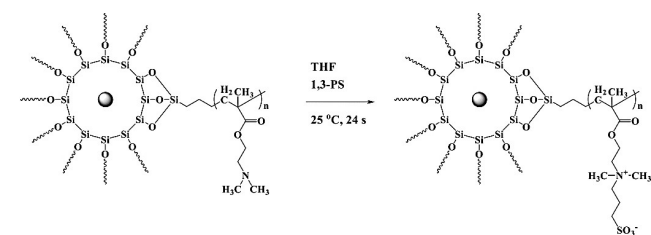


Figure 6. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ composite system.

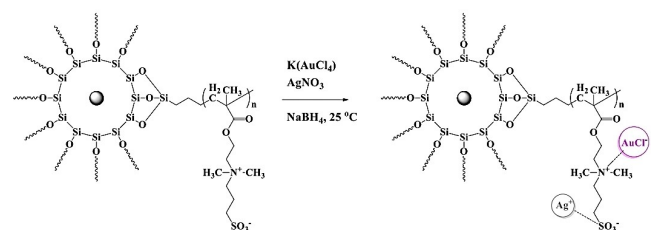


Figure 7. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(metal) nanoparticle synthesis.

Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Au) Composite System

0.1 g of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ nanoparticle was weighed and homogenized in 10 mL of water using an ultrasonic bath. The solution prepared by dissolving 0.1401 g $\text{K}(\text{AuCl}_4)$ in 1 mL of water was added dropwise to this mixture and homogenized using an ultrasonic bath at 30 °C for 60 minutes. Then, 0.05612 g NaBH_4 dissolved in 0.5 mL of water was added to the solution and homogenized for another 60 minutes and mixed well. In this way, the synthesis of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Au) composite system was carried out.

Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Ag) Composite System

The synthesis was carried out in the same way as the synthesis of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Ag) composite system, but 0.0630 g AgNO_3 was added instead of $\text{K}(\text{AuCl}_4)$.

Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Ag-Au) Composite System

0.1 g of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ composite system was taken and homogenized and dispersed in 10 mL of water using an ultrasonic bath. The solution prepared by dissolving 0.0630 g AgNO_3 and 0.1401 g $\text{K}(\text{AuCl}_4)$ in 3 mL of water was added dropwise to the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ solution. The prepared mixture was homogenized using an ultrasonic bath at 30 °C for 60 minutes. Finally, 0.112 g NaBH_4 dissolved in 0.5 mL of water was added to the mixture and homogenized and mixed for another 60 minutes. The synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Ag-Au) composite system was carried out.

Magnetic Field Effect on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Metal) Nanoparticles

The most important feature of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(metal) composite system is that it can be easily manipulated with a magnetic field. The nanoparticles exhibit rapid response to the applied magnetic field, forming a homogeneous dispersion, and readily redisperse with a gentle shake upon the removal of the magnetic field (Figure 8). This indicates the nanoparticles' outstanding magnetic responsiveness and redispersibility, presenting a favorable feature for their potential applications.

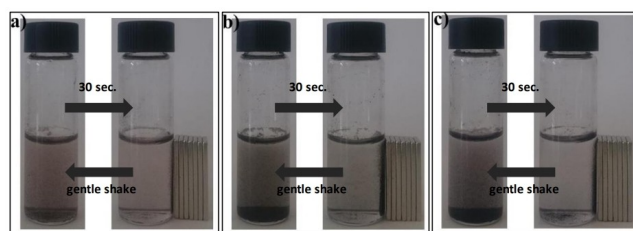


Figure 8. Magnetic field effect on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ (metal) nanoparticles [a) $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Au), b) $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Ag), and c) $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA}$ -(Ag-Au)].

Results and Discussion

Characterization of NPs by TEM

Fe_3O_4 Nanoparticles

In the experiments, the NPs, which aggregation was prevented by using an ultrasonic bath before synthesis, were ensured to have smaller core/shell structures after being synthesized with a mechanical stirrer. When the sizes of Fe_3O_4 NPs were examined by TEM, it was observed that they were in a homogeneous distribution between approximately 10–15 nm. In the experiments, it was observed that increasing the diameter of Fe_3O_4 NPs directly caused an increase in the diameter of the core/shell structure. In Figure 9, TEM images of Fe_3O_4 NPs are given using different magnifications.

$\text{Fe}_3\text{O}_4@\text{SiO}_2$ Nanoparticle

It is known from the experiments that mixing speed has an effect on NP sizes. It has been observed that the TEOS addition rate has a direct effect on NP diameters in $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NP synthesis. It was observed that when the TEOS addition rate increased, the diameters became larger and at the same time, the core/shell structure did not form and the SiO_2 remained free. The dimensions of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs were examined by TEM and their diameters were observed to be between approximately 120–150 nm. In TEM images (Figure 10), it is seen that Fe_3O_4 nanoparticles are inside the structure as dark spots.

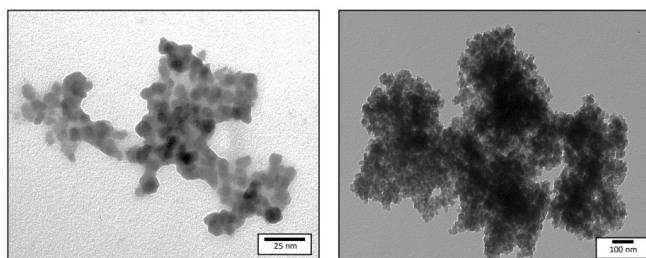


Figure 9. TEM images of Fe_3O_4 NPs.

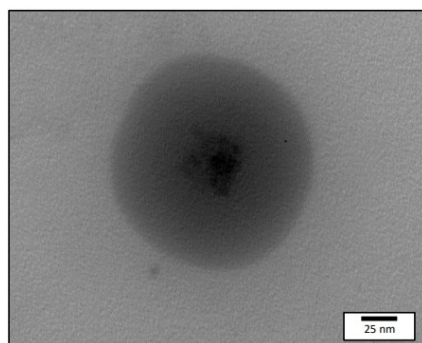


Figure 10. TEM image of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NP.

Examination of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -PDMA Composite System

When TEM images of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -PDMA NPs are examined; It is seen that the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -Br macroinitiator, which was synthesized and used as the macroinitiator, successfully polymerized the DMA monomer on the particle surface using the ATRP method. It is seen that before polymerization ($\text{Fe}_3\text{O}_4@\text{SiO}_2$ -Br) NP diameters are in the range of 120–150 nm, and after polymerization ($\text{Fe}_3\text{O}_4@\text{SiO}_2$ -PDMA) NP diameters vary between 145–160 nm. This increase in diameter proves that polymerization occurs on the particle surface. It was observed that there was a growth of approximately 26–30 nm in NP diameters, and as a result of this growth, a polymer layer with a thickness of 13–15 nm was formed. Additionally, looking at Figure 11, the lighter colored layer observed on the particle surface proves the formation of the polymer layer.

$\text{Fe}_3\text{O}_4@\text{SiO}_2$ -PDMA composite systems were betainated with 1,3-propane sultone and the end groups of the polymers were functionalized. The particle has become biocompatible, thanks to the betainization process. Synthesis studies of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ - β PDMA-(Au), $\text{Fe}_3\text{O}_4@\text{SiO}_2$ - β PDMA-(Ag) and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ - β PDMA-(Ag-Au) NPs were carried out using these functional end groups and as a result, metal nanoparticles were successfully synthesized.

$\text{Fe}_3\text{O}_4@\text{SiO}_2$ - β PDMA-(Au) Composite System

It was clearly seen in the TEM images that Au metal was successfully bonded to the structure thanks to the functional groups of the polymer. In Figure 12, TEM images of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ - β PDMA-(Au) composite system are given at different magnifications. The dark dots on the particle are Au metals

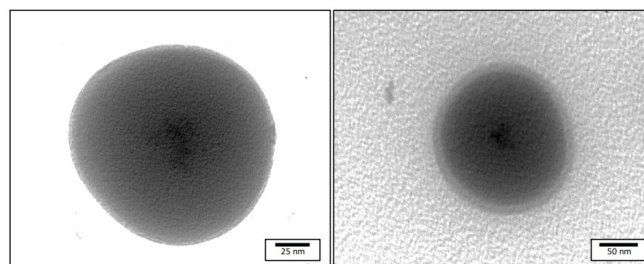


Figure 11. TEM image of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -PDMA NP.

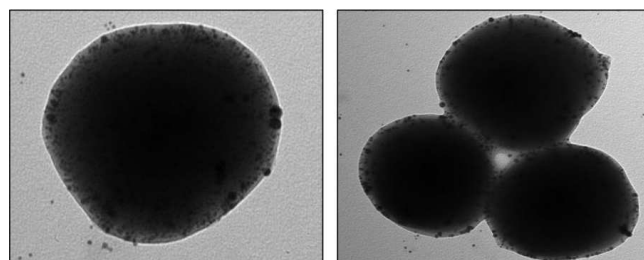


Figure 12. TEM images of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ - β PDMA-(Au) NP.

that have been reduced on the surface. The average size of Au metals is 3–8 nm.

$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Ag)}$ Composite System

Ag metal was successfully loaded into the polymeric structure, as seen in the TEM images (Figure 13). The sizes of Ag nanoparticles on the surface are in a wide range of 5–35 nm and have a polydisperse distribution.

$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Ag-Au)}$ Composite System

The TEM image of the composite system containing double metals, synthesized as a result of adding Au and Ag metal salts to the solution simultaneously, is given in Figure 14. It was observed that the metal nanoparticles accumulated on the particle surfaces were of two different sizes and homogeneously distributed. The smaller particles belong to Au and the larger particles belong to Ag metals.

These metal-loaded NPs were further investigated for use as catalysts in the reduction reaction of p-NP to p-AP and their differences as catalyst systems were revealed.

Characterization of Particles with TG-DTA

NPs were characterized by TG-DTA to determine their thermal stability. The thermal and gravimetric changes that occurred after the temperature increase were examined in the analyses and the determined thermal decomposition temperatures are

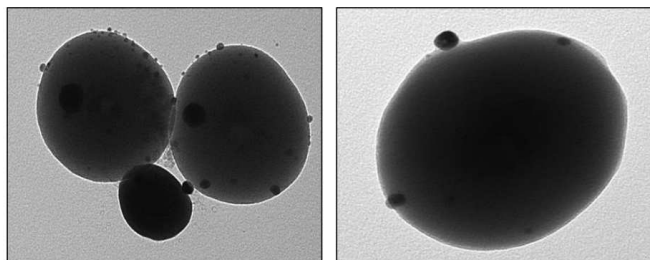


Figure 13. NP TEM images of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Ag)}$ NP.

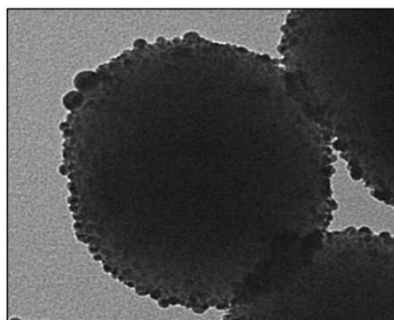


Figure 14. TEM image of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au-Ag)}$ NP.

given in Figure 15. In the TG% graph, it was seen that the thermal decomposition of Fe_3O_4 occurred in a single step and there was a 10% loss in mass. This loss is due to H_2O molecules trapped in the crystal structure and moisture in the environment. When the literature is examined, it has been reported that a loss of approximately 8% in mass after thermal decomposition is normal and that this loss is caused by H_2O crystals trapped in the structure.^[41] It was seen that the synthesis was successful when the results were examined. Likewise, when the TG% graphs of other particles are examined, $\text{Fe}_3\text{O}_4@\text{SiO}_2$ has a 13% loss by mass, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ has a 15% loss by mass, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Br}$ has a 16% loss by mass. It was observed that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PDMA}$ has a loss of 43% by mass. The reason for the increase in mass losses seen at each stage (synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$, synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Br}$ and synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PDMA}$) is that new groups are added to the structure after synthesis. When the TG-DTA graph was examined, it was seen that the synthesis of the targeted $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PDMA}$ composite system was successful. When the thermal characterization of NPs was examined, it was seen that the reactions were successful for each step and the planned structures were successfully synthesized.

Characterization of NPs by PXRD

In the Rietveld analysis of Fe_3O_4 NPs, it was seen that Fe_3O_4 NPs were 100% magnetite (Figure 16a). It was observed that the reaction was carried out successfully and the magnetic sample with the desired magnetic properties was synthesized. The X-ray diffraction (XRD) pattern of Fe_3O_4 exhibits diffraction peaks at 2θ values of 30.25, 35.64, 43.30, 53.67, 57.19, and 62.79 corresponding to crystallographic planes (220), (311), (400), (422), (511), and (440), respectively. These crystallographic planes, namely (111), (220), (311), (400) and (511) are identified as special planes for Fe_3O_4 . The (311) plane emerges as the primary peak in the XRD pattern, suggesting the presence of Fe_3O_4 . The results affirm the formation of Fe_3O_4 based on the observed diffraction pattern.^[42]

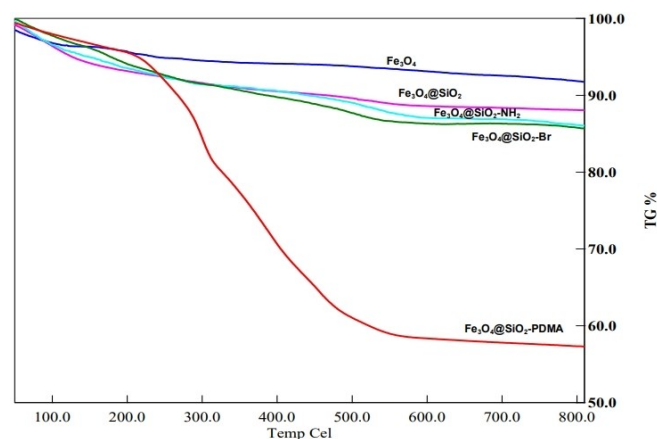


Figure 15. TG-DTA measurements of NPs.

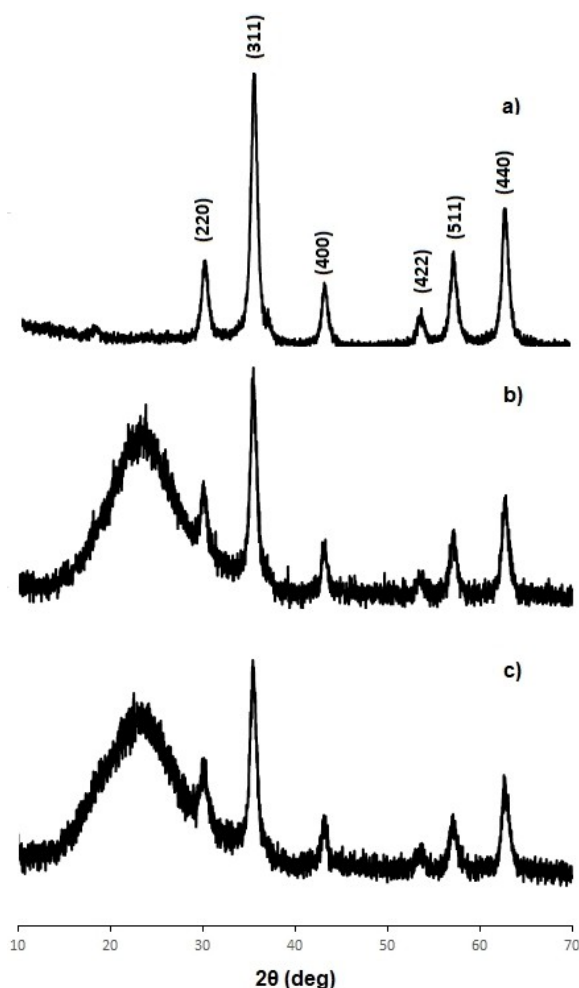


Figure 16. X-Ray diffraction analysis measurement of nanoparticle a) Fe_3O_4 , b) $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ and c) $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ -PDMA.

When the Rietveld analysis results in Figure 16b and c were examined, it was seen that the PXRD peaks are wide and broad since it is known that the synthesized NPs are not crystalline and are amorphous. Rietveld $2\theta = 5^\circ$ – 29° was analyzed by subtracting it from the diffractogram. In the XRD pattern of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ (Figure 16b), a wide peak at a 2θ range of 22 – 26° was indicative of the amorphous phase of SiO_2 . Subsequently, following the application of PDMA brushes, an additional diffused pattern emerged in the XRD spectrum of $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{PDMA}$ at a 2θ of 14 – 26° , representing the amorphous polymer layer (Figure 16c). When the integral areas of amorphous structures were examined, it was seen that the integral area of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ NP was smaller than the integral area of the $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ -PDMA composite system. The result here is that the amorphous structure increases and polymerization occurs.

Catalytic Activity Studies of NPs

Catalytic activity studies of NPs were carried out with a UV-Vis spectrophotometer. The reduction reaction of para-nitrophenol (p-NP) to para-aminophenol (p-AP) given in Figure 17 was used as a model reaction in catalytic studies. Moreover, a crucial factor in opting for the reduction reaction of p-NP lies in the applicability of UV-visible spectrophotometry for real-time monitoring of the reaction's progress. The transformation of p-NP to p-AP, as observed through UV-Vis spectroscopy, manifested distinct peaks at 400 and 300 nm, correspondingly. Upon introducing the NP catalyst into the reaction mixture, the intensity of the peak at 400 nm exhibited a gradual decline. The peak disappeared for different time as the nanoparticle changed. Concurrently, with the diminishing absorption peak of p-NP at 400 nm, a novel peak emerged at 300 nm, unequivocally signaling the reduction of p-NP to p-AP (Figure 17).

1.15 mmol p-NP solution was prepared by dissolving 0.0008 g p-NP in 5 mL water and 0.1 M NaBH_4 solution was prepared by dissolving 0.03783 g NaBH_4 in 10 mL water. 0.0022 g of each of the $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ -βPDMA-(metal) NPs was weighed into separate containers and dispersed in 5 mL of water. For all NPs; 1 mL NP solution, 1 mL H_2O and 0.1 mL NaBH_4 solution were mixed in the UV cuvette. 0.1 mL of p-NP solution was added to the mixture and UV absorbance measurements were recorded over time. UV-vis absorption spectra were measured at specific time intervals within a scanning range of 250–500 nm. A well-fitted linear relationship between $\ln(\text{Ct}/\text{Co})$ and the reduction time plot was observed, suggesting that the reaction follows pseudo-first-order kinetics. The negative exponential rate constant, denoted as k_{app} , was determined from the slope of the $\ln(\text{Ct}/\text{Co})$ versus time plot (Ct represents the concentration at a given time (t), Co represents the concentration at time $t = 0$, and k_{app} stands for the apparent rate constant). Furthermore, the reduction ratio was found to be independent of NaBH_4 concentration.^[43]

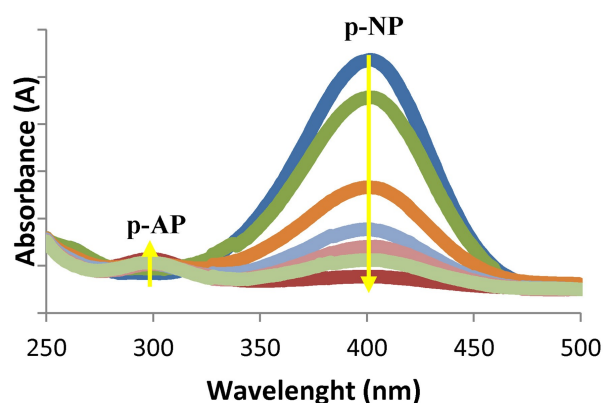
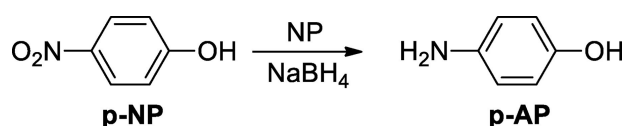


Figure 17. Reduction reaction and reduction graph of p-NP to p-AP.

By looking at the absorption spectra of NPs, the effect of Ag and Au salts on the catalyst role in the reduction reaction was determined. Adsorption spectra of NPs were obtained as a result of absorbance measurements with UV-Vis spectrophotometer using $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Ag)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au-Ag)}$ composite systems as catalysts. In this process, while the intensity of the peak at 400 nm of p-NP decreases, simultaneously a new peak at 300 nm of p-AP forms and the intensity of the peak increases over time. Reduction times for $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Ag)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au-Ag)}$ composite systems were determined as 45, 52 and 3 min, respectively. The conversion times and rate constants of the reduction of p-NP to p-AP are given in Table 1. Catalytic reduction rate of p-NP by $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au)}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Ag)}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au-Ag)}$ nanoparticles as catalyst was found as $0.11 \times 10^{-2} \text{ s}^{-1}$, $0.07 \times 10^{-2} \text{ s}^{-1}$ and $1.19 \times 10^{-2} \text{ s}^{-1}$, respectively. These results indicate that the catalytic reduction rate constants for NPs are $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au-Ag)} > \text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au)} > \text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Ag)}$. The system containing Au-Ag nanoparticles showed higher catalytic activity than the systems containing Au and Ag. Additionally, a comparison of the kinetic results of some SiO_2 -based metal catalysts in the literature in p-nitrophenol reduction reactions is given in Table 2.

When the three systems were evaluated, it was seen that the system in which Au and Ag were used together was the best catalyst system. It showed superior performance as a catalyst compared to systems in which Au and Ag salts were used alone. In the system containing Au metal, the conversion was completed in a shorter time due to the size of the metal nanoparticles being much smaller than the system containing Ag metal and the surface area being higher. The system containing both Ag and Au nanoparticles together showed much better performance compared to monometallic systems, thanks to the synergistic effect created.

The most important feature of Fe_3O_4 in its core structure is that it is magnetic, allowing NPs to be easily directed with an external magnetic field and removed from the environment. In the experiments, it was seen that the magnetic property of Fe_3O_4 worked successfully and facilitated the removal of NPs used as catalysts from the environment. An external magnetic field was applied to the solutions after the reduction reaction and the usability of the magnetic NPs removed from the solution medium as catalysts was examined. After the examinations, it was concluded that there was a slight loss in the efficiency of NPs when used repeatedly, but they could still be used as catalysts in reduction reactions. The reusability of NPs as catalysts was tested 3 times and the results are shared in the table (Table 3).

Table 1. The conversion times and rate constants of the reduction of p-NP to p-AP.

Composite System	Time (min)	k_{app}
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au)}$	45	$0.11 \times 10^{-2} \text{ s}^{-1}$
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Ag)}$	52	$0.07 \times 10^{-2} \text{ s}^{-1}$
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au-Ag)}$	3	$1.19 \times 10^{-2} \text{ s}^{-1}$

Table 2. Comparison of the kinetic results of some SiO_2 -based metal catalysts reported in the literature in the reduction reactions of p-NP to p-AP.

Catalyst	Catalyst amount	k	t	Ref.
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$	1 g	0.46 min^{-1}	10.7 min	[44]
$\text{SiO}_2/\text{Fe}_3\text{O}_4$	100 μg	$9 \times 10^{-3} \text{ s}^{-1}$	4 min	[45]
Au@hollow-SiO_2	2 mg mL^{-1}	0.527 min^{-1}	7 min	[46]
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Cu}_2\text{O}$	1 mg mL^{-1}	Not determined	5 min	[47]
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-Au}$	3 mg	$7.8 \times 10^{-3} \text{ s}^{-1}$	3.7 min	[48]
$\text{Mn@SiO}_2\text{-NH}_2\text{-Au}$	3 mg	$6.1 \times 10^{-3} \text{ s}^{-1}$	12 min	[49]
$\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2\text{-CS/Pd}$	23 mg	$1.2 \times 10^{-2} \text{ s}^{-1}$	4 min	[50]
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au-Ag)}$	2.2 mg	$1.19 \times 10^{-2} \text{ s}^{-1}$	3 min	This work

Table 3. Reduction times of p-NP to p-AP of composite systems (3 repetitions).

Composite System	Reduction Time (min)		
	1.	2.	3.
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au)}$	45	62	73
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Ag)}$	52	69	81
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-}\beta\text{PDMA-(Au-Ag)}$	3	7	8

Conclusions

Fe₃O₄ nanoparticles were synthesized and coated with silica to create a surface that would allow polymer synthesis. The formed Fe₃O₄@SiO₂ was modified and transformed into the Fe₃O₄@SiO₂-NH₂ structure. These modified particles were converted into Fe₃O₄@SiO₂-Br macroinitiator to be used as initiator in atom transfer radical polymerization. Finally, PDMA chains were grafted onto the particle. After the magnetic core/shell structured materials were betainized, Fe₃O₄@SiO₂-βPDMA structures were obtained, and these structures created a suitable surface for the synthesis of Au and Ag nanoparticles on their surfaces. The reduction reaction of p-nitrophenol to p-aminophenol was chosen as a model for the catalytic investigation of Fe₃O₄@SiO₂-βPDMA-(metal) particles. The nanoparticle system containing two metals together carries out the reduction reaction faster than nanoparticles containing a single metal. At the same time, due to its magnetic feature, it can be easily directed and separated from its environment when an external magnetic field is applied. In this way, the same sample could be reused as a catalyst, although there was some loss in the reduction reaction. The monometallic magnetic nanoparticle synthesized with Au metal salt gave a faster reduction reaction than the monometallic magnetic nanoparticle synthesized with Ag metal salt. When magnetic nanoparticles containing two metals and one metal are compared, the synergistic effect, homogeneous distribution and large surface area created by the simultaneous use of two metals in the monometallic nanoparticle make a difference by performing the catalytic reaction faster compared to single-metal systems.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Catalytic activity · Fe₃O₄@SiO₂ magnetic nanoparticles · p-Nitrophenol · SI-ATRP · Zwitterionic composite system

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