



Silver Nanoparticles Stabilized in Polymeric Resin: Synthesis, Characterization and Catalytic Activity Study for Reduction of *p*-Nitrophenol

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A facile method is reported to synthesize a stable dispersion of silver nanoparticles in polymeric resin and its catalytic activity studies. The average particle size of silver nanoparticles obtained was 30 nm. CHNS analysis, FTIR spectra SEM, EDX, TEM, UV-visible spectra were the various techniques used for characterization. Catalytic reduction of *p*-nitrophenol using the synthesized catalyst was the model reaction selected here. The efficiency of catalytic reduction was found to be 93 % in a total time of 24 min.

Keywords: Silver nanoparticles, Reduction, *p*-Nitrophenol.

INTRODUCTION

The properties of nanoparticles are different from those of bulk metal due to their small size [1]. These novel properties may find application in various fields such as photoelectronics, catalysis, magnetism and sensing [2-8]. Major problem with the synthesis of nanoparticles is their stabilization. Polymers are found to be efficient support for stabilization of nanoparticles. Polymer embedding represents the simplest way to protect the nanoparticles and providing a means of stabilization in handling and applications [9]. In heterogeneous catalysis, styrene-divinyl benzene (PS-DVB) copolymer is most commonly used as supporting system. Due to hydrophobic and rigid nature of polymer backbone, PS-DVB systems show low metal ion uptake.

1,6-Hexanediol diacrylate (HDODA) cross-linked polystyrene (PS-HDODA) possess optimum hydrophobic hydrophilic balance and is more flexible than PS-DVB system [10]. Thus, PS-HDODA has been introduced to be more convenient as catalyst support than PS-DVB system. The challenges in the application of nanoparticles could be overcome by incorporation into hydrogels [11]. Such polymer supported catalyst systems can separate from the products by means of simple filtration which leads to operational flexibility [12]. Immobilized metal

nanoparticles find application in several fields such as water treatment, food processing, catalysis, *etc.* [13]. Silver nanoparticles stabilized in sulphonated cross-linked polystyrene were obtained by *in situ* reduction of silver nitrate in hydrogel network. Hydrogel network is a carrier where *in situ* reduction of AgNO₃ in the presence of NaBH₄ as reducing agent occurred.

p-Nitrophenol is a toxic pollutant which causes harmful effects in living organisms [14]. These are widely used in the manufacturing of pesticides, insecticides, fungicides, and also used in the pharmaceuticals and synthetic dye industry [15]. Human exposure to *p*-nitrophenol takes place by inhalation, ingestion and dermal contact. Harmful effects of *p*-nitrophenol on health depends on duration, exposure dose, pathways and individual characteristic such as gender, nutritional status, life style *etc.* Short-term exposure of *p*-nitrophenol by inhalation or ingestion causes headache, drowsiness, nausea, cyanosis and eye irritation [16]. One of the most toxic derivative of parathion insecticide is *p*-nitrophenol and it is carcinogenic and cytotoxic [17]. It is highly soluble in water bodies such as fresh water, marine environments and in industrial wastewater. Thus traditional water purification methods for the removal of *p*-nitrophenol from waste water are not effective. There are many methods for the removal of *p*-nitrophenol which includes catalytic reduction by using microwaves, microbial degradation, photo-

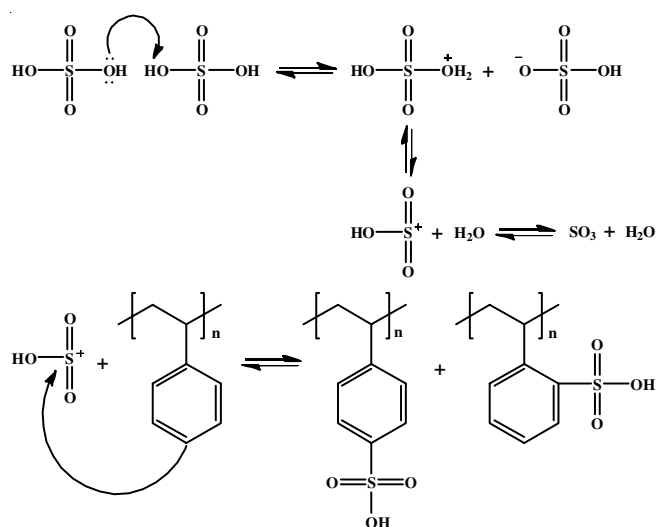
catalytic degradation, electro-fenton method, electro-coagulation and electro-chemical treatment [18-24]. Silver nanoparticles are widely used due to its size, shape and antibacterial properties. Herein, we report the catalytic reduction of *p*-nitrophenol using silver nanoparticles stabilized in polymeric 1,6-hexanediol diacrylate (HDODA) cross-linked polystyrene (PS-HDODA) resin.

EXPERIMENTAL

Styrene and 1,6-hexanediol diacrylate (HDODA) were purchased from Sigma Aldrich Company. Acetone, methanol, toluene, dimethyl formamide, dichloromethane, benzoyl peroxide, poly(vinyl alcohol), sulphuric acid and silver nitrate were obtained from Merck chemical company. The FTIR spectra were recorded on a Bruker IFS-55 spectrometer using KBr pellets. The scanning electron micrographs were taken using a Hitachi S-2400 instrument. The surface morphology of cross-linked polystyrene and sulphonated polystyrene were studied using SEM and TEM. The UV-visible spectra were recorded on a Shimadzu 160-A spectrometer. EDX image was obtained from EDX 800 Shimadzu, Japan instrument. CHNS analysis was done by Perkin-Elmer 2400 Series CHNS analyzer.

Copolymerization: Cross-linked polystyrene is synthesized by free radical suspension polymerization. For the synthesis of 2% HDODA cross-linked polystyrene, a mixture of styrene (98 mmol), HDODA (2 mmol), toluene (8 mL) and benzoyl peroxide (1 g) was prepared. Poly(vinyl alcohol) (1 %) solution is used as suspension medium. The above mixture is mechanically stirred at 80 °C for 6 h. The product was collected by filtration and then washed with hot water, acetone and methanol and dried at 80 °C.

Sulphonation: The copolymer was swelled in dichloromethane for 0.5 h. Conc. sulphuric acid was added and heated to 50 °C with periodic shaking, which is needed during sulphonation. The sulphonated resin was filtered, washed with distilled water and dried at 50 °C for 6 h [24] (Scheme-I).



Scheme-I: Sulphonation reaction [Ref. 24]

Ion-exchange capacity: Salt splitting titration is used for the determination of ion-exchange capacity of sulphonated resin. An accurate amount of sulphonated resin was weighed

and added into an Erlenmeyer flask containing 2 N NaCl solutions. It was stirred for 3 h and then titrated with standardized NaOH solution using phenolphthalein as indicator. The ion-exchange capacity of sulphonated resin (IEC, meq/g) was calculated from the following equation:

$$\text{IEC} = c \times v/w$$

where *c* is the standardized concentration of NaOH, *v* is the volume (mL) of NaOH solution at end point and *w* is the weight (g) of determined sulphonated resin.

Metal loading to polymeric support: The polymeric ligand was equilibrated with AgNO₃ solution (0.05 M 100 mL) at room temperature for 24 h. The metal loaded polymer was filtered, washed with water and dried under vacuum.

Synthesis of polymer supported metal nanoparticles: Metal ion loaded to polymer supported (1 g) was suspended in methanol (10 mL) taken in a round bottom flask and sodium borohydride (1 mL, 20 mmol) was added. The reaction mixture was stirred at room temperature for 2 h to ensure complete reduction. It was filtered under vacuum, washed with methanol (20 mL × 5) and dried under vacuum for 24 h.

Catalytic activity: For water purification from contaminants catalytic approach plays an important role. Here reduction of *p*-nitrophenol using silver nanoparticles stabilized in sulphonated PS-HDODA resin was selected as a model reaction. NaBH₄ was used as reducing agent. After catalysis, catalyst can be separated by simple filtration. The percentage catalytic efficiency was calculated.

RESULTS AND DISCUSSION

A polymeric 1,6-hexanediol diacrylate (HDODA) cross-linked polystyrene (PS-HDODA) hydrogel were synthesised by suspension polymerization and functionalized by sulphonation using conc. H₂SO₄, and the ion-exchange capacity of obtained resins were determined by salt splitting titration. Metal ion is loaded to the polymeric support by equilibrating the polymeric ligand with metal salt solution. The metal loaded to polymeric support was reduced into the nano-scale by sodium borohydride. Sulphonated resin showed swelling in polar solvents indicated the presence of hydrophilic group in polymeric system.

CHNS analyses (Table-1) gave sulphur content of 6.27% indicated the attachment of sulphur containing group. The PS-HDODA copolymer resin showed no ion-exchange capacity due to the absence of sulphononic acid group. The sulphonated copolymer showed an ion-exchange capacity of 3.50 meq/g (Table-2).

TABLE-1
CHNS ANALYSIS OF SULPHONATED PS-HDODA

C (%)	H (%)	N (%)	S (%)
56.11	8.14	Not detected	6.27

In FTIR spectra (Figs. 1-3), the resins exhibited a band around 1724-1720 cm⁻¹ indicating carbonyl stretching frequency, which is an indication HDODA cross-linking to the polymeric support system. Bands at 1657-1598, 1493-1473 and 1451-1443 cm⁻¹ corresponds to phenyl ring stretching vibrations of C=C-C conjugative system. The frequency in the range 1166

TABLE 2
ION-EXCHANGE CAPACITY OF SULPHONATED RESIN

Sample name	Sulphonating time (min)	Volume of sulphuric acid (mL)	Temperature (°C)	Ion exchange capacity (IEC) (meq/g)
PS-HDODA resin	—	—	—	0.00
PS-HDODA SO ₃ H	40	2	60	3.50

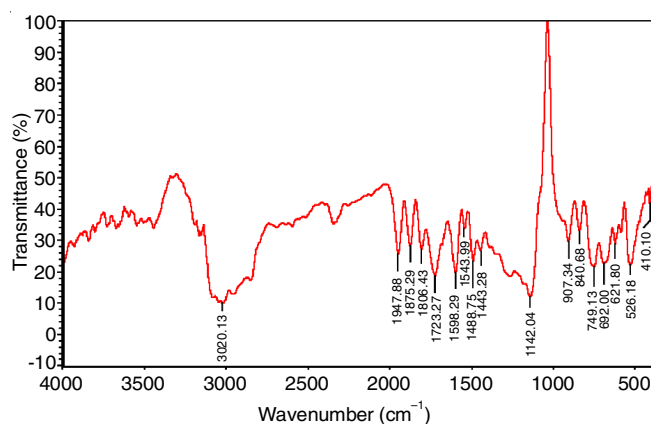


Fig. 1. FTIR spectra of PS-HDODA resin

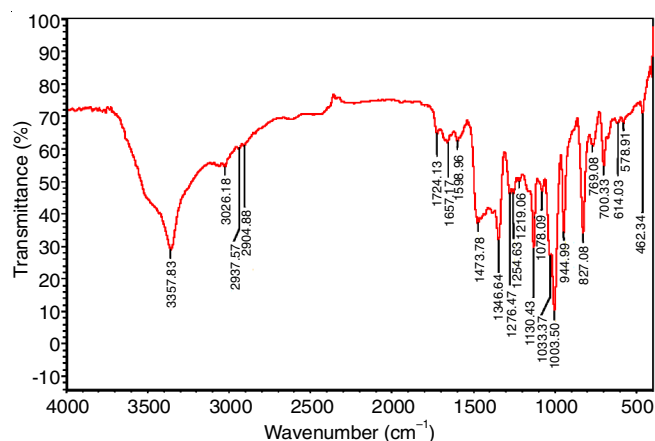


Fig. 3. FTIR spectra of silver nanoparticles loaded sulphonated PS-HDODA resin

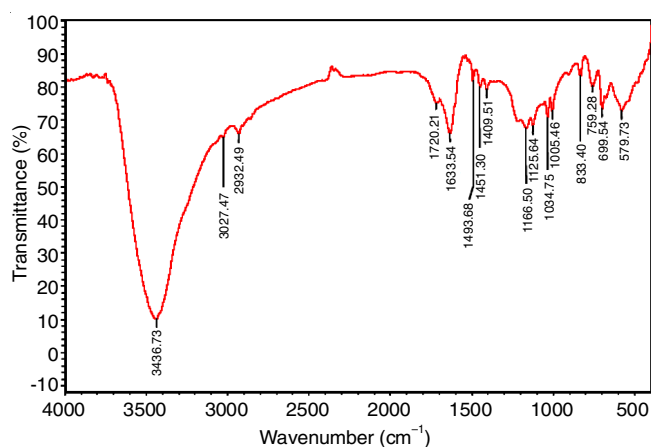


Fig. 2. FTIR spectra of sulphonated PS-HDODA resin

cm⁻¹ was attributed to S=O symmetric stretching vibration. On silver metal nanoparticles loaded, the S=O stretching frequency lowered to 1130 cm⁻¹ while the bands at 1078-1033 and 907 cm⁻¹ represented phenyl in-plane and out of plane C-H bending vibrations, respectively. Moreover, the band at 759-700 cm⁻¹ phenyl ring wagging and twisting, respectively (Table-3).

Scanning electron microscopy is used for surface morphological analysis of polymeric resin. All copolymer resin retained spherical morphology. PS-HDODA copolymer resin have very smooth surface. But the external surface of sulphonated copolymer resin showed scales and cracks probably by sulphonation process. When silver nanoparticles loaded, the external surface of polymeric resin became more and more rough (Fig. 4).

TABLE-3
KEY BAND (cm⁻¹) OF SILVER NANOPARTICLES STABILIZED IN POLYMERIC RESIN

System	$\nu(\text{C=O})$	$\nu(\text{S=O})$	$\nu(\text{OH})$	$\nu(\text{C-H})$
PS-HDODA resin	1723	—	—	3020
Sulphonated PS-HDODA resin	1720	1166	3436	3027
Silver nanoparticles loaded sulphonated PS-HDODA resin	1724	1130	3357	3026

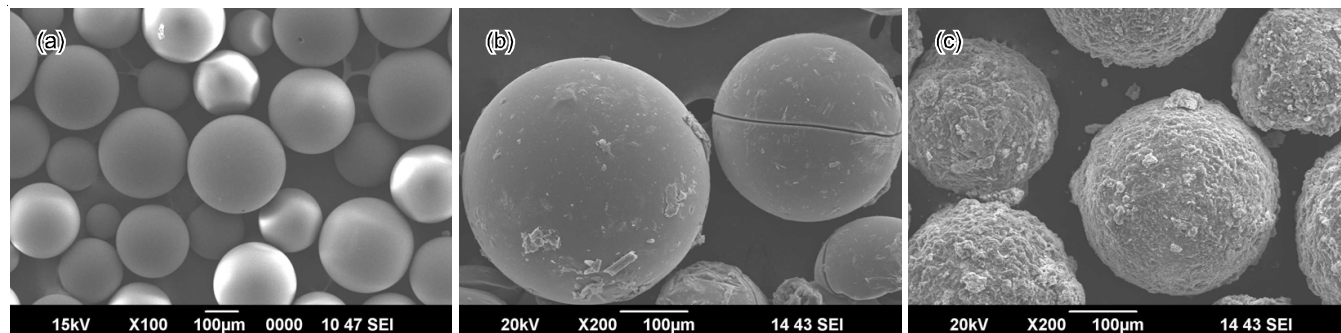


Fig. 4. SEM image of (a) PS-HDODA resin, (b) Sulphonated PS-HDODA resin, (c) Silver nanoparticles loaded sulphonated PS-HDODA resin

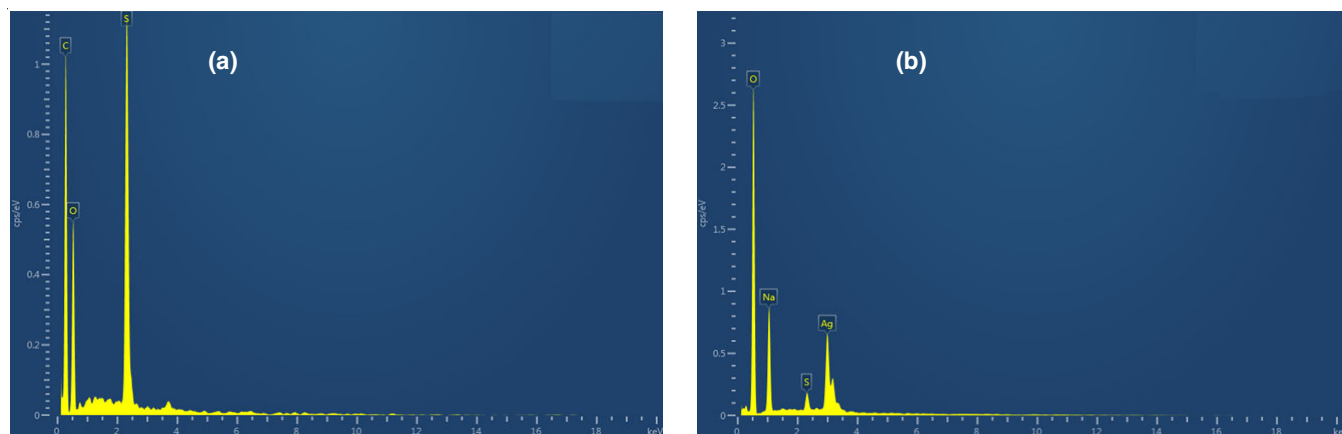


Fig. 5. EDX image of (a) Sulphonated PS-HDODA resin, (b) Silver nanoparticles loaded sulphonated PS-HDODA resin

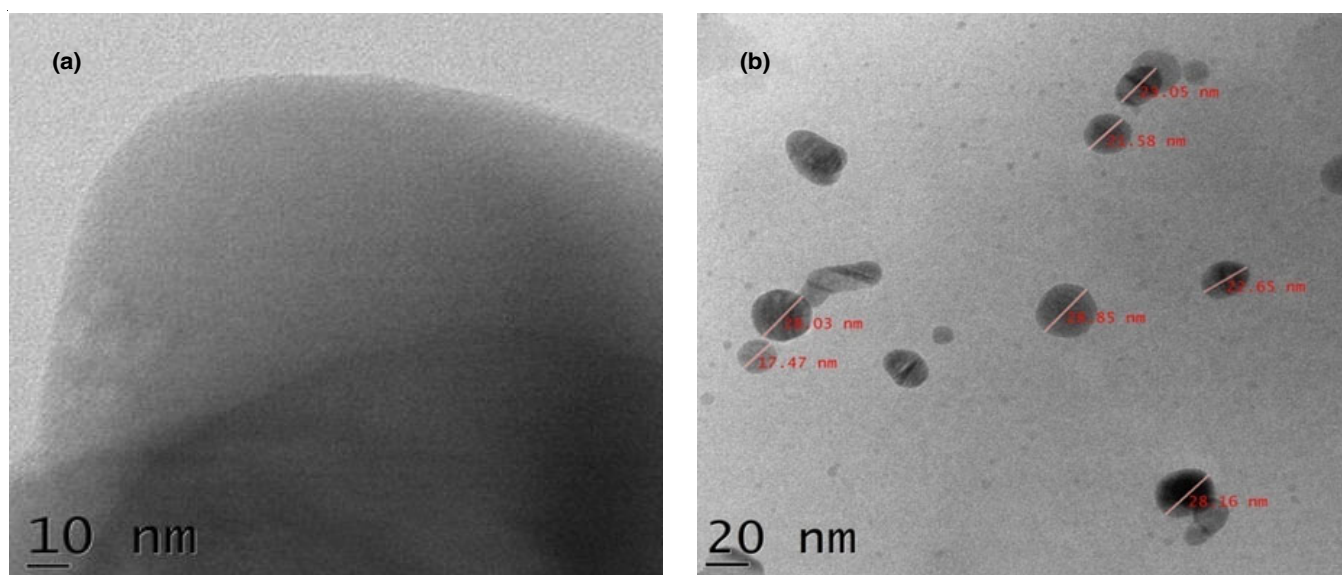


Fig. 6. TEM image of (a) Sulphonated PS-HDODA resin, (b) Silver nanoparticles loaded sulphonated PS-HDODA resin

Elemental analysis X-ray fluorescence analysis: The results obtained are shown in Fig 5. The presence of silver is confirmed by the peaks in the elemental analysis. The peaks for carbon oxygen sulphur sodium have also been observed.

TEM analysis: The TEM image of sulphonated PS-HDODA resin showed very smooth surface (Fig. 6). In metal loaded resin, silver nanoparticles appeared as dark spot inside sulphonated PS-HDODA resin with a size in the range of ~ 30 nm.

Catalytic activity: Herein, sodium brohydride reduction of *p*-nitrophenol using silver nanoparticles loaded sulphonated PS-HDODA resin was taken as the model reaction. The UV - visible spectra for the reduction reaction is shown in Fig. 7. Reduction of *p*-nitrophenol is observed by decreasing absorption peak at 400 nm. The percentage catalytic efficiency was calculated using the following equation:

$$\text{Efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 is the initial absorbance of *p*-nitrophenol and C is the absorbance of *p*-nitrophenol at time t . From the percentage efficiency plot (Fig. 8) as time increases, the efficiency of catalyst was also increased. From the experimental results, the rate of the reaction corresponds to the first order kinetics (Fig. 9).

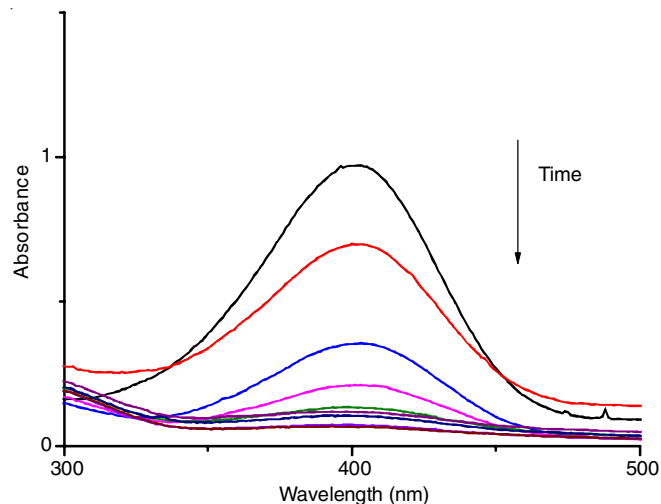


Fig. 7. UV-visible absorbance spectra for catalytic reduction of *p*-nitrophenol

$$\ln C/C_0 = -kt$$

where C_0 is the initial absorbance of reaction system, C is the absorbance at time t . From kinetic curve rate, constant k was calculated for the reaction system.

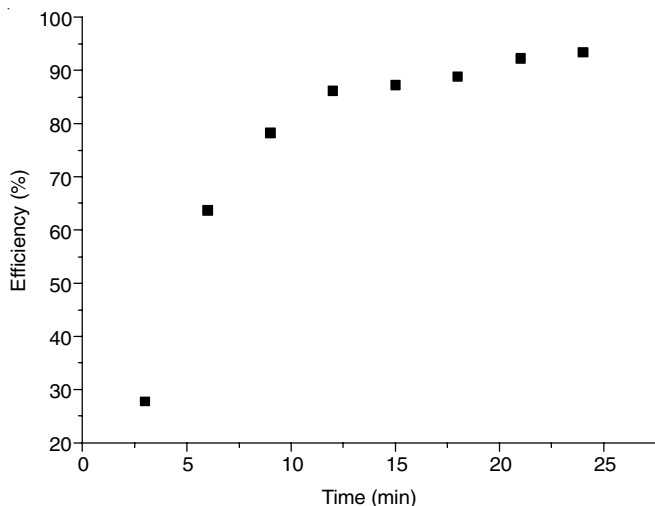


Fig. 8. Efficiency % with irradiation time for catalytic reduction of *p*-nitrophenol

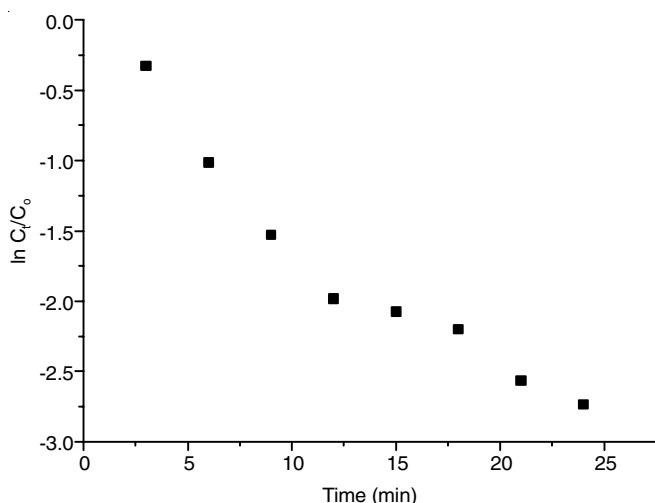


Fig. 9. Kinetic curves for *p*-nitrophenol reduction

Conclusion

In this study, preparation of silver nanoparticles stabilized in polymeric resin was presented. Suspension polymerization was used to synthesize polymeric 1,6-hexanediol diacrylate (HDODA) cross-linked polystyrene (PS-HDODA) resin. PS-HDODA copolymer were converted into polymeric resin by sulphonation of cross-linked polymer. Metal loaded to this polymeric support was converted into nanoscale by sodium borohydride reduction. The catalytic activity of prepared silver nanoparticles stabilized in polymeric resin was tested against *p*-nitrophenol reduction reaction. The catalyst showed 93 % efficiency in the reduction reaction within 24 min. Thus, this catalyst system can be efficiently used for the treatment of wastewater containing *p*-nitrophenol.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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