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An efficient adsorbent and catalyst: AgNPs fabricated in triaizne based conducting polymer for the reduction of 4-nitrophenol

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ABSTRACT

4-Nitrophenol (4-NP) is a highly toxic organic pollutant exists in several industries wastewater and harmful to the human health as well as to the ecosystem. The fast removal and coast effective reduction of 4-NP is great challenge, to solve the environmental and human health issues. In the present study, I have fabricated novel AgNPs into porous conducting polymer matrix without using any external stabilizer and reducing agents, because triaizne based conducting polymer behaves as a stabilizer and self-reducing agents. The FTIR and XPS analyses revealed that the polymer matrix not only contains aromatic moiety, but also have several imine groups. XRD results support the formation of AgNPs in to the polymer and show the FCC crystalline structure. The SEM and TEM results revealed that the spherical AgNPs are well dispersed in the polymer matrix and the average diameter of AgNPs was found to be 30 nm. The fabricated nano composite is a high prose materials and show excellent adsorption capacity and catalytic activity towards the reduction of 4-NP to 4-AP at room temperature. The catalytic activity factor was observed to be 1.668 s^{-1} g^{-1} and support outstanding catalytic activity of AgNPs@CP. This approach can be used to fabricate other catalysts and advance materials for potential applications in environmental chemistry.

Keywords: 4-nitrophenol; Triaizne; Silver nano particles; Reduction; Nano composite

1. Introduction

4-Nitrophenol (4-NP) is an intermediate or byproduct, widely produced in several industries such as drugs, leathers, chelating agents, dyes and pesticides. 4-NP is highly risky to the human health and the aquatic environments due to its highly toxicity, difficulty of natural degradation, and excellent chemical and good biological stability. The effect of 4-NP in humans causes vomiting, pains, cyanosis, tiredness and drowsiness [1–4]. Because of the toxicity, 4-NP has been recorded, as one of the basic industrialized pollutants by US environmental protection agency. Therefore, effective treatment of organic pollutants, such as 4-NP in wastewater is a big demand to protect the human health and the ecosystems. However, several techniques have used for the treatment of organic/inorganic pollutants such as ozonation, adsorption, microbial degradation, Fenton processes, photo-degradation and reduction [5–11]. Among these processes, the reduction of nitroarenes using metal-based catalysts including Au, Ag, Pt, Ni and Co is one of the best effective, ecofriendly friendly, and cost effective technique [12–16]. It is well known that the catalytic activities of the metal-based catalyst are dependent on the size, shape, and morphology of the catalyst. However, the high cost, typical synthetic methods of these metals nano particles prevents their use as catalyst. Thereby, the controlled synthesis of cheap and efficient catalyst material with highly efficient catalytic activity towards the reduction of 4-NP has received great interest of researcher. Metals nano particles have excellent electrical conductivity as well as excellent biocompatibility nano particles and have been explored traditionally, to be employed as catalysts for the reduction of nitrophenol [17–20].

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Herein, I fabricate novel AgNPs in polymer matrix, which, were reduced and stabilized by triaizne based conducting polymer. The key concept of our strategy is that the triaizne based conducting polymer (CP) performs the dual-functionalities during the fabrication of nano particles, one is reducing agents and the other stabilizing the silver nano particles (AgNPs) with controlled size at room temperature. More importantly, CP is not only a stabilizer that prevents AgNPs particles from agglomeration, but also ensures their good dispersion and accessibility of catalytic centers for the reduction of 4-AP. Additionally, the polymer have good adsorption capacity towards the 4-NP. The results suggest that the prepared nano composites exhibit excellent catalytic activity and good cycling stability due to the synergetic behavior of the AgNPs and the conducting polymers as compared with other catalytic structures reported in the literature.

2. Experimental

2.1. Materials and methods

Silver nitrate ($AgNO_3$), 2,4,6-trichloro-1,3,5-triazine, 4-nitrophenol (4-NP), terephthaldehyde, were purchased from Sigma-Aldrich. All chemicals used in the experiments were used without further purification. Deionized water was used throughout the experiment. The UV-Vis spectra were carried out on a SHIMADZU-1650 UV-vis spectrophotometer and the FTIR spectra were carried out on Bruker tensor-27 using KBr plates. Thermal stability of AgNPs@CP was determined using SDTQ-600 thermogravimetric analyzer (TA instrument) in inert atmosphere. The morphologies and structures of AgNPs@CP were measured using scanning electron microscopy (SEM, JEOL JSM-6700) and high-resolution TEM (HR-TEM, JEOL). X-ray diffraction (XRD) results were collected from a PANalytical X'Pert Pro diffractometer using Cu-Kα radiation (λ = 1.5418 Å). X-ray photo electron spectroscopy (XPS) experiments were performed on an ESCA 3400 X-ray photo electron spectrometer (Shimadzu). Surface area and porosity analyses were performed using Micro meritics Tristar. Specific surface, pore size as well as pore size distribution were determined using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods respectively. The percentage of AgNPs in the polymer matrix was estimated using inductive coupled plasma-optical emission spectroscopy (ICP-OES) using a Spectro Arcos ICP-OES FSH 12 instrument.

2.2 Synthesis

2.2.1 Synthesis of silver nano particles in the conducting polymer matrix

The triazine derivatives (2,4,6-trihydrazinyl-1,3,5-triazine) was prepared using the reported methods [21]. The polymer matrix was prepared by 2,4,6-trihydrazinyl-1,3,5-triazine (40 mmol) with p-terephthaldehyde (60 mmol) in DMSO (100 mL) under the inert conditions, a yellow solid powder was obtained in 69% yield. The AgNPs were fabricated in the polymer matrix using silver nitrate (10^{-3} M) and the polymer (0.1 g) in a mixture of water and methanol (50:50 v/v). The mixture was stirred at room temperature for 1 h and then sonicated for 4 h at 40°C. The color of solution was changed for light yellow suspension to yellowish black. The mixture was left to stand at room temperature for 12 h and centrifuged at 8000 rpm for 10 min to collect the polymeric matrix with AgNPs, which was washed with water and methanol several times and dried under vacuum for 24 h.

2.3. Adsorption test

The batch adsorption procedure was employed to measure the adsorption capacity of the AgNPs@CP using different experimental conditions such as the effect of pH and time. In a conical flask, 5 mg of AgNPs@CP and 20 mL aqueous solutions of 4-NP with various concentrations have been mixed and shacked in water bath for 120 min at different pH of 4-NP (3.0 to 9.0). The concentrations of 4-NP were measured via a UV-vis spectrophotometer at maximum adsorption wavelength of 317 nm in acidic medium and 400 nm in basic medium and calculated by the following equation (1) [22]:

$$q_e = (C_0 - C_e)\, V/W \tag{1}$$

where q_e (mg/g) is the adsorption capacity onto the adsorbents; C_0 and C_e (mg/L) are the initial and equilibrium concentration of 4-NP, respectively; V (mL) is the volume of the solution; W is the weight of adsorbent in gram.

2.3. Catalytic tests

The reduction of 4-NP to 4-aminophenol (4-AP) was monitored using UV-vis spectroscopy. 1 mL (5 mM) freshly prepared of 4-NP and 1 mL (40 mM), $NaBH_4$ aqueous solution and 2 mL distilled water were added into a quartz cuvette. Then, 5 mg mL^{-1} of AgNPs@CP was added into the solution to initiate the reduction process. The progress of the reaction was observed by UV-Vis spectroscopy [23]. The yellow color of 4-nitrophenolate ionic the solution gradually disappeared due to the formation of 4-aminophenol.

3. Results and discussions

3.1. Characterization of AgNPs@CP

The AgNPs were fabricated in the triaizne based conducting polymer matrix and the said polymer matrix has been used as a self-reducing as well as capping agent for AgNPs as shown in Fig. 1a. The formation of the AgNPs@CP was supported by UV-vis absorption spectra. Characteristically UV-adsorption band of the synthesized AgNPs was observed λ_{max} around 422 nm as shown with the Fig. 1(b) [24]. While the FTIR spectra of prepared AgNPs@CP is presented in Fig. 2(a), the FTIR absorption bands at 1620 and 1334 cm^{-1} represent the C=N and aromatic C–N stretching. Another peak at 3300–3500 cm^{-1} exhibits a characteristic stretching vibration of N-H groups [25,26]. After the adsorption of p-nitrophenol, the FT-IR spectrum of AgNPs@CP showed the shifting in several peaks. The presence of a stretching vibration at 1505 cm^{-1} and 1345 and the peak corresponding to the deformation vibrations of the C–H bond

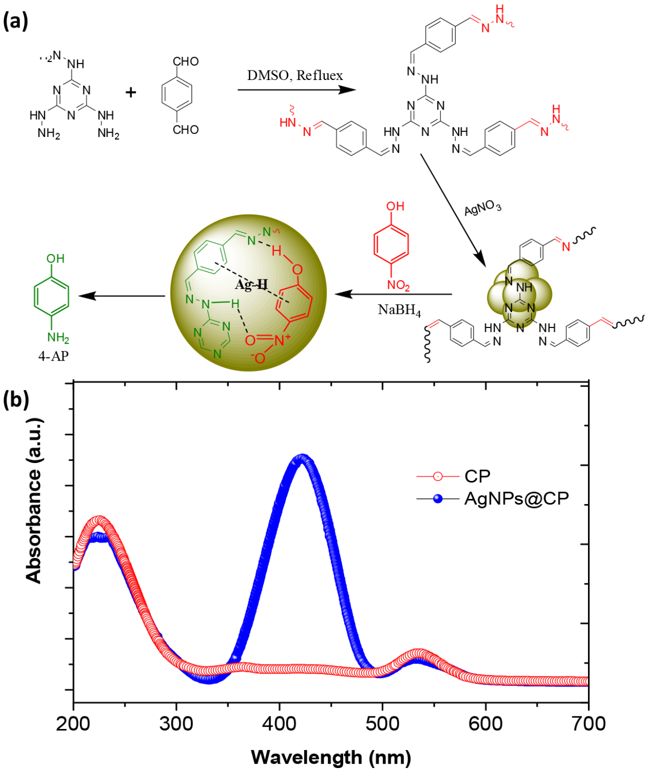

Fig. 1. (a) Typical synthetic route of AgNPs@CP and it adsorption and catalytic behavior towards 4-NP (b) the UV-visible spectra of AgNPs@CP and CP.

in the benzene rings also shifted to from 840 to 858 cm^{-1} in the AgNPs@CP@NP, spectrum support the adsorption of 4-NP.

The TGA of AgNPs@CP and AgNPs@CP@NP is shown in Fig 2(b), the TGA results revealed that thermal degradation was carried out in three degradation stages in the case of AgNPs@CP, while, four degradation stages in the case of AgNPs@CP@NP. In the case of AgNPs@CP, the first degradation was observed up to 200°C, in this stage about 25.28% weight loss was observed. The second degradation stage is the main degradation stage and in this stage, about 22.51% weight loss was found at 400°C, due to the degradation of organic part of the nano composite. The last degradation was cracking of the polymer and about 29.32% weight loss was observed between 400°C to 790°C. The formation of Ag nano particles in the polymer matrix was supported due to the presence of residue 23.05% weight at 790°C correspond to the AgNPs and other residue. On the other hand in the case of AgNPs@CP@NP show lower thermal stability then that of AgNPs@CP due to the presence of less thermal stable organic groups of 4-NP and 17.07% weight was observed at 792.05°C. The X-ray diffraction pattern of AgNPs@CP is shown in Fig. 2(c). The XRD pattern of AgNPs@CP shows peaks at 2θ values of 38.2°, 44.3°, 64.5° and 77.5° due to the (111), (200), (220) and (311) planes and support the formation of face centered cubic (fcc) for AgNPs in the conducting polymer matrix [27]. In case of AgNPs@CP@NP, no change was observed in the peak position only the intensity of some peaks decreased due to the presence of amorphous contents in the nano composite. The nitrogen adsorption-desorption isotherms were measured

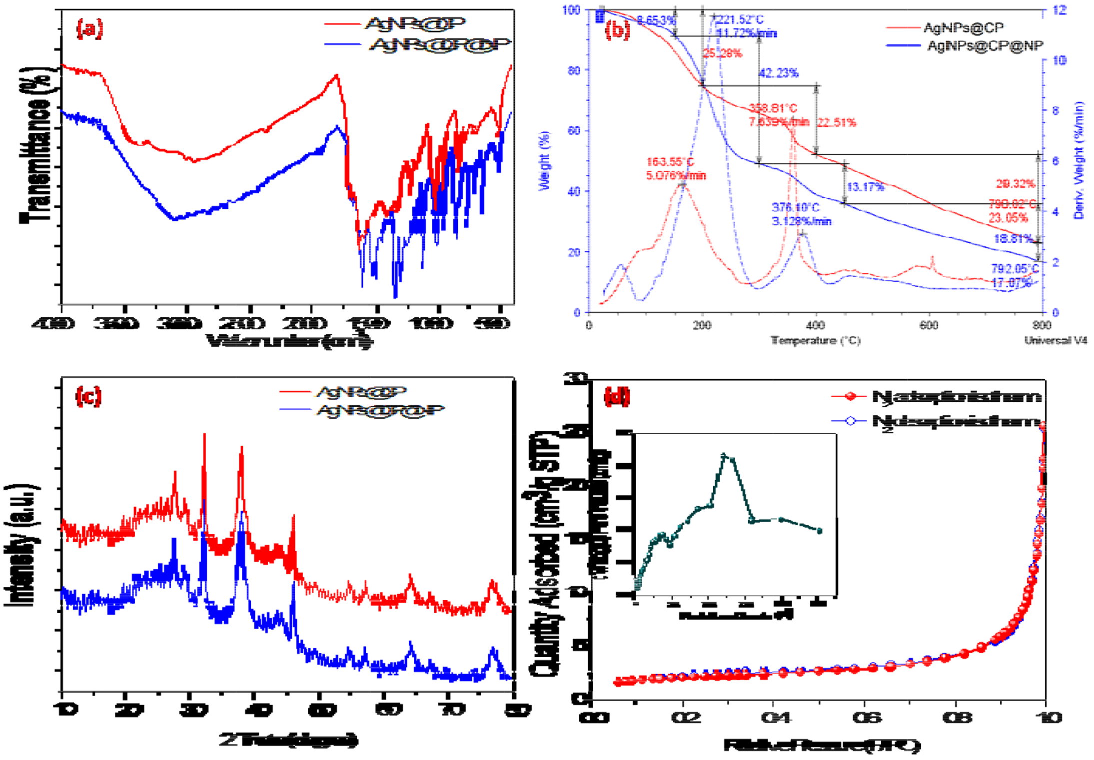

Fig. 2. (a) FTIT spectra (b) DTA and DTA (c) XRD spectrum of AgNPs@CP and AgNPs@CP@NP (d) N$_2$ adsorption and desorption and the insert corresponding pore volume distribution of of AgNPs@C.

to characterize the specific surface area and the pore size distribution of AgNPs@CP and represented in Fig. 2d. The BET surface area and the total pore volume of AgNPs@CP were determined to be 72.6 m^2 g^{-1} and 0.40 cm^3 g^{-1}, respectively, suggesting the mesoporous structure characteristic.

The morphologies of AgNPs in the polymer matrix were characterized by SEM and TEM analysis. As shown in Fig. 3a, the SEM image of AgNPs@CP show that the spherical AgNPs are well disperses in the porous conducting polymer matrix. Fig. 3b shows that the adsorption of NP decreases the porous nature of the AgNPs@CP. The AgNPs inserted between the conducting polymers increase the conductivity as well as increase the catalytic activities of AgNPs. The TEM image of AgNPs@CP is shown in Fig. 3c and the average size of nanoparticles were observed about 30 nm according to the particles size distribution. The HRTEM image of AgNPs as shown in Fig. 3d revealed that the fabricated AgNPs are crystalline in nature and the distance between lattice fringes is 2.35 Å, can be assigned to (111) plane of face center cubic as show in inserted Fig. 3d [28,29]. The EDX spectra of the AgNPs@CP revealed that the nanocomposite surface contains Ag, N, and C elements and the percentage of Ag support the results of ICP and found to be 8.42%.

The XPS analysis was used to determine the surface composition of AgNPs@CP. The wild range XPS spectra of AgNPs@CP is shown in Fig. 4a, indicating the presence of N,C, O and Ag. As shown in Fig. 4b, two characterize regions of Ag 3d was found at 368.10 and 374.14 eV are assigned to Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ respectively and support the presence of the metallic silver nano particles [30,31]. The deconvoluted spectra of N1s as shown in Fig. 4c, and fitted four peaks at 420.3, 400.5, 399.4 and 398.2 eV and support two different electronic states including the –NH/NH$_2$, HN-C, -C-N- and C=N respectively. The high-resolution C1 s XPS spectra as shown in Fig. 4d, the fitted peaks at 287.3, 286.4 eV, and 284.7 eV can be attributed to the C-N, =C-N and C=N respectively, which indicated the existence of hydrazine based conducting polymer.

3.2. Absorption of 4-NP using AgNPs@CP

The absorption of 4-NP from aqueous solution using AgNPs@CP and pure silver nano particles have been studied and the results revealed that no significant adsorption was observed over the pure silver nano particles. On the other hand in the case of AgNPs@CP a promising adsorption was found which is significantly affected the excremental condition such as pH and time. The pH of the solution create the protonation in the polymer matrix and the ionization of 4-NP. As shown in Fig. 5a, when the pH of the solution was increased from 4.5 to 7.5, the absorption capacity increased from 28.24 to 70.79 mg/g, when the pH of the solution was further increased no significant effect on the adsorption capacity was observed, and the adsorption capacity tends to be a constant with a slight decrease and observed 62.13 mg/g at pH 10. When the initial concentrations of 4-NP were change no effect of the concentration was observed and show similar pH effect. The equilibrium time during the adsorption of 4-NP was observed, and the results are illustrated in Fig. 5b, the absorption equilibrium in the absorption of 4-NP was obtained within only 12 s and

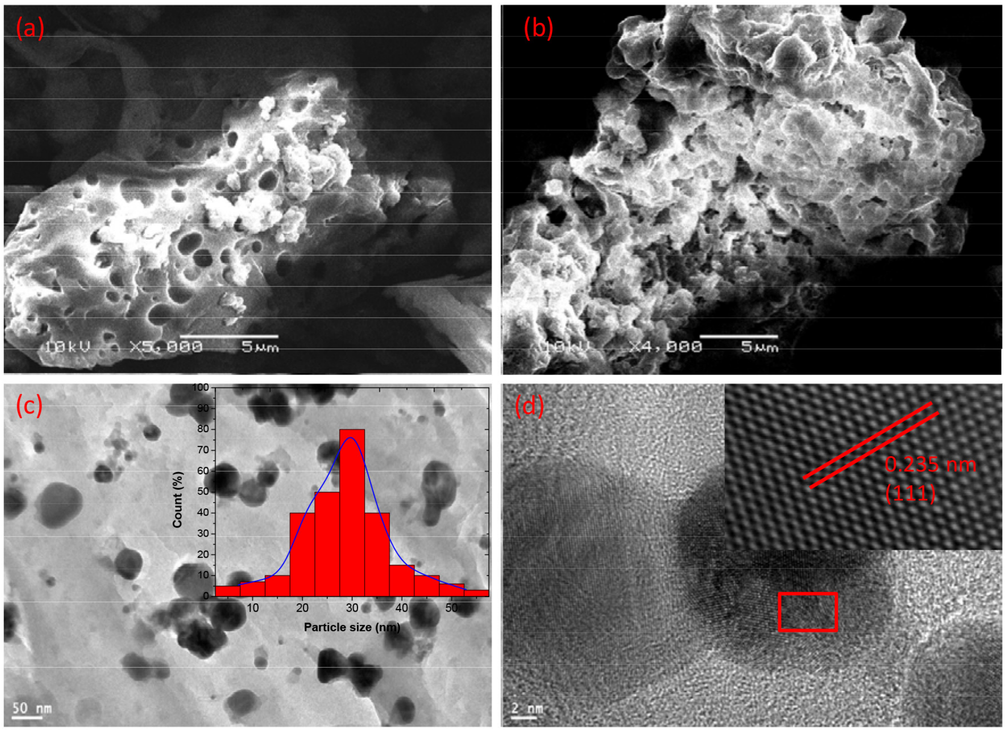

Fig. 3. (a) SEM image of AgNPs@CP (b) SEM image of AgNPs@CP@NP (c) TEM image of AgNPs@CP (d) HRTEM image of AgNPs@CP, the insert corresponding to d spacing of selected AgNPs.

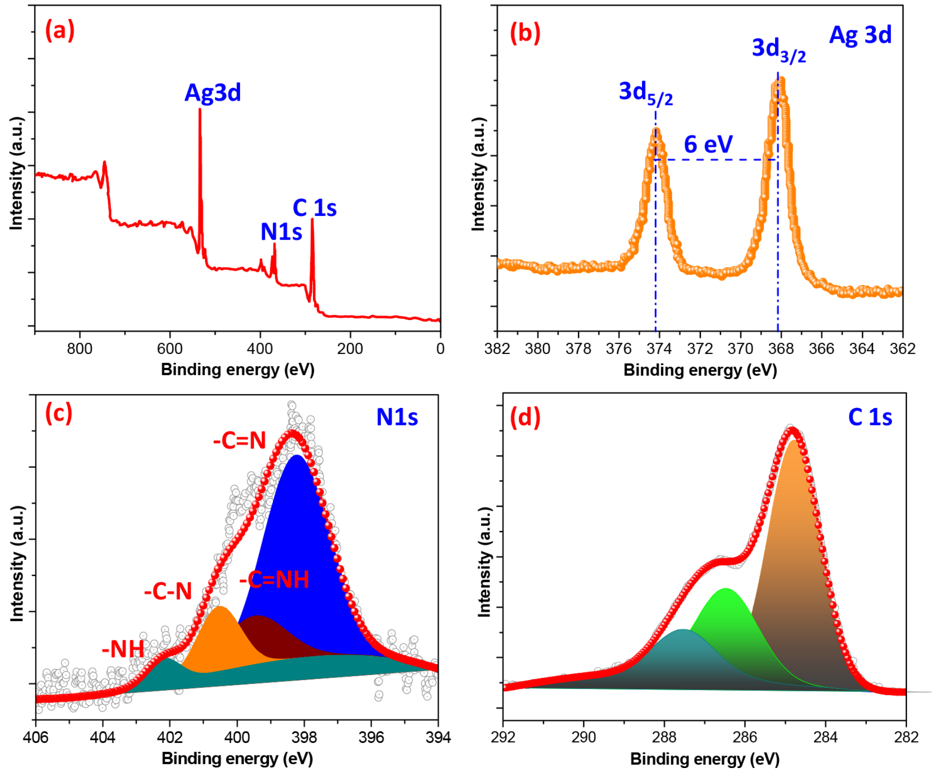

Fig. 4. (a) Wide XPS spectra of AgNPs@CP (b) XPS spectra of Ag$_3$d (c) XPS spectra of N1S (d) XPS of O 1S.

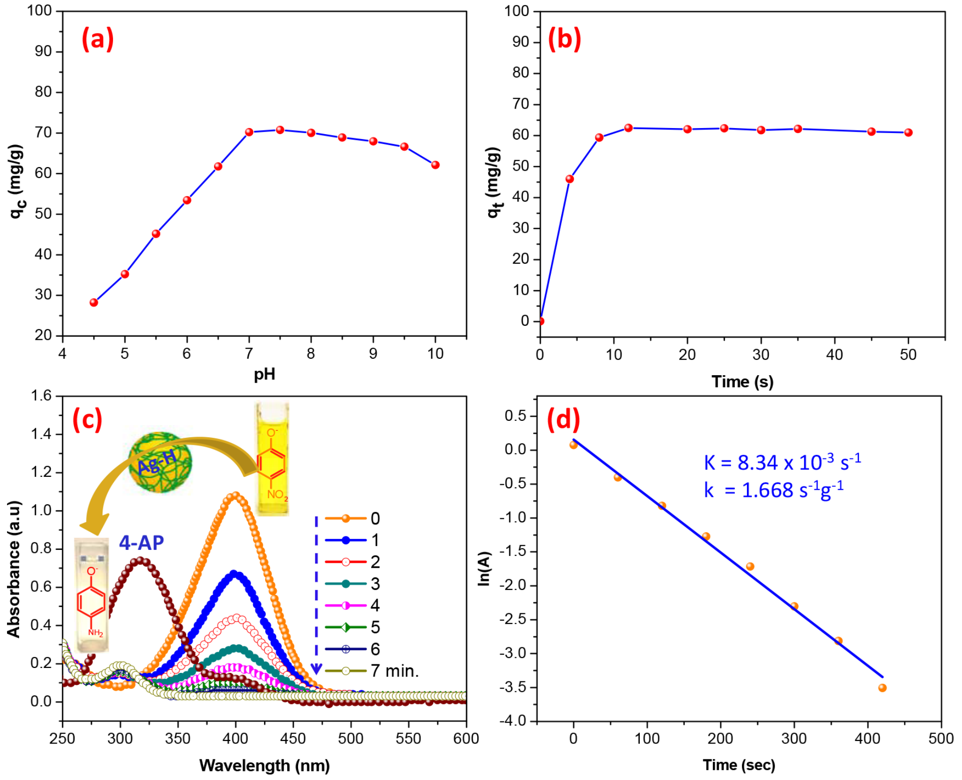

Fig. 5. (a) Effect of initial pH during the adsorption of 4-NP by AgNPs@CP (b) Effect of time (s) during the adsorption of 4-NP by AgNPs@CP (c) the reduction of 4-NP to 4-AP using AgNPs@CP catalyst and NaBH4 as a co-catalyst (d) the logarithm dependence of the absorbance with the reduction time.

support the ultrafast absorption process. The effect of initial concentration with respect of time was observed up to 4 g/L of 4-NP and no significant effect on the adsorption rate. It was observed that 4-NP was absorbed by the porous conducting polymer matrix via hydrogen bonding and π–π interaction between the automatic and imine groups of the polymer as shown in scheme - 1.

3.3. Catalytic reduction of 4-NP

The reduction of 4-NP to 4-AP is monitored by UV-Vis spectroscopy; the absorption peaks at 400 nm and 300 nm are corresponding to 4-nitrophenolate ion and 4-aminophenol ion respectively [32]. The time-dependent absorption results are shown in Fig. 5c and the peak intensity of 4-nitrophenolate ions is gradually decreased while the intensity of 4-aminophenol ions peak at 300 is gradually increased that support the reduction of 4-NP to 4-AP. The catalytic reduction is very fast and within 800 s, 95% conversion of 4-NP in to 4-AM was observed the support the excellent catalytic activity of AgNPs@CP. However, the effect of the $NaBH_4$ concentration was also examined and no effect of $NaBH_4$ concentration was observed during the reduction of 4-NP that support the pseudo-first-order reaction [23]. As shown in Fig. 5d, the linear plot of ln (C_t/C_0) vs. time is fitted in the following Eq. (2):-

$$\ln(C_t/C_0) = \ln(A_t/A_0) = -k_t \tag{2}$$

where C_t and C_0 denote the concentration of 4-NP at time *t* and *0*, and A_0 and A_t represent the absorbance of 4-NP at time *0* and *t*, respectively. *k* is the reaction rate constant in 8.34×10^{-3} s^{-1}. The catalytic activity factor *k* during the reduction of 4-NP was calculated using linear correlation between ln (C_t/C_0) and the reaction time *t* and it was found to be 1.668 s^{-1} g^{-1}.

The catalytic mechanism of AgNPs@CP can be explained via Langmuir–Hinshelwood (LH) model. The BH^{4-} ions and 4-NP react together over the surface of AgNPs. Firstly, the BH^{4-} reacts with H_2O to produce hydrogen and the produce hydrogen react with AuNPs to form Ag–H. Secondly, the adsorbed 4-NP reacts with the Ag–H and resulting produce 4-AP.

The excellent porosity of polymer matrix develops more active sites to form Ag–H and space for the reaction between 4-NP with active sites of AgNPs. It is well known, that the nitro group is electron-accepting group and ammine groups are electron-donating groups, due to the formation of electron donating groups in the case of 4-AP remove easily from the polymer matrix and show promising adsorption as well as the catalytic reduction of 4-NP in comparison with previously reported works [33–36]. This is because after reduction the hydrogen bonds has been broken in the case of 4-AP and increase the affinity of 4-AP and aqueous solvent is more than that of 4-NP [37].

4. Conclusions

In summary, I developed a novel rout to fabricate the AgNPs in a porous conducting polymer matrix. The polymer matrix was behaving as a stabilizer as well as reducing agents without introducing other expensive and harmful reducing agent. The prepared nano composite exhibits excellent porosity and shows excellent and fast adsorption of 4-NP from aqueous solution. The polymer matrix contains spherical AgNPs with a size distribution from 10 to 50 nm but the average size was observed 30 nm (AgNPs@CP) and shows excellent catalytic activity towards the reduction of 4-NP with activity factor of 1.668 s^{-1} g^{-1}. The excellent adsorption capacity of the polymer matrix and excellent catalytic activity of AgNPs may result of synergetic behaviors between AgNPs and the polymer matrix. Additionally, the small size of AgNPs, the high surface area, and porous nature of the polymers support the further use in environmental chemistry and using this method; the metal nano particles can be fabricated in the porous organic polymer matrix and can be used for the removal and reduction of organic pollutants from aqueous solution.

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