short term inhalation of 4-NP can cause headaches, nausea, drowsiness, cyanosis, stomach, and chest pain. Nonetheless, 4-NP is still used in the production of dyestuffs, pharmaceuticals, cosmetics, and pesticides. 4-NP may enter soil through the hydrolysis process of organophosphorus insecticides, and it is carcinogenic at a low concentration of 20 µg/L. Due to these facts, wastewater containing nitroaromatic compounds has attracted excessive global attention. The hydrogenation or reduction of 4-NP to 4-aminophenol (4-AP) was considered an effective strategy to get rid of this pollutant. In addition to that, 4-AP is safer than 4-NP and could also be used in various fields, including dye manufacturing, corrosion inhibitors, photographic developers, hair colouring agents, antipyretics, and analgesic drugs [1–3, 6–8].

Chitosan (Cs) is obtained from chitin, which is the 2nd most abundant natural bio-polymer (polysaccharide) on the Earth, following cellulose, through enzymatic or alkaline deacetylation methods. Cs is soluble in weak acidic solutions due to protonation of amino groups, forming a soluble positively charged polysaccharide, and it is insoluble at pH > 7. It has numerous attractive properties, including
non-toxicity, film-forming ability, biocompatibility, biodegradability, wide availability, low price, and coupling with its multifunctional groups. It was used in various fields like food, cosmetics, medicine, and wastewater treatment, where it was considered a natural biosorbent material. Cs and its composites have excellent adsorption properties toward inorganic and organic contaminants from aqueous environments. Its amino and hydroxyl groups may interact with pollutants through a variety of mechanisms, including hydrogen bonding, electrostatic attraction, ion exchange, and van der Waals force [6, 7, 9–14]. Several studies have been published on the synthesis of chitosan-based composites for environmental applications, including the removal of organic dyes [15–18], metal ions [15, 19–23], tetracycline [24], phenolic compounds [25, 26], nitrocompounds [27, 28], pesticides [29], and pharmaceutical products [30, 31]. Despite the use of chitosan based composites to get rid of numerous highly hazardous materials, the separation and recovery of the powdered composites in the treated-water for reuse through radiation filtration and sedimentation methods is difficult, can block filters, and may lead to secondary pollution [27]. In addition, its acid instability can be improved by chemical modification, for instance, cross-linking, carboxyalkyl substitution, and incorporation of nano-fillers [32]. Thus, as alternatives to these powdered catalysts, researchers have developed crosslinking of chitosan in the form of hydrogel beads to enable easy separation from the purified water after the treatment process and for cyclic utilization of chitosan based materials on a large scale. Regarding this, several chitosan composite beads were prepared. Among these compounds, Ag@Cs have attracted the most attention due to their multifunctionality, biocompatibility, high catalytic activity, nontoxic behavior, and antimicrobial activity [9, 11, 33–35]. It was reported that silver nanoparticles can destroy more than 650 kinds of pathogenic microbes, including bacteria, fungi, and viruses [11].

A variety of strategies were utilized to modify Cs hydrogels with Ag nanoparticles. For example, sodium borohydride was used for reduction of Ag ions in the presence of GO powder to get GO-Ag nanocomposites, which were dispersed in chitosan solution (2 wt% acetic acid). Then this dispersion was dropped into sodium tripolyphosphate solution as a crosslinker to prepare Cs-GO-Ag nanocomposite hydrogel beads for the release of anticancer drugs [36]. Recently, Zhou et al. [33] synthesized Cs hydrogels using epichlorohydrin as a crosslinking agent, and after that, Ag nanoparticles were deposited by thermal reduction through heating of hydrogels in AgNO₃ solution for 6 h at 80 °C. The obtained Cs/Ag nanocomposite was used as wound dressing. In another study, Ag-chitosan beads were prepared for reduction of nitroaromatic compounds in two-steps; (1) synthesis of Cs beads using glutaraldehyde as a cross-linker and (2) deposition of Ag by thermal treatment [28]. Yadollahi et al. [37] synthesized Ag/Cs nanocomposite beads for drug delivery applications through the addition of Ag⁺/chitosan solution dropwisely into a solution containing a mixture of sodium tripolyphosphate as a crosslinker and sodium borohydride for reduction of Ag ions to Ag nanoparticles. Another researchers revealed that the Ag⁺/chitosan solution was microwave irradiated to synthesize Ag nanoparticles impeded in Cs matrix, and after that, this dispersion was dropped into NaOH solution to get Ag/Cs composite beads [29]. In conclusion, most of the presented methods involved the use of organic materials and took place in multisteps to prepare Ag@Cs beads. As a result, establishing a more simple and safe way to make Ag@Cs biocomposite hydrogel beads, such as employing mild conditions and non-toxic chemicals, remains a significant challenge.

The present study focuses on developing Ag@Cs biocomposite beads, which are prepared in a one-step process, as environmentally friendly, recyclable, and biodegradable catalysts for the catalytic hydrogenation of 4-nitrophenol for the first time. Our procedure is very simple for scaling-up, environmentally safe not using aggressive or organic chemicals, and also low cost, not requiring heat, energy, or multisteps. It can be summarized as follows; AgNO₃ as a source for Ag nanoparticles was dissolved in a Cs/acetate acid solution and dropped into a basic alcohol solution to achieve two tasks; the formation of spherical hydrogel beads and the reduction of silver ions to metallic silver. The XRD, EDS, UV-vis, and HRTEM proved the in-situ synthesis of Ag nanoparticles impeded in Cs beads. The optimal Ag@Cs biocomposite exhibited acceptable thermal stability, higher surface area, enhanced catalytic activity, easy reusability, and good stability. Thus, the proposed process offers the synthesis of various Ag/Cs based nanocomposite beads for several applications.

Materials and methods

Materials

Chitosan was purchased from Alamia company for chemicals. Silver nitrate was obtained from Sigma-Aldrich. Sodium borohydride was supplied by Merk. Sodium hydroxide was provided by SD Fine-Chem Limited. Nitrophenol was obtained from LOBA Chemie.
**Synthesis of chitosan (Cs) and silver@chitosan (Ag@Cs) beads**

Chitosan was dissolved in a 1% acetic acid solution at 60 °C with stirring until complete solubility. Then, different weights of silver nitrate (0, 3, 5, 10, 15, and 20% w/w) relative to chitosan were added under stirring. This solution was dropped into a 1 M NaOH ethanol solution using a glass syringe. The obtained spherical beads were washed with deionized water and freeze dried at −50 °C for 48 h. The photos of the Cs and Ag@Cs nanocomposite hydrogel beads are presented in Fig. 1. Pure chitosan (Cs) beads have a white colour, whereas the colour of Ag@Cs beads changes from light brown to dark brown, and finally to black with increasing the added amount of AgNO₃. This colour change demonstrates the formation of Ag nanoparticles in the polymer matrix. The samples are coded as Ag@Csₓ, where x is the weight% of AgNO₃.

**Characterization**

Fourier transform infrared (FTIR) spectra of pure Cs and Ag@Cs nanocomposite beads were measured using a Bruker VERTEX 80 instrument equipped with an attenuated total reflection (ATR) unit. The optical properties of the Ag@Cs composites in comparison to the unmodified Cs beads were studied to confirm the presence of metallic silver by recording the UV–vis absorption spectra from 200 to 800 nm on a Shimadzu 2401 UV–vis spectrophotometer using 2.5% acetic acid as a solvent. Field emission scanning electron microscopy (FESEM, Quanta 250 FEG FEI) was used to examine the microstructure and the surface morphology of the prepared chitosan beads before and after Ag sensitization. The prepared beads were coated with a thin layer of gold using a sputter coater after mounting on a carbon tape. The elemental composition of pristine Cs beads and Ag@Cs was determined by an energy dispersive spectrometry (EDS) analyzer integrated in FESEM. To gain more information about the size and shape of the synthesized Ag particles into Cs matrix, the composite was studied by high resolution transmission electron microscopy (HRTEM). The beads were dissolved in 2.5% acetic acid using a vortex mixer and finally dropped on the grid for observation. The crystallinity studies were done by measuring the X-ray diffraction (XRD) profiles of pure Cs and Ag@Csₓ composite beads using a Panalytical X’Pert PRO diffractometer with Cu Kα source and 10−70° scanning range. The Brunauer-Emmett-Teller (BET) specific surface area was determined by using a Quantachrome apparatus, and the pore size distribution was estimated using the DFT method. Thermogravimetric analysis (TGA) of pure chitosan and Ag@chitosan composite beads was carried out on a thermal analyzer SDT Q600 V 20.9 Build 20. The heating rate was 10 °C/min and a temperature range of 30–800 °C in flowing N₂ gas.

**Catalytic activity experiments**

Catalytic hydrogenation/reduction of nitro compounds to their aniline derivatives is a significant pathway to evaluate the activity of various metal based catalysts. Herein, 4-nitrophenol (NP) was taken as a target contaminant to evaluate the catalytic activity of the prepared silver@chitosan composite beads (Ag@Cs3, Ag@Cs5, Ag@Cs10, Ag@Cs15, and Ag@Cs20) in comparison with pure chitosan (Cs) beads. Typically, 40 mg of the beads were added to a solution of 4-nitrophenol and 0.1 mM NaBH₄ with stirring. At specific time intervals, 2.5 ml was suctioned off and its UV-Vis absorption spectra were recorded by using Shimadzu 2401 UV-Vis spectrometer.

**Results and discussion**

**XRD analysis**

The XRD profiles of pure chitosan (Cs) and silver chitosan (Ag@Cs5, Ag@Cs15, and Ag@Cs20) nanocomposite hydrogel beads are presented in Fig. 2. Unmodified Cs beads exhibited only one peak at 20 value 20°, Fig. 2a. This peak is characteristic to (110) reflection crystal plane of chitosan, which indicating its semi-crystalline structure and crosskling [10, 14, 32, 33, 35, 37–39]. The pattern of Ag@Cs5 composite, Fig. 2b, showed a new peak at about 38°, which might be indexed to (111) planes of the face-centered-cubic structure of metallic silver. Whereas, this peak becomes stronger in the case of Ag@Cs15 nanocomposite, indicating increasing the Ag content in the beads. XRD pattern of
Ag@Cs20 composite exhibited two new peaks at ~44.3° and 64.4° attributed to (200) and (220) crystal planes of Ag, which further demonstrates the successful preparation of Ag crystal nanoparticles in the Cs [33–36, 38, 40, 41]. The peaks of Ag nanoparticles are matched with JCPDS Card No. 04–0783 [34, 36]. Additionally, increasing the Ag contents in the composite beads results in a significant decrease in the intensity of the chitosan characteristic peak and a blueshift. These results indicating the interaction between the Cs chains and Ag nanoparticles may be via coordination bond and Van der Waals force [33, 35]. The same observation was presented previously [33, 35]. Whereas, the silver peaks become more obvious, demonstrating increasing the amount of Ag with increasing the added concentration of AgNO₃. The above results confirmed the successful in-situ formation of Ag nanoparticles in the Cs beads using basic ethanol solution.

**SEM analysis**

The morphology and surface structure of the material are vital factors in the catalytic processes. The FESEM images of pure chitosan (Cs) beads, Fig. 3(a,b), along with the Ag@chitosan (Ag@Cs15) composite beads, Fig. 3(c, d), were studied. It is obvious that the Ag@Cs nanocomposite beads display a more porous structure, more wrinkles, and Ag particles are observed on the surface of Cs. This might lead to an increase in the surface area and active sites [42] as will be proved in the BET analysis section. By comparing Fig. 3(a) and (c), it is clear that pure Cs beads have a distorted spherical shape with diameter 2.9±0.3 mm whereas, Ag@Cs beads have an ideal spherical shape with a diameter of 2.4±0.1 mm. It was reported that freeze dried beads were characterized by great homogeneity in spherical shape, contained many cavities, higher porosity, and their size was almost the same as before drying. On the other hand, air dried beads have lower porosity and are smaller in size. This is owing to that there is no time for the beads to shrink due to the rapid sublimation of frozen water from the beads, thus the areas of the earlier ice-crystals were transformed into structured cavities [43].

**EDS analysis**

Energy dispersive X-ray spectroscopy (EDS) analysis was carried out for both pure Cs and Ag@Cs15 to determine their chemical composition, as shown in Fig. 4. The EDS spectrum of pure Cs (Fig. 4a) shows that the amount of C, N, and O is 42.1, 11.2, and 46.6 wt%, respectively. For the composite beads, the amount of C, N, O and Ag is 36.6, 7.9, 46.1, and 9.2 wt%, respectively, Fig. 4b. The obtained data agree with the XRD results and prove the successful in-situ growth of Ag nanoparticles impeded into the chitosan beads in a one-step process using an ethanol solution of NaOH.

**UV-visible measurements**

Optical properties of various Ag@Cs biocomposites relative to pure Cs were studied by measuring the UV-vis absorption spectrum to verify the formation of Ag as shown in Fig. 5. For the unmodified Cs beads, inset Fig. 5a, there is a shoulder in the UV region that may correspond to the CO group [39]. Whereas, Ag@Cs3 composite, which is prepared by the addition of a small amount of AgNO₃, shows a weak peak at 405 nm related to the plasmon absorption peak of Ag particles [27, 35], inset Fig. 5b. Cs/Ag synthesized

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** XRD patterns of (a) pure Cs beads, (b) Ag@Cs5, (c) Ag@Cs15, and (d) Ag@Cs20 nanocomposite beads

![Fig. 3](https://example.com/fig3.png)

**Fig. 3** FESEM images of pure Cs beads (a,b) and Ag@Cs15 composite beads (c,d) at different magnifications

![Fig. 4](https://example.com/fig4.png)

**Fig. 4** EDS spectra of (a) pure Cs beads and (b) Ag@Cs15 nanocomposite beads
and well dispersed with no aggregation [29, 35, 44]. Hidayat et al. found that the plasmon peak of silver nanoparticles was shifted to a longer wavelength, indicating the agglomeration of Ag particles by increasing reduction time, as also confirmed this by TEM images [11]. These results are consistent with the XRD and EDX analyses, proving the in-situ growth of Ag nanoparticles.

**HRTEM analysis**

The size and morphology of the in-situ grown Ag nanoparticles, as well as their dispersion in the Cs polymer matrix, were investigated using HRTEM analysis. HRTEM micrographs of the Ag@Cs15 nanocomposite, Fig. 6(a, b), revealed that the synthesized Ag particles had a spherical shape. The particle size distribution of silver nanoparticles is depicted in Fig. 6c based on the study of 50 particles. The estimated mean diameter of Ag was ~6.7 nm. It is obvious that there is no agglomeration and the Ag nanoparticles are excellent dispersed in the Cs polymeric matrix, which serves as a good stabilizer and support for the formation of inorganic nanoparticles, in agreement with the literature [12, 35]. This implies the synthesis of well dispersed Ag nanoparticles within the Cs beads in one-step. The SAED pattern in Fig. 6d proved the presence of (111) and (200) planes of Ag, which matched well with the XRD results.

**Fig. 5** UV–visible absorption spectra of (a) CS and (b) Ag@Cs3 in the inset figure and (c) Ag@Cs5, (d) Ag@Cs10, (e) Ag@Cs15, (f) Ag@Cs20 nanocomposites.

**Fig. 6** (a,b) HRTEM images of Ag@Cs15 nanocomposite. (c) The particle size histogram of the grown Ag nanoparticles. (d) SAED pattern of Ag nanoparticles.
The peak that can be due to the saccharide group appeared at 897 cm$^{-1}$ [9, 46].

The FTIR spectra of Ag@Cs composites, Fig. 7b–f, showed the characteristic absorption peaks of neat Cs beads with significant changes. For example, two absorption bands of the stretching vibrations of N–H and O–H groups were overlapped together and appeared as a single broad absorption band ranging from 3000 to 3420 cm$^{-1}$ as clearly seen for the nanocomposite beads containing the highest amount of Ag (Ag@Cs20), Fig. 7f. In addition, the absorption band of N–H (amide II) is blue-shifted to 1582 cm$^{-1}$. These observations indicated the interaction of the formed Ag nanoparticles with the Cs functional groups (O–H and N–H) [35]. This band alteration is consistent with the previous work [35, 44, 49].

**TGA analysis**

The thermal stability of the pure Cs beads and Ag@Cs15 nanocomposite was evaluated by measuring TGA as shown in Fig. 8. The TGA thermograms of (a) pure Cs and (b) Ag@Cs15 nanocomposite beads were recorded. The specific surface area, mean pore diameter, and total pore volume were determined from the nitrogen adsorption–desorption isotherms (Fig. 9).

**Fig. 7** FTIR spectra of (a) pure Cs and various Ag@Cs composite beads including (b) Ag@Cs3, (c) Ag@Cs5, (d) Ag@Cs10, (e) Ag@Cs15, and (f) Ag@Cs20.

**Fig. 8** TGA thermograms of (a) pure Cs and (b) Ag@Cs15 nanocomposite beads.

**Fig. 9** Nitrogen adsorption–desorption isotherms of (a) pure Cs, (b) Ag@Cs15, and (c) Ag@Cs15 nanocomposite beads. In the inset figure, you can see the pore size distribution. (d) The values of specific surface area, mean pore diameter, and total pore volume.
in Fig. 8. Thermograms of pure Cs, Fig. 8a, showed three degradation steps; the first one is attributed to the loss of water molecules; the second step is associated with the deacetylation and degradation of chitosan, and the last one corresponded to the oxidative degradation of the carbonaceous residue. The same trend was observed by Lavorgna et al. [49]. Whereas, the nanocomposites have only two decomposition regions and the third thermal degradation step disappeared after the incorporation of Ag nanoparticles. This phenomenon may be related to strong interactions between chitosan chains and the formed Ag nanoparticles. At 850 °C, the weight loss for Cs and Ag@Cs15 beads was 21.9% and 24.2%, respectively. This slight higher weight loss may be as a result of the reduction the intra-/intermolecular hydrogen bonding in the chitosan chains after the insertion of Ag nanoparticles. This observation agrees with previous study [35].

Surface area analysis

The textural parameters, including specific surface area ($S_{BET}$), mean pore diameter, and total pore volume, of pure Cs, Ag@Cs15, and Ag@Cs20 nanocomposite beads were estimated as shown in Fig. 9. The nitrogen adsorption–desorption isotherms of all samples in a good agreement with type IV. The $S_{BET}$ of pure Cs and Ag@Cs15 was 45.06 m$^2$/g and 69.63 m$^2$/g, respectively. Increasing surface area confirming the development of more porous structure, which is matched with the FESEM images. On the other hand, Ag@CS20 composite has a lower surface area of 30.13 m$^2$/g. From this phenomenon, it may be speculated that the Ag@CS20 composite has a lower active surface area, thus it may exhibit lower catalytic activity relative to Ag@CS15 nanocomposite. The inset figures show the corresponding pore diameter distribution of every sample. The estimated pore diameter was 9.6, 5.4, and 0.7 nm and total pore volume was 0.185, 0.247, and 0.114 cc/g for Cs, Ag@Cs15, and Ag@Cs20, respectively.

Catalytic activity studies

Generally, hydrogenation (or reduction) of nitrophenol to amino phenol is frequently used to assess the catalytic activity of various metal nanoparticles embedded in several materials. Figure 10a shows the absorption spectrum of nitrophenol solution in the absence and presence of NaBH$_4$. Nitrophenol has a characteristic peak at ~318 nm as shown in Fig. 10a. Whereas, after the addition of NaBH$_4$, Fig. 10b, the maximum absorbance peak appeared at 400 nm and the solution’s color changed from light yellow to intense yellow. This is attributed to the formation of phenolate ions [6, 27, 50]. In the absence of a catalyst, the solution that contains nitrophenol and NaBH$_4$ was continuously monitored by recording the UV-visible data with the passage of time as presented in Fig. 10b. It is seen that with increasing time from 0 to 40 min, the intensity of the characteristic peak at ca. 400 nm is not affected as presented by Tian et al. [51], i.e., the chemical reaction will not occur (Fig. 10c). This trend proves that NaBH$_4$ alone can’t reduce nitrophenol to aminophenol. The transformation of 4-nitrophenol to 4-aminophenol is thermodynamically favourable (4-NP/4-AP $E_0^0=−0.76$ V) [52] but kinetically unfavourable due to the high kinetic energy barrier by using only NaBH$_4$ without the use of a suitable and efficient catalyst, as previously reported [27]. For this reason, the addition of a catalyst is necessary to accelerate electron transfer from donor (NaBH$_4$) to acceptor (nitrophenol) after the sorption of both onto its surface [3, 52].

4-nitrophenol was used as a model of organic pollutants to assess the catalytic activity of the prepared Ag@chitosan composites (Ag@CS3, Ag@CS5, Ag@CS10, Ag@CS15, and Ag@CS20) in comparison with pure chitosan (Cs) beads. For unsensitized Cs beads, there was no change in the intensity of the 4-nitrophenolate ion peak at 400 with increasing time as presented in Fig. 11a. This indicates that pure Cs beads have no catalytic activity toward the reduction of nitrophenol. According to the UV-visible spectra in Fig. 11b–f, the intensity of the 4-nitrophenolate ion peak at 400 nm declined regularly, whereas the intensity of the aminophenol peak at ~300 nm was enhanced with time. It is seen that all Ag@Cs composites show the same trend, which proves the catalytic reduction of nitrophenol to aminophenol in the presence of the prepared Ag@Cs composite beads as shown in chemical Eq. 2, Figs. 10, [7]. These
nearly turned to aminophenol. Therefore, the Ag@Cs15 nanocomposite was chosen as the optimal one. By increasing the Ag concentration up to 20% w/w, the composite beads still acquire higher catalytic activity relative to the unmodified Cs beads but not as high as the Ag@Cs15 sample. Similar results have been reported by Chen et al. [6]. The authors showed that decoration of TiO₂ nanowires with high amounts of Ag nanoparticles decreased the catalytic activity for the removal of 4-nitrophenol.

The kinetics, linear fitted curves, regression coefficients ($R^2$), rate constant values, and reduction efficiency of nitrophenol using pure Cs and Ag@Cs composites (Ag@Cs3, Ag@Cs5, Ag@Cs10, Ag@Cs15, and Ag@Cs20) were studied as displayed in Fig. 12. The pseudo-first order kinetic assumption is applied for the reduction of nitrophenol and can be described by Eq. 1. In which $C_0$ and $C_t$ are the initial concentration of nitrophenol and at contact time $t$ min. $K$ (min⁻¹) is the reaction rate constant. The conversion efficiency was estimated from the UV-Vis spectra based on Eq. 2. As demonstrated in Fig. 12, all Ag@Cs composites showed a gradual decrease in nitrophenol concentration with the passage of time. Figure 12b reveals that $\ln(C/C_0)$ is directly proportional to time, which indicates that the hydrogenation reaction of nitrophenol is a pseudo first-order reaction owing to the much lower concentration of nitrophenol relative to the reducing agent.

$$-\ln\frac{C_t}{C_0} = Kt$$

The results also demonstrate that Ag content has a significant role in the reduction process. The UV–visible spectra in Fig. 11e showed almost no 4-nitrophenolate ion absorbance peak at 400 nm after 20 min indicating that nitrophenol was
As shown in Fig. 12c, the values of the rate constant (K) and the regression coefficient (R²) were calculated for different catalysts. It is noticeable that all the Ag@chitosan composite beads exhibited a higher catalytic activity compared to neat Cs beads. These results suggest that, generally, the Ag sensitization of Cs beads increases the value of the rate constant and Ag content has a pronounced effect on the catalytic activity of the prepared Ag@chitosan composites (Ag@CS3, Ag@CS5, Ag@CS10, Ag@CS15, and Ag@CS20). According to the obtained results, by increasing the Ag amount until 15% w/w, the prepared Ag@Cs beads exhibited higher catalytic activity. However, a further increase in the Ag amount resulted in a small decrease in the catalytic activity. Among the Ag@Cs biocomposites, the optimal Ag@CS15 has the highest rate constant and the reduction efficiency reached 0.143 min⁻¹ and 94.4%, respectively. However, in the case of pure Cs beads, these values are 0.0001 min⁻¹ and 0.27%, respectively. When the Ag content was increased to 20% (w/w), these values were 0.13 min⁻¹ and 93%, respectively. Decreasing catalytic activity from Ag@CS15 to Ag@CS20 may be attributed to the decrease in the surface area from 69.63 m²/g to 30.13 m²/g, respectively.

**Reusability study**

The stability and easy recovery of the catalyst are very important factors for its wide application. The designed Ag@Cs composite catalysts are designed mainly to enable its easy separation after the reduction process. Thus, the performance of the optimal Ag@Cs biocomposite catalyst was tested in five subsequent hydrogenation cycles, and the removal efficiency versus the cycle number is presented in Fig. 13. After the first catalytic process, the Ag@CS15 composite beads were collected by a sieve and washed twice with distilled water and collected as shown in Scheme 1a. Herein, cross-linked Ag@Cs biocomposite hydrogel beads were fabricated via a one-step simple route. The anchoring of Ag nanoparticles and the cross-linking of chitosan beads happened at the same time and can be explained as follows. Firstly, a solution containing chitosan powder dissolved in acetic acid (1%) with or without the addition of silver ions was prepared and put into a glass syringe. Scheme 1a. After that, chitosan is crosslinked once dropped into the NaOH solution and gelled spheres form immediately, Scheme 1b. At the same time, ethanol at alkaline conditions can reduce silver ions, which are coordinated into the lone pair electrons of amino groups (NH₂) in chitosan chains, to form Ag nanoparticles [11, 35, 37, 55, 56]. Chitosan also has hydroxyl groups, but silver ions as a soft acid favored to coordinate with nitrogen as a softer base instead of bonding with oxygen atom [11]. Previously, ethanol was used for reduction of other metal ions such as Pd [3]. Also, the reduction of AuCl₄⁻ ions into Au particles was carried out in a basic methanolic solution [57]. Jiang et al. deposited Ag nanoparticles over a silica surface through reduction of Ag⁺ with ethanol/water at basic condition [55]. Recently, Hidayat et al. used methanol solution of AgNO₃ and visible light irradiation for deposition of Ag nanoparticles over the surface of chitosan-coated white silica-gel beads [11]. Additionally, chitosan serves as a good stabilizer for the synthesized metal nanoparticles such as copper, cobalt, and Ag nanoparticles to restrict their grow up [7, 12, 27, 58]. In addition to the chitosan stabilizing effect, Biao et al. used chitosan as a reducing agent for silver ions to produce Cs-Ag colloid through hydrothermal treatment [44]. Herein, after 24 h, the obtained hydrogel beads were washed with distilled water and collected as shown in Scheme 1c. In this way, the Ag⁺/chitosan soluble solution has been transformed into Ag@chitosan insoluble gel beads.
Conclusions

In summary, recyclable Ag@Chitosan nanocomposite beads with different Ag contents were synthesized via a simple one-step method using basic ethanol solution as a physical crosslinking and reducing agent for the first time. XRD, EDX, and UV-Visible measurements demonstrated that Ag particles are successfully impeded into Cs beads. HRTEM revealed that the formed Ag particles are spherical in shape with a diameter ~6.7 nm. FTIR results confirmed the interaction between the grown Ag nanoparticles and chitosan function groups. The specific surface area was 45.06 m²/g, 69.63 m²/g, and 30.13 m²/g for pure Cs, Ag@Cs15, and Ag@CS20 nanocomposite, respectively. These results suggest that the Ag@CS20 composite has a smaller active surface area in comparison to the Ag@CS15, which may result in decreased catalytic activity as confirmed by the values of the reduction efficiency and rate constant. Among the Ag@Cs biocomposites, the optimal Ag@Cs15 has the highest rate constant and the reduction efficiency reached 0.143 min⁻¹ and 94.4%, respectively. When the Ag content was increased to 20% (w/w), these values were 0.13 min⁻¹ and 93%, respectively. Decreasing catalytic activity from Ag@Cs15 to Ag@Cs20 may be attributed to the decrease in the surface area. Additionally, the designed Ag@Cs15 catalyst is characterized by easy reuse and was tested in five subsequent hydrogenation cycles. It was found that the composite beads still acquire 90% removal efficiency, which is somewhat lower than the removal efficiency (94.4%) of the first cycle. These results indicate that the proposed new/simple assembly of Ag nanoparticles into chitosan beads produces an Ag@Cs catalyst with high efficiency and good recycling durability for hydrogenation of nitrophenol to aminophenol.

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Declarations

Conflict of interest The authors declare that they have no competing interests.

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References

1. Anusuya N, Pragathiswaran C, Thulas G (2021) Catalytic reduction of 4-nitrophenol to 4-amino phenol by chitosan/TiO₂-Fe₂O₃ nanomaterial, Mater. Today: Proc. 37 3759 – 3763
2. Fatima R, Afridi MN, Kumar V, Lee J, Ali I, Kim KH, Kim JO (2019) Photocatalytic degradation performance of various types of modified TiO₂ against nitrophenols in aqueous systems. J Clean Prod 231:899–912
3. Ayad MM, Amer WA, Kotp MG (2017) Magnetic polyaniline-chitosan nanocomposite decorated with palladium nanoparticles for enhanced catalytic reduction of 4-nitrophenol. Mol Catal 439:72–80
4. Gemini VL, Gallego A, De Oliveira VM, Gomez CE, Manfio GP, Koral SE (2005) Biodegradation and detoxification of p-nitrophenol by Rhodococcus wratislaviensis. Int Biodeterior Biodegradation 55:103–108
5. Donlon BA, Razo-Flores E, Lettinga G, Field JA (1996) Continuous detoxification, transformation, and degradation of nitrophenols in upflow anaerobic sludge blanket (UASB) reactors, Biotechnology. Bioeng 51:439–449
films: an effective photocatalyst under nanowire nanofibers with 21. Li T, Liu X, Li L, Wang Y, Ma P, Chen M, Dong W (2019) Polyvinyl alcohol/chitosan hydrogels on the recyclable adsorption of Cu (II), Pb (II) and cd (II) from aqueous solution. J Polym Res 26:1–12
22. Liu L, Li C, Bao C, Jia Q, Xiao P, Liu X, Zhang Q (2012) Preparation and characterization of chitosan/graphene oxide composites for the adsorption of Au (III) and Pd (II). Talanta 93:350–357
23. Yu B, Xu J, Liu JH, Yang ST, Luo J, Zhou Q, Wan J, Liao R, Wang H, Liu Y (2015) Adsorption behavior of copper ions on graphene oxide–chitosan aerogel. J Environ Eng 1:1044–1050
24. Zhao L, Dong P, Xie J, Li J, Wu L, Yang ST, Luo J (2013) Porous graphene oxide–chitosan aerogel for tetracycline removal. Mater Res Express 1:015601
25. Javadi E, Baghdadi M, Taghavi L, Panahi HA (2020) Removal of 4-nonylphenol from surface water and municipal wastewater effluent using three-dimensional graphene oxide–chitosan aerogel beads. Int J Environ Res 14:513–526
26. Kafshgari MM, Tahermansouri H (2017) Development of a graphene oxide/chitosan nanocomposite for the removal of picric acid from aqueous solutions: Study of sorption parameters. Colloids Surf B Biointerfaces 160:671–681
27. Bakhsh EM, Ali F, Khan SB, Marwani HM, Danish EY, Asiri AM (2019) Copper nanoparticles embedded chitosan for efficient detection and reduction of nitroaniline. Int J Biol Macromol 131:666–675
28. Sargin I (2019) Efficiency of Ag (0)@ chitosan gel beads in catalytic reduction of nitroaromatic compounds by sodium borohydride. Int J Biol Macromol 137:576–582
29. Saifuddin N, Nian CY, Zhang LW, Ning KX (2011) Chitosan-silver nanoparticles composite as point-of-use drinking water filtration system for household to remove pesticides in water. Asian J Biochem 6:142–159
30. Mojiri A, Kazerooni RA, Gholami A (2019) Cross-linked magnetic chitosan/activated biochar for removal of emerging micropollutants from water: Optimization by the artificial neural network. Water 11:551
31. Delhiraja K, Vellingiri K, Boukhvalov DW, Philip L (2019) Development of highly water stable graphene oxide-based composites for the removal of pharmaceuticals and personal care products. Ind Eng Chem Res 58:2899–2913
32. Jayalakshmi R, Jeyanthi J (2021) Spectroscopic investigation of carbon nanotube as nano-filter entrapped in chitosan hydrogel beads. J Mol Struct 1237:130856
33. Zhou P, Xia Z, Qi C, He M, Yu T, Shi L (2021) Construction of chitosan/Ag nanocomposite sponges and their properties. Int J Biol Macromol 192:272–277
34. Kanniah P, Chelliah P, Thangapandi JR, Gnanadhas G, Mahendran V, Robert M (2021) Green synthesis of antibacterial and cytotoxic silver nanoparticles by Piper nigrum seed extract and development of antibacterial silver based chitosan nanocomposite. Int J Biol Macromol 189:18–33
35. Chen J, Fan L, Yang L, Wang C, Zhang M, Xu J, Luo S (2020) Facile synthesis of Ag nanoparticles-loaded chitosan antibacterial nanocomposite and its application in polypropylene. Int J Biol Macromol 161:1286–1295
36. Rasoulozedehzali M, Namazi H (2018) Facile preparation of antibacterial chitosan/graphene oxide-Ag bio-nanocomposite hydrogel beads for controlled release of doxorubicin. Int J Biol Macromol 116:54–63
37. Yadollahi M, Farhoudian S, Namazi H (2015) One-pot synthesis of antibacterial chitosan/silver bio-nanocomposite hydrogel beads as drug delivery systems. Int J Biol Macromol 79:37–43
38. Tomke PD, Rathod VK (2020) Facile fabrication of silver on magnetic nanocomposite (Fe3O4@ Chitosan–AgNP nanocomposite) for catalytic reduction of anthropogenic pollutant and agricultural pathogens. Int J Biol Macromol 149:989–999
39. Vaezifar S, Razavi S, Golozar MA, Karbasi S, Morshed M, Kamali M (2013) Effects of some parameters on particle size
distribution of chitosan nanoparticles prepared by ionic gelation method. J Clust Sci 24:891–903

40. Vanaamudan A, Sadhu M, Pamidimukkala P (2018) Chitosan-Guar gum blend silver nanoparticle bionanocomposite with potential for catalytic degradation of dyes and catalytic reduction of nitrophenol. Mol Liq 271:202–208

41. Syed B, Prasad N, Dhananjaya BL, Yallappa S, Satish S (2016) Synthesis of silver nanoparticles by endosymbiont Psedomonas fluorescens CA 417 and their bacterial activity. Enzyme Microb Technol 95:128–136

42. Bagheri H, Roodaiea A, Baktash MY (2014) A chitosan–poly-pyrrole magnetic nanocomposite as μ-sorbent for isolation of naproxen. Anal Chim Acta 816:1–7

43. Zare-Akbari Z, Farhadnejad H, Furughi-Nia B, Abedin S, Yadollahi M, Khorsand-Ghayemi M (2016) PH-sensitive bionanocomposite hydrogel beads based on carboxymethyl cellulose/ZnO nanoparticle as drug carrier. Int J Biol Macromol 93:1317–1327

44. Biao L, Tan S, Wang Y, Guo X, Fu Y, Xu F, Zu Y, Liu Z (2017) Synthesis, characterization and antibacterial study on the chitosan-functionalized Ag nanoparticles. Mater Sci Eng C 76:73–80

45. Shehap AM, Nasr RA, Mahfouz MA, Ismail AM (2021) Preparation and characteristics of high doping chitosan/MMT nanocomposites films for removing iron from ground water. J Environ Chem Eng 9:104700

46. Altunkaynak F, Okur M, Saracoglu N (2022) Controlled release of paroxetine from chitosan-montmorillonan nanocomposite. J Drug Deliv Sci Technol 68:103099

47. Queiroz MF, Melo KRT, Sabry DA, Sassaki GL, Rocha HAO (2015) Does the use of chitosan contribute to oxalate kidney stone formation? Mar Drugs 13:141–158

48. Yasmeen S, Kabiraz MK, Saha B, Qadir MR, Gafur MA, Masum SM (2016) Chromium (VI) ions removal from tannery effluent using chitosan-micrcocrystalline cellulose composite as adsorbent. Int. Res. J. Pure Appl. Chem. 1–14

49. Lavoroga M, Attianese I, Buoncore GG, Conte A, Del Nobile MA, Tescione F, Amendola E (2014) MMT-supported Ag nanoparticles for chitosan nanocomposites: structural properties and antibacterial activity. Carbohydr Polym 102:385–392

50. Nasrollahzadeh M, Atradi M, Jaleh B, Gandomirizbahi M (2016) In situ green synthesis of Ag nanoparticles on graphene oxide/TiO. nanocomposite and their catalytic activity for the reduction of 4-nitrophenol congo red and methylene blue. Ceram Int 42:8587–8596

51. Tian X, Zahid M, Sun W, Zhu Y (2021) Facile fabrication of TiO. with 3D hierarchical structure and its supported Pd catalysts for high catalytic hydrogenation performance of 4-Nitrophenol to 4-Aminophenol. Appl Surf Sci 566:150615

52. Ravi G, Sarasija M, Ayodhya D, Kumari LS, Ashok D (2019) Facile synthesis, characterization and enhanced catalytic reduction of 4-nitrophenol using NaBH₄ by undoped and Sm 3+ Gd3+ Hf3+ doped La2O3 nanoparticles. Nano Converg 6:1–9

53. Liu DM, Dong C, Xu B (2021) Preparation of magnetic kaolin embedded chitosan beads for efficient removal of hexavalent chromium from aqueous solution. J Environ Chem Eng 9:105438

54. Anusuya N, Pragathiswaran C, Mary JV (2021) A potential catalyst-TiO₂/ZnO based chitosan gel beads for the reduction of nitro-aromatic compounds aggregated sodium borohydride and their antimicrobial activity. J Mol Struct 1236:130197

55. Jiang X, Chen S, Mao C (2008) Synthesis of Ag/SiO₂ nanocomposite material by adsorption phase nanoreactor technique, Colloids Surf. A Physicochem Eng Asp 320:104–110

56. Hashemian S, Shahedi MR (2013) Novel Ag/kaolin nanocomposite as adsorbent for removal of acid cyanine 5R from aqueous solution. J. Chem. (2013) 7 pages

57. Quinn M, Mills G (1994) Surface-mediated formation of gold particles in basic methanol. J Phys Chem 98:9840–9844

58. Zienkiewicz-Strzałka M, Deryło-Marzęwska A, Skorik YA, Petrova VA, Choma A, Komaniecza I (2020) Silver nanoparticles on chitosan/silica nanofibers: Characterization and antibacterial activity. Int J Mol Sci 21:166

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