Karaj branch

Journal of Applied Chemical Research, 15, 1, 46-63 (2021)

Journal of Applied Chemical Research
jacr.kiau.ac.ir

Biosynthesis of Ag Nanoparticles at Ziziphus Jujuba Kernel Substrate using *Tilia platyphyllos* Extract: Catalytic Activity for Reduction of Organic Dyes

Bahar Khodadadi*, Mohammad Sabeti, Omulbanin Norozi

Department of Chemistry, Faculty of Science, University of Qom, Qom, Iran

(Received 14May 2020; Final revised received 17Aug.2020)

Abstract

For the first time the extract of the plant of *Tilia platyphyllos* was used to green synthesis of Ag nanoparticles (NPs) supported on Ziziphus jujuba kernel as an environmentally benign support. Ag NPs/ Ziziphus jujuba kernelas an effective catalyst was prepared through reduction of Ag^+ ions using *Tilia platyphyllos* extractas the reducing and capping agent and Ag NPs immobilization onZiziphus jujuba kernel surface in the absence of any stabilizer or surfactant. According to FT-IR analysis, the hydroxyl groups of phenolics in *Tilia platyphyllos* extract as bioreductant agents are directly responsible for the reduction of Ag^+ ions and formation of Ag NPs. The as-prepared catalyst was characterized by Fourier transform infrared (FT-IR) and UV-Vis spectroscopy, field emission scanning electron microscopy (FESEM) equipped with an energy dispersive X-ray spectroscopy (EDS), Elemental mapping, X-ray diffraction analysis (XRD) and transmittance electron microscopy (TEM). The synthesized catalyst was used in the reduction ofCongo Red (CR), and Methyl Orange (MO) at room temperature.The Ag NPs/Ziziphus jujuba kernelshowed excellent catalytic activity in the reduction of these organic dyes. In addition, it was found that Ag NPs/Ziziphus jujuba kernelcan be recovered and reused several times without significant loss of catalytic activity.

Keywords: Ag nanoparticles, Ziziphus jujuba kernel, *Tilia platyphyllos*, $NaBH_4$, Organic dyes.

---

*[*] **Corresponding author:** Bahar Khodadadi, Department of Chemistry, Faculty of Science, University of Qom, Qom, Iran. Email: Bkhodadadi98@yahoo.com, Tel.: +98 2532103792.*

Introduction

In the past decades, dyes are the major effluents from various industries such as ceramics, paper, plastic, cosmetics, leather, food, and textiles are considered one of the major water pollutants in the environment. These compounds are well known as toxic, non-biodegradable and carcinogenic pollutants in wastewaters and have potential toxicity toward humans, animals and plants [1-6].Since organic dyes possess high resistance, high stability and low solubility in water, the conventional wastewater treatment methods in the literature including adsorption, reverse osmosis, or chemical coagulation cannot be sufficient and effective in the degradation of these. [1-9]. Nevertheless, these methods solely transfer pollutants from the liquid to the solid phase. This causes secondary pollution and further treatment is required. Therefore, the effective methods to remove these contaminants are an important challenge in ecological systems, due to their toxicity and carcinogenic properties [5-7].

Over the past few years, researchers have mainly focused on decolorization or detoxification of these compounds using a strong reducing agent in the presence of noble metals such as Pt, Au, Ag and Cu which can catalyze the reaction by facilitating electron relay from the donor BH_4^{-} to overcome the kinetic barrier [8, 9].Moreover, heterogeneous catalysts are more and more used in the form of NPs due to their higher available catalytic surface. The major drawback for use of MNPs is their agglomeration. To decrease MNPs agglomeration and overcome the drawbacks concerning stability and recovery of MNPs could be solved by applying an ideal support, which decreases nanoparticle agglomeration [9, 10]. Up to now, several inorganic compounds such as zeolite, graphene oxide, TiO_2 and Fe_3O_4 have been used as supports for the MNPs [11-13].In recent years, researchers have mainly focused on the application of biowaste materials as supports that are the best candidates because of their low cost, accessibility and inexpensive adsorbent for removal of ionic pollutants and dyes from aqueous media. Newly, our research group reported the green synthesis of MNPs supported on the various inorganic supports such as clinoptilolite, TiO_2/SiO_2, and agricultural biowaste involve some of the fruit kernel shells and overcome the drawbacks concerning stability and recovery of MNPs[4, 6, 9,14, 15].

To date, a number of physical and chemical methods for the synthesis of M NPs are available; for example, sol-gel, quick precipitation, thermal decomposition, electrochemical, sonochemical, and microwave assisted processes. These methods which are extremely expensive and also is required high temperature and pressure conditions and mainly use toxic and hazardous reactants and starting materials. Moreover, environmental and biological risks that limit their usage in medical applications. Therefore, environmentally benign production methods of MNPs are very attractive. Recently, the green method that employing microorganisms and plant extract for synthesis of MNPs with suitable catalytic activity have drawn attention as a good alternative to chemical and physical methods due to several advantages such as environmentally friendly, simple methodology, very moderate reaction conditions, easy to control, energy-efficient and organic solvent-free as well as compatibility for biomedical and pharmaceutical applications. It has been found that plant extracts act both as reducing and capping agents in the synthetic process of the nanoparticles. Several plants have been successfully used for efficient and rapid extracellular synthesis of Ag NPs [4-9, 13-17]. Hitherto, there has been no report on the biosynthesis of Ag NPs using the *Tiliaplathyphyllos* extract.*Tilia platyphyllos*belongs to Tiliaceae family, which consists of several species, distributed in Europe, North America and Asia. *Tilia platyphyllos*is a large deciduous tree *Tilia platyphyllos*grows in Baluchestan, Bandar Abbas and north parts of Iran. Flowers and flowering branches of this tree are used in Iranian traditional medicine. *Tilia platyphyllos*, is used as diaphoretic, appetizer, diuretic, expectorant, antispasmodic and sedative in phytotherapy. It has been also used for the treatment of cough, nervous tension, migraine, insomnia, and different types of spasms in traditional medicine. Medicinal properties of Tilia species have been attributed to some active ingredients including flavonoids, volatile oil and mucilage. Quercitrin (as the main flavonoid), hyperoside, tiliroside, kaempferol derivatives, isoquercitrin, as tragalin and rutin are the most important compounds in Tilia species[18-21].

According to these literatures, phenolic compounds such as flavonoids and phenol carbonic acids constitute one of the most important groups in *Tilia platyphyllos.* Therefore, the present work focused on the use of *Tilia platyphyllos* extract as an important source for bioreduction of metallic ions and production of nanoparticles. The agglomeration of MNPs is inevitable. According to the literature and our previous works, Ziziphus jujuba kernel powder as a biowaste material seems to be suitable support for adsorption purposes due to its high surface area.Thus, in this work, firstly Ag NPswere synthesized via reduction of Ag^+ ion by *Tilia platyphyllos* extract as a reducing and stabilizing agent. Ag NPs/Ziziphus jujuba kernel was then prepared by *Tilia platyphyllos* extract. Through biological reduction of Ag^+ ions, highly dispersed Ag NPs are formed *in situ* on the Ziziphus jujuba kernel surface. Furthermore, the catalytic activity and recyclability of Ag NPs/Ziziphus jujuba kernel in the reduction of CR and MO in aqueous medium at ambient temperature using $NaBH_4$ as the hydrogen source have been investigated. The catalyst can be easily recycled following the reaction completion.

Experimental

Instruments and reagents

Chemical reagents obtained from Merck and Aldrich Chemical Companies and used without further purification. All materials were of commercial reagent grade. Products were characterized by comparison of their physical and spectral data with those of authentic samples. FT-IR spectra were recorded on a Nicolet 370 FT/IR spectrophotometer (Thermo Nicolet, USA) using pressed KBr pellets. X-ray Diffraction (XRD) measurements were carried out using a Philips model X'Pert Pro diffractometer employing Cu Kα radiation (λ=1.5418Å) at a scanning rate of 2º/min inthe 2θ range from 10 to 80˚. UV-Visible spectral analysis was carried out using a Shimadzu UV-2500 double-beam spectrophotometer in the wavelength range of 200-700 nm. Scanning electron microscopy (SEM) was performed on a Cam. Scan MV2300. The chemical composition of the prepared nanostructures was measured by EDS (energy dispersive X-ray spectroscopy) performed in SEM.The shape and size of samples were identified by transmission electron microscopy (TEM) using a Zeiss-EM10C operating at an accelerating voltage of 80 kV.

Preparation of Tilia platyphyllos extract

Dried powder of *Tilia platyphyllos*(10 g) refluxed at 80°C in 75% (V/V) ethanol solution(100 ml) for 30 min and the resulting mixture was allowed to cool to ambient temperature. *Tilia platyphyllos* extract was centrifuged at6500 rpm and the supernatant was separated by filtration.

Preparation of AgNPs/Ziziphus jujuba kernel using the Tilia platyphyllos extract

Typical Ag NPs/Ziziphus jujuba kernel synthesis consisted of separate synthesis of the Ag NPs using the plant extract as follows: Typical AgNPs synthesis consisted of separate synthesis of the Ag NPs using the plant extract as follows:10 mL of 0.2 M $AgNO_3$was added dropwise to 50 mL of *Tilia platyphyllos* extract underconstant stirring at 75°C. The solution color gradually changed from yellow to dark brown during the heating process, because of the excitation of surface plasmon resonance (SPR), indicating the formation ofthe Ag NPs(as monitored by UV-Vis spectra of the solution).Finally, the colored solution of silver nanoparticles was centrifuged at 6500 rpm for 30 min for complete separation. The obtained precipitate was washed several times with distilled water and one time with ethanol and then air dried for 24 h at 50°C in oven. Typical synthesis of the AgNPs/Ziziphus jujuba kernel was carried out as follows: prior to use, the Ziziphus jujuba kernel was washed and air dried ground with a high speed rotary cutting mill and sieved into fractions of < 0.45 micrometer in size. 0.5 g of Ziziphus jujuba kernelthen was dispersed in 50 mL of the *Tilia platyphyllos* extract under continuous stirring. After 5 min, 10 mL of 0.2 M $AgNO_3$ were added to the mixture at 70 °C and vigorously shaken for 1.5 h. After 10 min., the solution color changed from yellow to black because of the excitation of SPR, indicating nanoparticle formation. Subsequently, the prepared Ag NPs/Ziziphus jujuba kernel was centrifuged at 6500 rpm for 30 min for complete separation. Finally, the obtained precipitate was washed several times with distilled water and one time with ethanol and then air dried for 24 h at 50°C in an oven. All the steps are summarized in Figure 1.

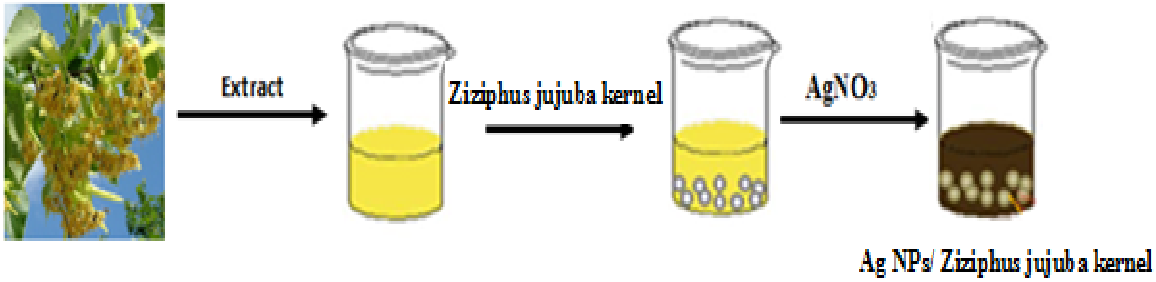


Figure1. Diagrammatic synthesis of Ag NPs/Ziziphus jujuba kernel.

Procedure for the reduction of CR, and MO

In typical experiments, the catalytic activities of the Ag NPs/Ziziphus jujuba kernel samples were evaluated by the degradation of an aqueous solution of 10 ppm CR, and MO. Typically,25 mL of freshly prepared aqueous solution of 5.3×10^{-3} M $NaBH_4$wasmixed with 25 mL of the prepared dye solution in a beaker. After 1 min of stirring, different amounts of the catalyst were added and the mixture was stirred at room temperature until the color of the solution vanished, indicating that degradation of the dye was complete. The reduction was monitored with a UV-Visible absorption spectrophotometer. Finally, after the degradation was complete, the catalyst was separated from the reaction system by brief centrifugation, washed with ethanol and dried for the next cycle.

Results and discussion

In this research, we report an environmentally friendly, low-cost andeasy method for the preparation of AgNPs/Ziziphus jujuba kernel using *Tilia platyphyllos* extract as a reducing and cappingagent is reported. SEM, EDS, elemental mapping, TEM andXRD has been used in the characterization of the stable AgNPs/Ziziphus jujuba kernel. AgNPs have been separately synthesized and characterized using FT-IR and UV–Vis for further monitoring. Moreover, the presence of polyphenolic compounds of *Tilia platyphyllos* extract as antioxidant sources in the green synthesis of Ag NPS was shown by FT–IR and UV–Vis analysis.

Characterization of Tilia platyphyllos extract and Ag NPs

As shown in the UV–Vis spectrum of the *Tilia platyphyllos* extract (Figure 2.a), the fingerprint signals appearing around 330 nm and 275 nm are assigned to the $\pi \rightarrow \pi^*$ transitions, of conjugated double bounds of polyphenolics as antioxidant for green synthesis of nanoparticles [9, 22].The reduction of the Ag ions by *Tilia platyphyllos* extract and formation of Ag NPs was monitored by UV-Vis spectroscopy, as well (Figure 2. b).

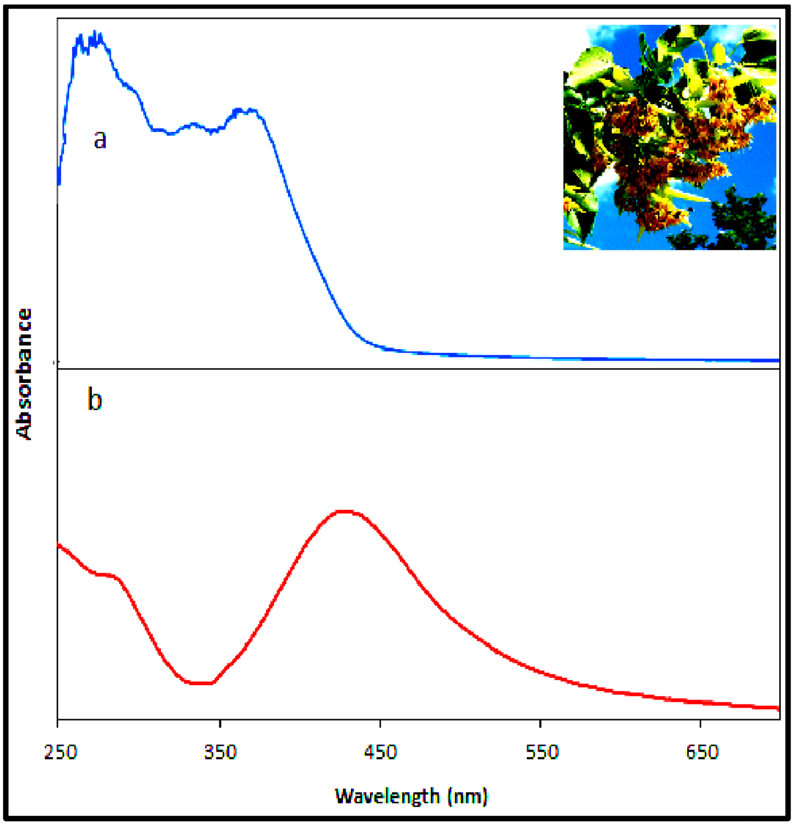
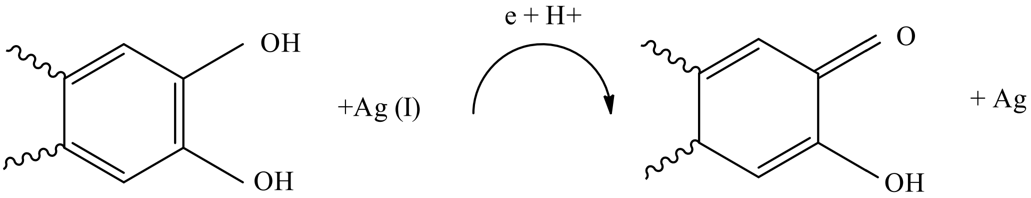


Figure 2. UV-Vis spectra of *Tilia platyphyllos* extract (a) and green synthesized Ag NPs using *Tilia platyphyllos* extract (b).

After completion of the reaction, UV-Vis spectrum showed a maximum absorbance at about 440 nm, which can be assigned to the surface plasmon absorption of silver nanoparticles [9, 23, 24].FT-IR analysis was carried out to determine the phenolic content of the *Tilia platyphyllos* extract and its effect on Ag NPs biosynthesis.



Scheme1. Mechanism for green synthesis of Ag NPs using *Tilia platyphyllos* extract.

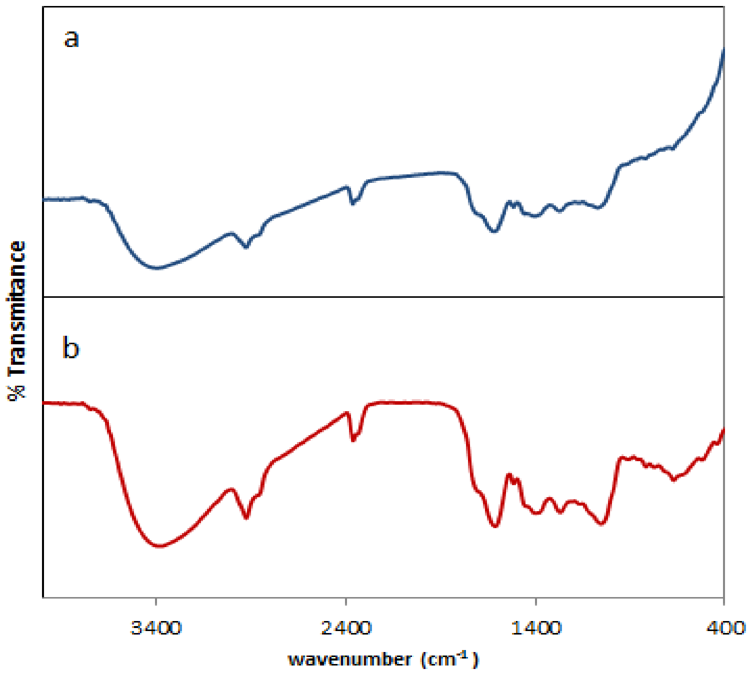


Figure 3. FT-IR spectra of *Tilia platyphyllos* extract (a) and green synthesized Ag NPs using *Tilia platyphyllos* extract (b).

The FT-IR spectrum of *Tilia platyphyllos* extract(Figure 3(a)) shows peaks at 3400–3500, 1680, 1450, and 1050–1270 cm^{-1} which correspond to the free OH in molecule and OH group forming hydrogen bonds, carbonyl group (C=O), stretching C=C aromatic ring, and C–OH stretching vibrations, respectively. These peaks can show the presence of flavonoid and phenolic acids in the *Tilia platyphyllos* extract which responsible for the reduction of Ag$^+$ ions and formation of the corresponding Ag NPs (Scheme 1) [6, 7, 9].According to the FT-IR spectrum of synthesized Ag NPs by using *Tilia platyphyllos* extract (Figure 3(b)), the positions of observed peaks are almost similar to the corresponding peaks in the FT-IR spectrum of *Tilia platyphyllos* extract, which shows adsorbent of organic compounds in the extract on the surface of Ag NPs, possibly through π-electrons interaction in the absence of other strong ligating agents [9, 13].

Characterization of Ziziphus jujuba kernel and Ag NPS/Ziziphus jujuba kernel

FT-IR spectroscopy has been used to monitor the functional groups of Ziziphus jujuba kernel as support and Ag NPS/Ziziphus jujuba kernel and results are shown in Figure 4. a.

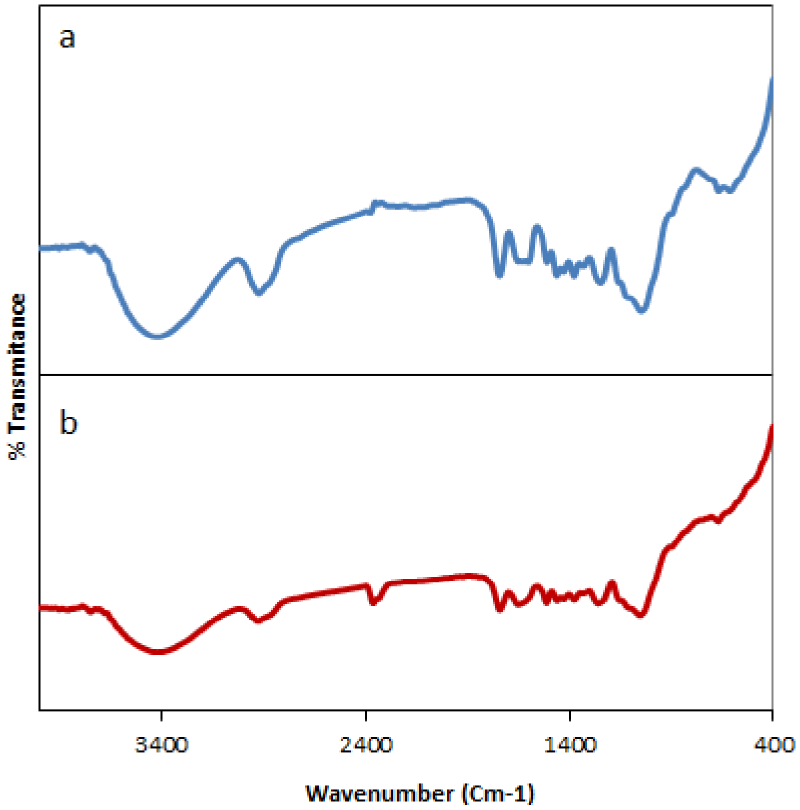


Figure 4. FT-IR spectra of Ziziphus jujuba kernel (a) andAg NPS/Ziziphus jujuba kernel (b).

According to literatures, cellulose, hemicellulose and lignin are three main components of biomass in the Ziziphus jujuba kernel. It has been well recognized that, the typical functional groups for these compounds are expected in FT-IR spectra. As seen in Figure 4.a, the broad peak observed at 3500 to 3100 cm^{-1} in the spectra of the Ziziphus jujuba kernel and AgNPs/Ziziphus jujuba kernelis related to free OH in molecule and OH group forming hydrogen bonds. The absorption band at 2928 cm^{-1} is related to the C-H stretching vibrations. In addition,a small absorption peak at 1632 cm^{-1}is due to the bending vibrations of H_2O molecules. Moreover, the absorption bands at 1372 and 1488 cm^{-1} indicate the presence of the chemical functional groups, – CH_3, –CH_2 and –CH, which are characteristic for alkanes, cellulose, hemicellulose, and lignin. In addition, the absorbance at 1738 cm^{-1} is due to the C=O stretching vibrations. Moreover, the peaks at 1254 and 1056 cm^{-1} can be attributed to the C–O–C and C–O–(H) functional groups [6, 9, 25, 26]. In comparison with Ziziphus jujuba kernel, the FT-IR analysis of Ag NPs/Ziziphus jujuba kernel(Figure 4. b) confirms that no obvious changes can be seenin the functional groups after the immobilization of AgNPs on the Ziziphus jujuba kernel.

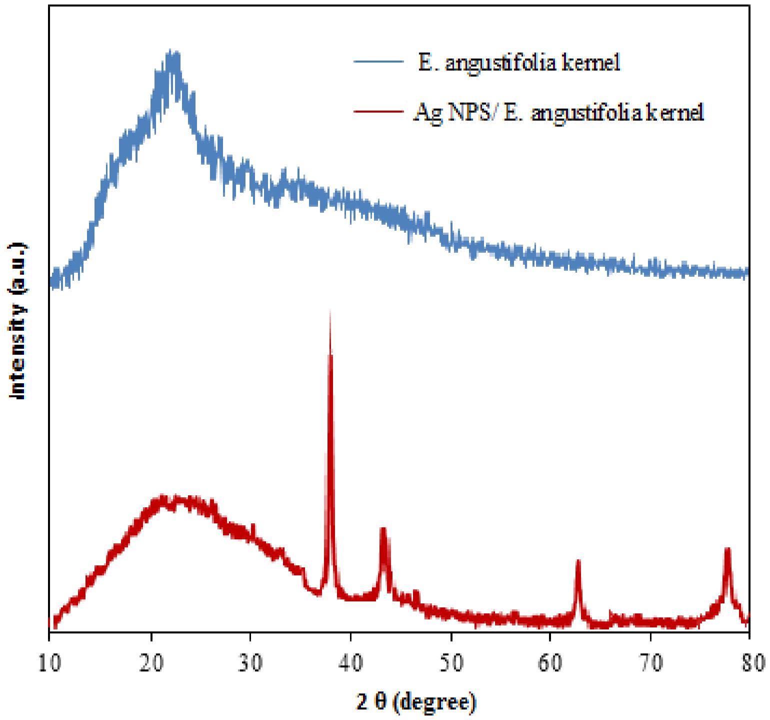


Figure 5. XRD pattern of Ziziphus jujuba kernel andAg NPS/Ziziphus jujuba kernel.

In order to evaluate the crystalline nature of the Ziziphus jujuba kernel and Ag NPs/Ziziphus jujuba kernelby X-ray diffraction (XRD) analysis was performed and the results are presented in Figure 5. Considering the fact that cellulose is the main component of Ziziphus jujuba kernel and according to the XRD result in Figure 5, the peak at 2θ around 22° is an evidence of cellulose. [27, 28]. The synthetic Ag NPs are crystalline in nature, as verified by the XRD pattern. As it can be observed in the XRD results of the Ag NPs/Ziziphus jujuba kernel (Figure 5),the diffraction peaks at 38.68°, 44.18°, 64.52°, and 78.12°were assigned to the Ag NPs, JCPDS no. 04-0783), which exhibits face centered cubic (FCC) structure for the metallic silver NPs immobilized on the surface of Ziziphus jujuba kernel without the formation of impurities like silver oxide (Ag_2O) [4, 9].Scanning electron microscopy (SEM) analysis was carried outin order to determine the size and morphologies of Ziziphus jujuba kernel andAg NPS/Ziziphus jujuba kernel. Figure 6shows the typical FE-SEM image of samples.

FE-SEM images indicate that the Ag NPs and Ziziphus jujuba kernel show spherical morphology with diameters of less than 20 nm with very narrow diameter distributions. From SEM images, it is clear that Ag particles are deposited on the surface of Ziziphus jujuba kernel without being incorporated in Ziziphus jujuba kernel. Moreover, Figure 7 illustrates the elemental mapping images, which demonstrate that Ag NPs are dispersed on the surface of Ziziphus jujuba kernel.

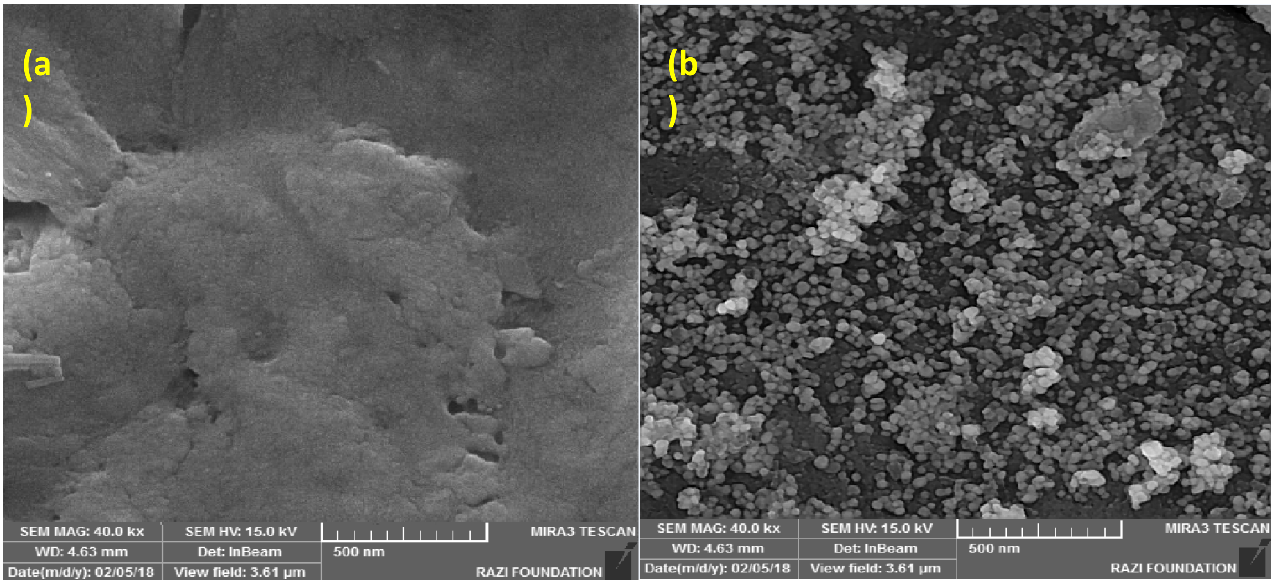


Figure 6. FE-SEM image ofZiziphus jujuba kernel andAg NPS/Ziziphus jujuba kernel.

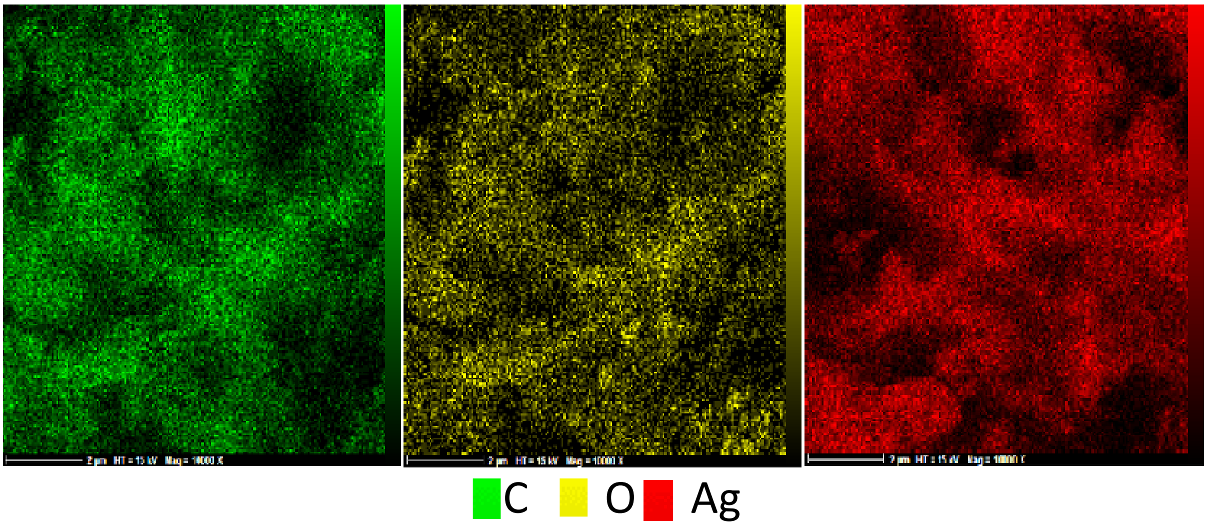


Figure 7. Elemental mapping of Ag NPS/Ziziphus jujuba kernel.

The elemental composition of Ag NPS/Ziziphus jujuba kernel was also characterized by EDS spectrum (Figure 8). EDS analysis confirms the presence of C, O, and Ag elements in the Ag NPS/Ziziphus jujuba kernel sample.

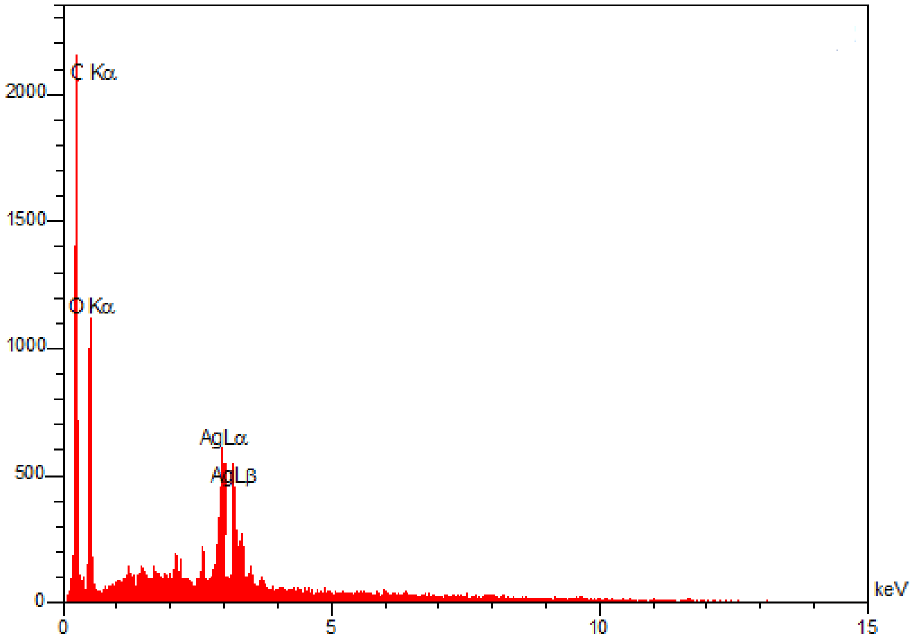


Figure 8. EDS spectrum of Ag NPS/Ziziphus jujuba kernel.

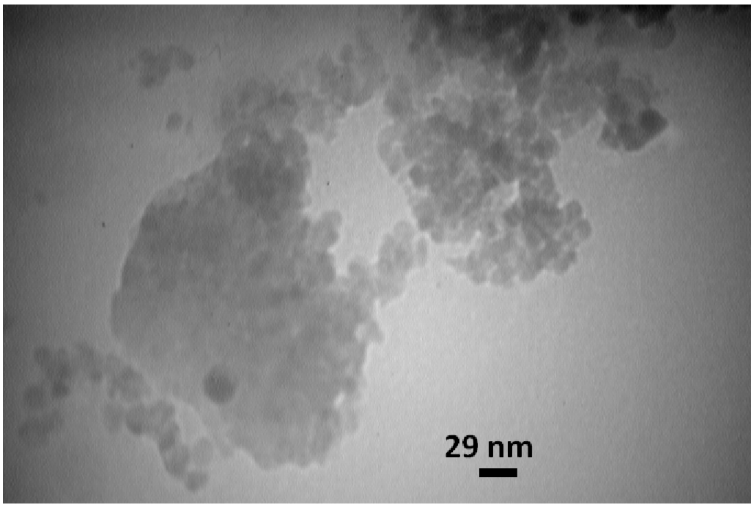


Figure 9.TEM image ofAg NPS/Ziziphus jujuba kernel.

Transmission electron microscopy (TEM) was employed in order to perform a more detailed study of the morphology and size of Ag NPS/Ziziphus jujuba kernel sample. Figure 9 shows TEM image of typical Ag NPS/Ziziphus jujuba kernel, in which Ag nanoparticles appear as dark dots over the surface of Ziziphus jujuba kernel with average sizes of less than 20 nm.

Catalytic behavior of green synthesized Ag NPS/Ziziphus jujuba kernel for reduction CR and MO

In this part, the reduction of CR and MO dyes by $NaBH_4$at room temperature was chosen to evaluate the catalytic activity of Ag NPS/Ziziphus jujuba kernel. The reaction progress was monitored by UV-Vis spectroscopy, as illustrated in Figures 10 and 11.

Table1. Completion time for the reduction of 10 ppm CR and MO dyes (25 mL) using 10 mg of Ziziphus jujuba kernel or 10 mg of Ag NPs in the presence of 25 mL of $NaBH_4$(5.3 ×10^{-3} M).

	Time (min)	
Catalyst	CR	MO
Ag NPs	29	34
Ziziphus jujuba kernel	200[a]	200[a]
-------	200[a]	200[a]

[a]Not completed.

Firstly, the reduction of 10 ppm CR and MO dyes (25 mL) using 10 mg of Ziziphus jujuba kernel or 10 mg of Ag Ps in the presence of 25 mL of $NaBH_4$ (5.3 ×10^{-3} M) was examined. Completion time for the reduction of CR and MO using Ag NPs and Ziziphus jujuba kernel and without any catalyst is given in Table 1.

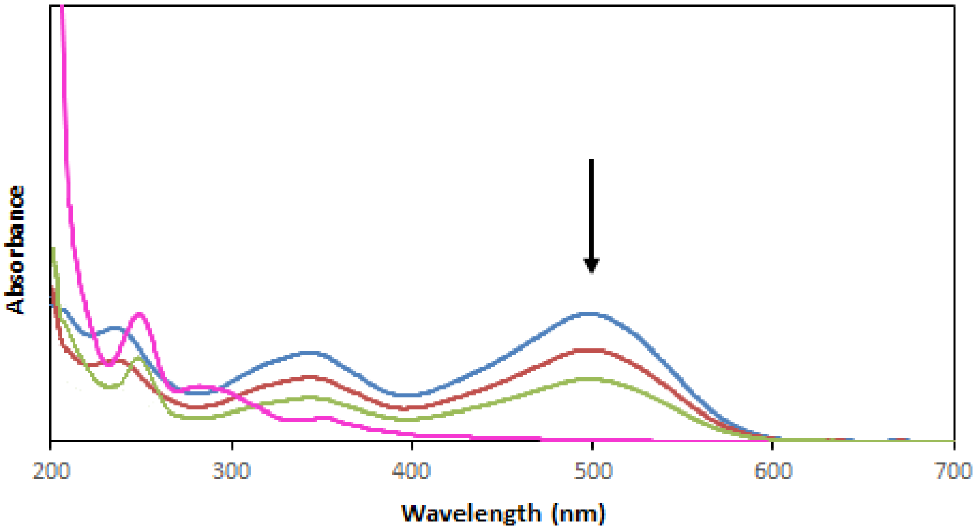


Figure 10. The UV-Vis spectra of CR aqueous solution in the presence of AgNPS/Ziziphus jujuba kernel.

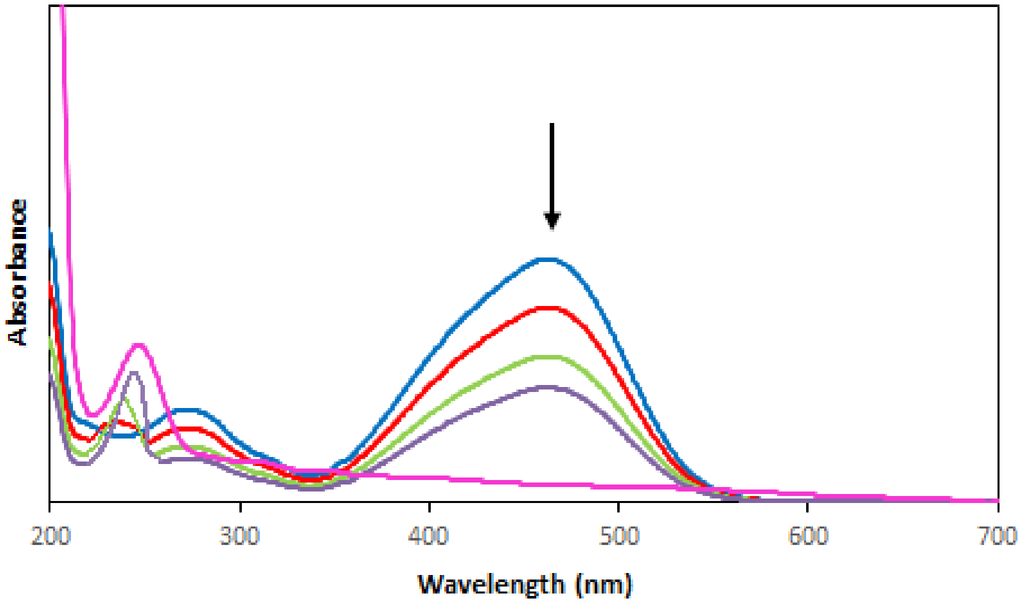


Figure 11. The UV-Vis spectra of MO aqueous solution in the presence of Ag NPS/Ziziphus jujuba kernel.

In addition, constant amounts of $NaBH_4$ and different amounts of catalyst were then applied in the catalytic reduction of CR or MO dyes. Completion times for the reduction of CR and MO using different amounts of catalyst are shown in Figures 12 and 13.

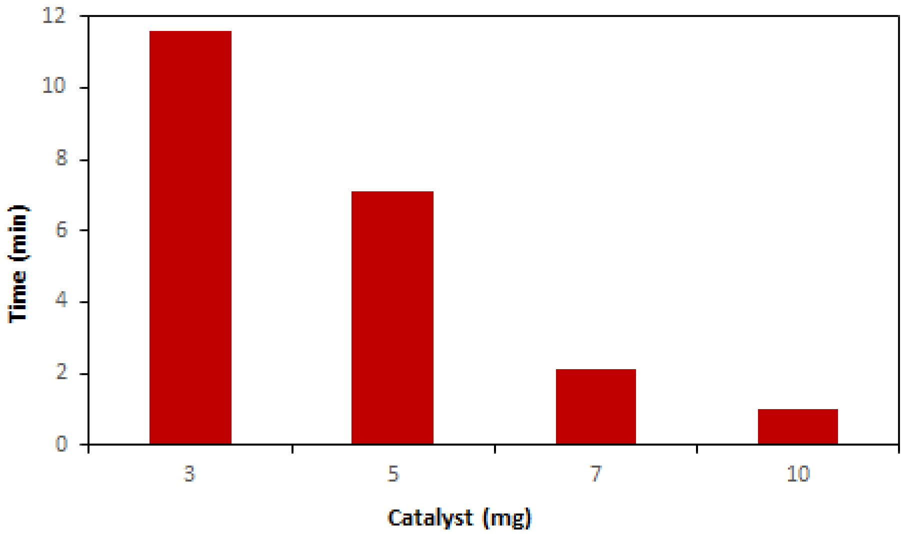


Figure 12. Competition time for the reduction of CR (10 ppm)using$NaBH_4$(5.3×10^{-3} M) and different amountsof Ag NPS/Ziziphus jujuba kernel.

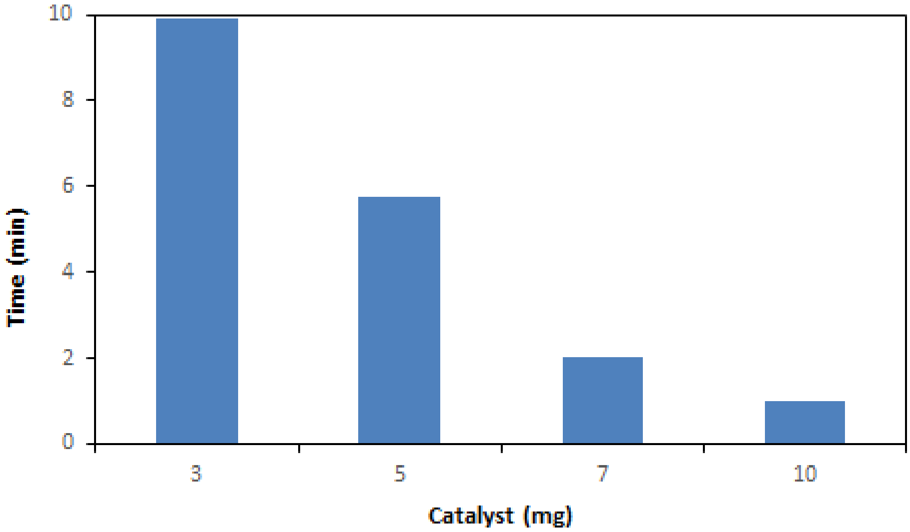
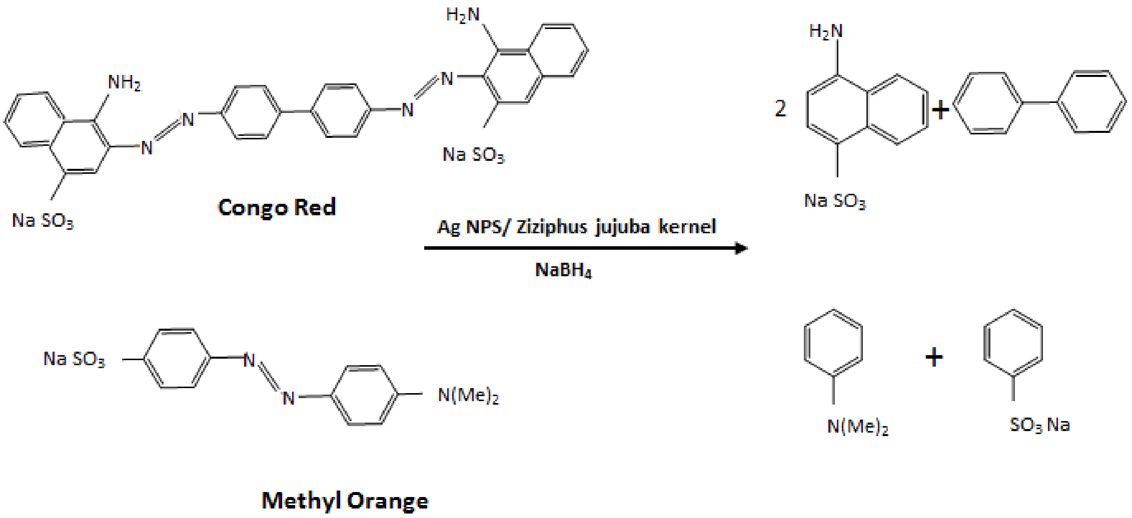


Figure 13. Competition time for the reduction of MO (10 ppm) using$NaBH_4$(5.3×10^{-3} M) and different amountsof Ag NPS/Ziziphus jujuba kernel.

According to UV-Vis spectra, aqueous solutions of CR and MO exhibit peaks at λ_{max} 493 and 466 nm, which disappear when the reduction of dyes is complete. According to these results, it can be concluded that, Ziziphus jujuba kernel as a support could be employed successfully to decreases Ag NPs agglomeration and increases catalyst surface area. Moreover, as the best result, reduction of CR and MO using 10.0 mg of Ag NPS/Ziziphus jujuba kernel was complete within 1.01min and 58 s, respectively. It seems that the following steps are assumed to be involved in this reaction: First, adsorption of $NaBH_4$onto the surface of the catalyst and formation of metal hydride; then, adsorption of CR or MOonto the surface of the catalyst; finally, reduction of CR or MO and desorption in order to create a free space for the reaction to continue. The mechanism of the catalytic reduction and degradation of dyes with Ag NPS/Ziziphus jujuba kernel is shown in scheme 2.



Scheme 2. Mechanism of the catalytic reduction and degradation of dyes with Ag NPS/Ziziphus jujuba kernel.

In order to illuminate the applicability and efficiency of green catalyst in this work, the results are compared with those of some of the recently reported methods for the reduction of variety of dyes by $NaBH_4$ in Table 2 [13, 14, 24, 29,30]. Obviously,Ag NPS/Ziziphus jujuba kernelshowsthe shortest time forthe reduction of organic dyes in comparison with literature methods.

Table 2. Comparison of results for this work with other reported methods inthe reduction of MO, and CR (3.0 mg catalyst).

	Catalyst	Time	Reference
Mo	Cu@SBA-15	5 min	29
Mo	Ag NPs/seashell	11 min	24
Mo	Ag/TiO2 nanocomposite	9 min	13
Mo	Cu/eggshell nanocomposite	2 min	14
Mo	Ag NPS/Ziziphus jujuba kernel	59 S	This Work
CR	Cu@SBA-15	7 min	29
CR	copper nanocrystals	500 S	30
CR	Ag NPs/seashell	3 min	24
CR	Cu/eggshell nanocomposite	65 S	14
CR	Ag NPS/Ziziphus jujuba kernel	60 S	This Work

Catalyst recyclability

Obviously, the reusability of the heterogeneous catalysts is one of the most important factors; especially for commercial and industrial applications. After each cycle, Ag NPS/Ziziphus jujuba kernel catalyst can be easily separated by mild centrifugation and washing several times with distilled water and drying for the successive reactions. The catalyst at least four times for 100% reduction of CR and RhBwithout significant loss of catalytic activity. Little loss of catalytic activity was observed after the 4th cycle which shown in Figure 14.

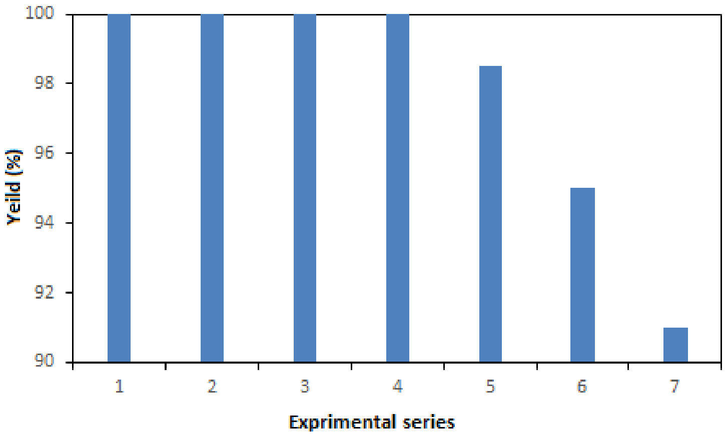


Figure 14. Reusability ofAg NPS/Ziziphus jujuba kernelcatalyst.

Conclusions

In this work, AgNPs, and Ag NPs/Ziziphus jujuba kernel were synthesized using *Tilia platyphyllos* extract as reducing and stabilizing agents. Ag NPs/Ziziphus jujuba kernel was utilized in the reduction of CR, and MO, in water at room temperature. Results revealed that Ag NPS/Ziziphus jujuba kernel had the high catalytic activity in comparison with the other literature works on the reduction of CR, and MO. Moreover, recycling results confirm that the catalyst can be recycled at least four times for 100% reduction of organic dyes. On the other hand, some of advantages for this work are listed below:

(I) Fast and clean synthesis without the use of hazardous, toxic and dangerous compounds or surfactants.

(II) The use of *Tilia platyphyllos* extract as an economic and effective reducing and stabilizing agent.

(III) The use of waste Ziziphus jujuba kernel as a natural and inexpensive valuable resource and environmentally benign support.

(IV) The synthesized catalysts are stable and could be easily recovered and reused.

Acknowledgments

We gratefully acknowledge the University of Qom and Payame Noor University for the support of this work.

References

[1]Z. Han, L. Ren, Z. Cui, C. Chen, H. Pan, J.Chen, *Appl. Catal. B: Environ.*, 126, 298 (2012).

[2]H.Y. Zhu, L. Xiao, R. Jiang, G.M. Zeng, L. Liu, *Chem. Eng. J.*, 172(2-3), 746 (2011).

[3] R.Saravanan, V.K. Gupta,T.Prakash, V.Narayanan, A.Stephen, *J. Mol. Liq.*, 178, 88(2013).

[4]B. Khodadadi, *Iranian J. Catal.,* 7 (2), 111(2017).

[5]M. Nasrollahzadeh, T. Baran, M. Sajjadi, N.Y. Baran, M. Shokouhimehr, *J. Mater. Sci.: Mater.Electron.*, 3, 1 (2020).

[6]B. Khodadadi, M. Bordbar, M.Nasrollahzadeh, *J. Colloid Interface Sci.*, 490, 1(2017).

[7]M.Atarod, M. Nasrollahzadeh, S.M.Sajadi, *J. Colloid Interface Sci.*, 465, 249(2016).

[8]M.Nasrollahzadeh, S.M. Sajadi, M.Khalaj,*RSC Adv.*, 4(88), 47313(2014).

[9]B.Khodadadi, M. Bordbar, M.Nasrollahzadeh, J. *Colloid Interface Sci.*, 493, 85(2017).

[10]M. Nasrollahzadeh, R. Akbari, Z. Issaabadi, S. M. Sajadi, *Ceram. Int.*, *46*(2), 2093 (2020).

[11]B. Zahed, H. Hosseini-Monfared, *App. Surf. Sci.*, 328, 536 (2015).

[12]M.Zargar, A.A.Hamid, F.A.Bakar, M.N.Shamsudin, K.Shameli, , F.Jahanshiri, F.Farahani, *Molecules*, 16(8), 6667(2011).

[13]M.Atarod, M. Nasrollahzadeh, S.M.Sajadi,*J. Colloid Interface Sci.*, 462, 272(2016).

[14]M. Nasrollahzadeh, S.M. Sajadi, A. Hatamifard, *Appl. Catal. B: Environ.*, 191,209 (2016).

[15] B.Khodadadi, M.Bordbar, A. Yeganeh-Faal, M.Nasrollahzadeh, *J. Alloys Compd.*, 719, 82(2017).

[16]R.Sathyavathi,M.B. Krishna,S.V.Rao, R.Saritha, D.N. Rao, *Adv. Sci. Lett.*, 3(2), 138(2010).

[17]R.K.Petla, S.Vivekanandhan, M.Misra, A.K. Mohanty, N.Satyanarayana, *J. Biomater. Nanobiotechnol.*, 3(1), 14(2012).

[18]E. Aguirre-Hernández, A.L. Martínez, M.E.González-Trujano, J.Moreno, H. Vibrans, M.Soto-Hernández, *J. Ethnopharmacol.*, 109(1), 140(2007).

[19]H. Fluke, *Medicinal plants,* Tehran, Roozbahan publication (2000).

[20]A. Zargari, *Medicinal plants,* Tehran University Publications (1997).

[21]B. Khodadadi, *Nanochem. Res.,* 2(1), 140 (2017).

[22]M. Bordbar, N. Negahdar, M. Nasrollahzadeh, *Sep. Purif. Technol.*, 191,295 (2018).

[23]V. Manonmani, V. Juliet. *Int. Conf. Innov.Manag. Serv. IPEDR* (2011).

[24] A.Rostami-Vartooni, M.Nasrollahzadeh, M. Alizadeh, *J. Colloid Interface Sci.*, 470, 268(2016).

[25]H.Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, *Fuel*, 86(12-13), 1781 (2007).

[26]I. Demiral, S.C.Kul, *J. Anal. Appl. Pyrolysis*, 107, 17(2014).

[27]H.Zhao, J.H.Kwak, Z.C.Zhang, H.M.Brown, B.W. Arey, J.E.Holladay, *Carbohydr. Polym.*, 68(2), 235(2007).

[28]K. Das, D.Ray, N.R. Bandyopadhyay, S. Sengupta, *J. Polym. Environ.*, 18(3), 355(2010).

[29]B.K. Ghosh, S.Hazra, B.Naik, N.N. Ghosh, *Powder Technol.*, 269, 371(2015).

[30]P. Zhang, Y. Sui, C. Wang, Y. Wang, G. Cui, C. Wang, B. Liu, B. Zou, *Nanoscale*, 6(10), 5343(2014).