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ORIGINAL ARTICLE

Highly effective heterogeneous doxycycline stabilized silver nanocatalyst for the degradation of ibuprofen and paracetamol drugs

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Antimicrobial activity

Abstract In this work, a new doxycycline stabilized silver nanocatalyst (Dox-Ag (0) NPs) was synthesized in aqueous solution (green method) by one-pot simple synthetic method for the ultra-fast catalytic degradation of ibuprofen and paracetamol. The formation of the Dox-Ag (0) NPs was monitored using UV–Vis absorption spectroscopy which confirmed the formation of Dox-Ag (0) NPs by exciting the typical surface plasmon absorption maxima at 404 nm. Transmission electron microscopy (TEM) confirmed the spherical morphology and monodispersed Dox-Ag (0) NPs with particle size 6.87 ± 2.2 nm. The newly synthesized Dox-Ag (0) NPs had an excellent catalytic activity as a catalyst for the 100% degradation of ibuprofen and paracetamol, which was carried out in 60 s. The antimicrobial activities of this catalyst were also evaluated against Gram-negative bacteria *Mycoplasma hominis*, *Escherichia coli*, *Pseudomonas aeruginosa* and Gram-positive bacteria *Staphylococcus aureus*, *Micrococcus flavus* and *Micrococcus luteus* by the disk diffusion method. Whereas standard antibiotic showed no zone of inhibition, the Dox-Ag (0) NPs showed good inhibition zone. The antimicrobial results therefore reveal that newly synthesized Dox-Ag (0) NPs had a tremendous catalytic and antimicrobial activity as a catalyst. They were recovered easily from reaction medium and reused with enhanced catalytic potential seven times. The current findings are equally extendable for safeguarding the aquatic environment against the pollution caused by drugs and microbial activity via a facile, highly economical, rapid and efficient reduction/degradation method based on the catalytic potential of Dox-Ag (0) NPs.

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1. Introduction

Many of pharmaceutical residues in water, wastewater, sludge and sediments are considered "emerging contaminants" even at ng l^{-1} levels owing to their adverse health effects (Jones et al., 2002; Koh et al., 2008; Cooper et al., 2008). Analgesic drugs with more than 70 million global prescriptions annually

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are a special group of pharmaceuticals that exhibit "persistent toxic waste" character (Takagi et al., 2006; Mendez-Arriaga et al., 2008). Ibuprofen (IBP) and paracetamol are widely consumed analgesic drugs that are available without prescription and found commonly in domestic sewage as a persistent and environmentally stable pharmaceutical (Kummerer et al., 2004; Hirsch et al., 1999). Its existence in the water even at very small concentrations is a consequence of direct disposal from households and effluent discharge from municipal/industrial wastewater treatment plants (Nikolaou et al., 2007; Cooper et al., 2008). Moreover, multidrug resistance is a rising problem in the treatment of infectious diseases. The wide use of broad-spectrum antibiotics has led to resistance to traditional antimicrobial agents for many bacterial human pathogens and has created a major threat to the global health care. In this background, there is a need of a rapid, economic and highly effective method for the degradation of various pharmaceutical analgesic drugs as well as antimicrobial activity in wastewaters simultaneously.

Many processes have been implemented for the elimination of many pharmaceutical analgesics drugs such as conventional unit processes (Trovo et al., 2008; Mendez-Arriaga et al., 2008), advanced oxidation processes (AOPs) (Naddeo et al., 2010), hybrid processes such as sonocatalysis (using TiO_2, SiO_2, SnO_2) and sono-ozonolysis (Hartmann et al., 2008; Naddeo et al., 2009), ultrasound (Ince et al., 2001), but its ultimate partial degradation, high time and cost signifying the need for innovative processes to save energy, and having more safer operations together with avoiding use of organic solvents. Furthermore, aqueous phase removal percentage is often used as the only parameter for elimination efficiencies of pharmaceutical drugs in wastewater treatment plant (Minh et al., 2010; Chong et al., 2010). In fact an aqueous removal percentage cannot comprehensively evaluate the elimination of pharmaceutical drugs in wastewater treatment plant, since some pharmaceutical drugs have a tendency to partition into the sludge (Jia et al., 2012). Mass balance approach would be an effective way to understand the fate of pharmaceutical drugs in wastewater treatment plant and their mass loading to the receiving environment (Zhou et al., 2013; Garcia-Segura et al., 2012). Elimination of organic compounds in the environment is the result of different processes. These processes can be biotic ones, i.e. biodegradation by bacteria and fungi. Non-biotic elimination processes are sorption, hydrolysis, photo-lysis, oxidation and degradation.

Recently, nanotechnology has been developed quickly in various fields such as in medicine, optics biology and electronics. Elemental or compound inorganic nanoparticles exhibit exclusive physical and chemical characteristics, creation possible to the development of novel and remarkable applications in catalysis (Junejo et al., 2013a,b), antimicrobial properties (Pang et al., 2011), drug delivery system (Kreuter, 2014), sensors (Zulfiqar et al., 2011, 2012) and antibacterial materials (Zhao et al., 2013; Pang et al., 2009). One of the interesting studies of nanoparticles is of silver (Ag) nanoparticles because the antimicrobial properties of Ag NPs are considered non-toxic and environmentally friendly in biomedical applications. A number of methods are existing for the synthesis of Ag (0) NPs; hydrothermal (Aksomaityte et al., 2013), sonochemical (Darroudi et al., 2012), electron beam irradiation (Kim et al., 2012), extraction of leave (Kouvaris et al., 2012), seed extract methods (Jagtap and Bapat, 2013), and so on. However, the recovery of noble metal nanoparticles from such stabilizers-containing systems is not easy. As compared to these synthesis routes, one of the recyclable, effective, green, cheaper and simplest methods for the synthesis of Ag (0) NPs is the use of antibiotic as reducing and capping agent. Previously, silver nanoparticles were synthesized and used as a catalyst for the degradation some nitro-compounds (Junejo et al., 2013). Whereas in the present work we applied analgesic drugs as model compound to monitor the catalytic efficiency of fabricated Dox-Ag (0) NPs.

In this work, we report a very simple one-pot method for the synthesis of silver nanocatalysts by green and biological method using doxycycline antibiotic and their effective application as heterogeneous, recoverable and reusable catalyst for remarkably faster and complete degradation of ibuprofen and paracetamol drugs. The entire research work is based on excellent economy of the process in terms of using cheaper chemicals, facile and simpler synthesis of catalyst, with shorter time for product formation (quicker procedure) and easy recovery and recycle of catalyst. Moreover, the Dox-Ag (0) NPs were also evaluated for antimicrobial activity against some Gram-positive and Gram-negative pathogens.

2. Materials and methods

2.1. Chemicals

All chemicals and reagents used in this study were of high purity and Analytical grade. NaOH, methanol and $AgNO_3$ were purchased from Merck. Standards of all antibiotic and analgesics such as doxycycline, Ibuprofen and paracetamol were purchased from Fluka.

2.2. Instrumentations

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku SmartLab Diffractometer operated at 40 kV and 35 mA using Cu Ka radiation. High resolution transmission electron microscopy (HRTEM) analysis was performed using a JEOL JEM 2100 microscope. A drop of diluted sample in alcohol was dropped on a TEM grid.

Fourier transform infrared (FT-IR) spectra were recorded in transmission mode with a Bruker ATR-FT-IR spectrometer. FT-IR spectra in the range 4000–400 cm^{-1} were recorded in order to investigate the nature of the chemical bonds formed.

The UV–Vis measurement was done using a Shimadzu UV–Vis 2600.

2.3. Synthesis of doxycycline-derived Ag (0) NPs

For a typical synthesis, 0.02 ml of doxycycline standard solution was mixed with 0.03 ml of 0.1 M of $AgNO_3$ solution to added 0.01 ml of NaOH solution as Dox-Ag (0) NPs accelerating agent observed by measuring the UV–Vis spectra of the solution. Here we report the use of doxycycline as reducing and capping agent for fabrication of silver nanoparticles.

2.4. Degradation study of Dox-Ag (0) NPs

The catalytic effect of silver nanoparticles was monitored for the analgesics such as ibuprofen and paracetamol. The catalytic degradation of these analgesics was carried out in a

standard quartz cell with 1 cm path length and about 3 ml volume containing Dox-Ag (0) NPs encumbered pieces of glass. The reaction was performed in the presence of small quantity of $NaBH_4$ only and Dox-Ag (0) NPs. Under optimized conditions, the catalytic reaction procedures were as follows for ibuprofen and paracetamol. The amount of individual reagent was taken as 0.2 ml from 10 mg/L analgesic which was taken in quartz cell followed by the addition of 2.80 ml milli Q water and then by 0.1 ml of 0.02 M $NaBH_4$. Carefully and immediately after the addition of 0.9 mg, Dox-Ag (0) NPs were immobilized on pieces of glass and put in quartz cell for the degradation process. The absorption spectra were monitored by a UV/Vis spectrophotometer.

2.5. Antimicrobial activity

All the compounds have been screened for antimicrobial activity using disk diffusion method by measuring the inhibition zone in mm against *Mycoplasma hominis* ATCC 27545, *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* ATCC 27853 (as Gram-negative bacteria) and *Micrococcus flavus* ATCC 10786, *Micrococcus luteus* ATCC 53598, and *Staphylococcus aureus* ATCC 25923 (as Gram-positive bacteria) in Tryptic soy agar (BDDifcoTM) medium. The sterilized agar media were poured into Petriplates and allowed to solidify. On the surface of the media fresh microorganism cultures (108 CFU ml^{-1}, CFU, colony-forming units) were spread with the help of sterilized L-shaped glass loop. A cylinder glass pipette of 5 mm diameter (pre-sterilized) was used to bore cavities. Both the standard antibiotic doxycycline and Dox-Ag (0) NPs (0.10 mg/ml each) were placed serially in the cavities with the help of micro-pipette and allowed to diffuse for 1 h. The standard antibiotic doxycycline was used as controls in each replicate. These plates were incubated at 37 °C for 18–24 h for antibacterial activity. The inhibition zone of the compounds was measured and evaluated. Each prepared sample was measured in five replicates.

2.6. Recovery and reuse of Dox-Ag (0) NPs as a catalyst

After completion of catalytic reaction, the broken pieces containing immobilized Dox-Ag (0) NPs were taken out of the cell, washed 6 times by deionized water and dried under N2 as before. These glass pieces having Dox-Ag (0) NPs were reused in a fresh analgesics solution for checking its second performance as a catalyst in a solution prepared by the procedure given in Section 2.3. Similar process was repeated 6 times to see any change in the performance of catalytic activity of reused Dox-Ag (0) NPs.

3. Results and discussions

3.1. UV–Visible study

UV–visible spectroscopy is a key technique to determine the formation and stabilization of aqueous metal nanoparticles. So UV–Vis spectrometry was performed to know the effect of concentration of silver nitrate, doxycycline, and NaOH in solution. The UV–Vis spectra were recorded after 1 h of mixing the solution, the color of solution was yellow, which is the indication of synthesized Dox-Ag (0) NPs (Junejo et al., 2013a,b). UV–Vis spectra showed absorbance peak of Dox-Ag (0) NPs at 404 nm as shown in Fig. 1. The time study of Dox-Ag (0) NPs was observed until 6 month, the wavelength was shifted to words blue shift from 408 to 404 nm. The λ_{max} after formation of one hour of Dox-Ag (0) NPs was at 408 nm which was slowly increased in absorbance and shifted to words blue shift after 24 h until one weak it reached at 405 nm. Finally, the λ_{max} was at 404 nm after six months and the color of the solution was dark yellow, it shows the stability with blue shifted formation of Dox-Ag (0) NPs (Junejo et al., 2014a,b).

3.2. FT-IR analysis

The FTIR study was used to disclose the surface interaction of doxycycline standard to doxycycline stabilized Ag (0) NPs and the results are displayed in Fig. 2.

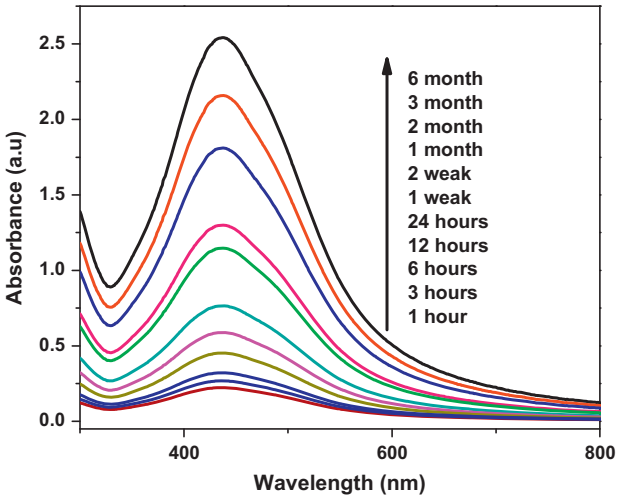

Figure 1 The UV–vis spectra recorded for time study of Dox-Ag (0) NPs samples showing stable absorption band at 404 nm after 1 h to till 6 months successively.

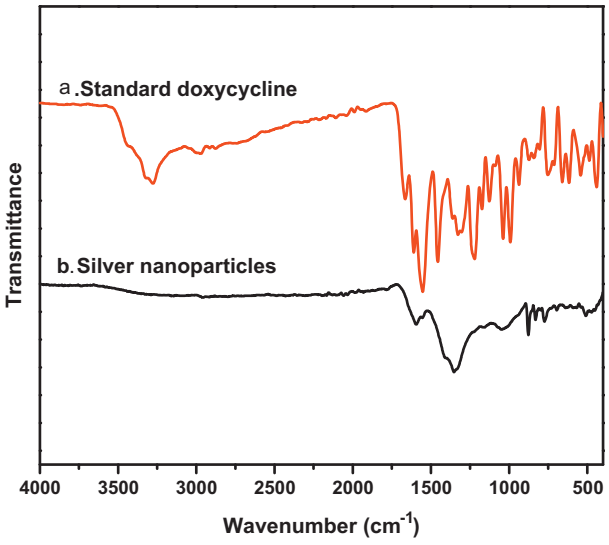

Figure 2 FTIR Spectra of doxycycline antibiotic (red) and silver nanoparticles (black).

The FT-IR spectra of doxycycline standard and Dox-Ag (0) NPs were presented in Fig. 2 (red) and (black) respectively. FT-IR spectra doxycycline standard showed the two broad and strong signals at 1666 cm^{-1} and 1390 cm^{-1} which can be assigned to hydroxyl groups (Zha et al., 2013; Hobart et al., 1986) (Fig. 2a). Related peaks have been seen at 1651 cm^{-1} and 1382 cm^{-1} by other workers (Janardhanan et al., 2009). That one broad band above 3000 cm^{-1} is present with no changes corresponding to the presence of O–H (3400 cm^{-1}) and N–H (3166 cm^{-1}) stretching frequencies experienced by NH_2 groups (Kalwar et al., 2013; Hassan et al., 2012). The broad band at 3166 cm^{-1}, 3036 cm^{-1} and 2966 cm^{-1} represents the N–H and O–H stretching frequencies (Lee et al., 2007). On the other hand, the bands of the C–H and N–H in-plane bend vibrations are at 1450 cm^{-1} (Birsöz et al., 2010; Hirsch et al., 1999), but in our case this band appears at 1340 cm^{-1} which shows slight shift of the band in sample (Fig. 2b).

3.3. HRTEM study

The size and morphology of the synthesized Dox-Ag (0) NPs were confirmed by HRTEM analysis. It was observed that small size and monodispersed Dox-Ag (0) NPs were synthesized by the help of antibiotic. The particle size of Dox-Ag (0) NPs was calculated as 10.87 ± 2.2 nm and spherical in shape as shown in Fig. 3. A number of methods have been reported for the synthesis of Dox-Ag (0) NPs and characterized by TEM (Junejo et al., 2013a,b; Junejo et al., 2014a,b). Typical TEM images and a corresponding histogram for Dox-Ag (0) NPs are given in Fig. 3.

3.4. XRD study

XRD pattern of Dox-Ag (0) NPs obtained using solid product as the result of drying of Dox-Ag (0) NPs (Fig. 4). Nearly 2 mg of dark black solid sample was analyzed Dox-Ag (0) NPs with face centered cubic (fcc) structure. The average crystallite size of the product was calculated using Line profile fitting (Wejrzanowski et al., 2006), and found as 11 ± 3 nm for observed 3 peaks with the following miller indices: (1 1 0), (2 0 0), (2 2 0) (Peng et al., 2013). These observed miller indices

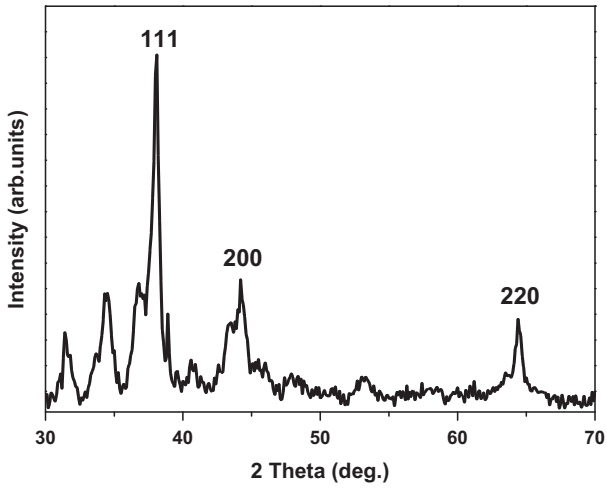

Figure 4 XRD powder pattern of doxycycline derived Ag (0) NPs.

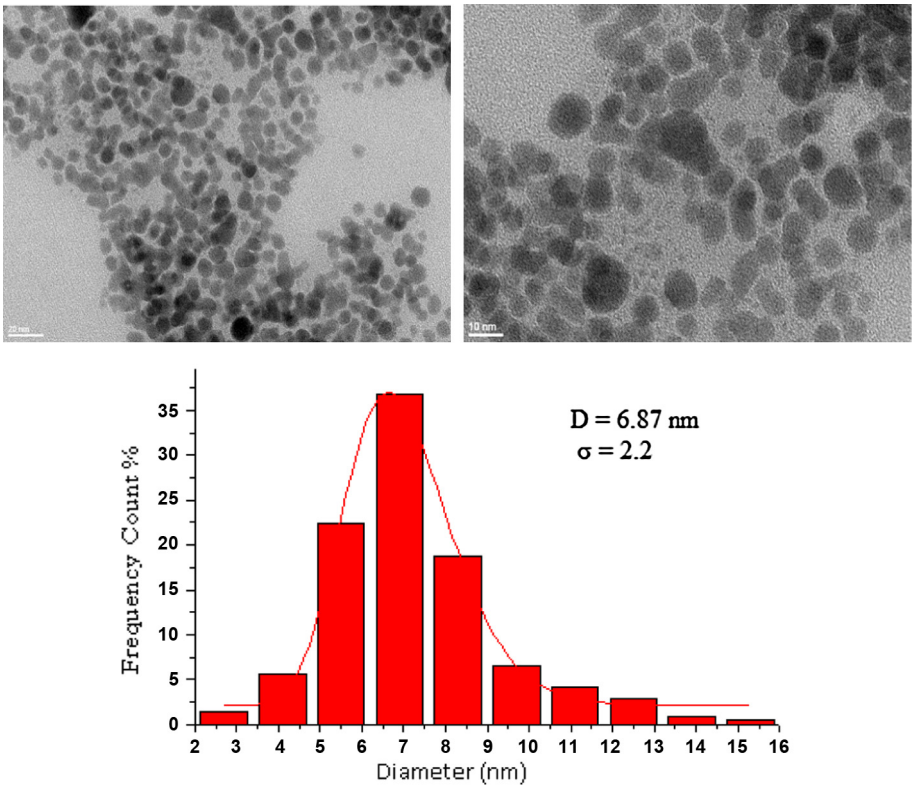

Figure 3 HRTEM images and particle size distribution diagram of doxycycline derived Ag (0) NPs.

matched with the ICDD card no. 99-200-4306 and confirm the crystalline nature of Amo-Ag (0) NPs (Junejo et al., 2013a,b).

3.5. Heterogeneous degradation study of Dox-Ag (0) NPs

UV–vis spectral studies were carried out to check the performance of Dox-Ag (0) NPs for the catalytic reduction/degradation of ibuprofen and paracetamol as a model reaction in the presence of 0.02 M $NaBH_4$ as illustrated in Figs. 5 and 6.

3.5.1. Heterogeneous catalysis of ibuprofen

To explore the efficiency of Dox-Ag (0) NPs in aqueous system for the degradation of ibuprofen (10 mg/L) that showed the surface plasmon resonance at 225 and 263 nm. Fig. 5 describes various aspects of catalytic degradation of ibuprofen in the presence/absence of Dox-Ag (0) NPs and $NaBH_4$ using UV–vis spectrometry as diagnostic tool. Fig. 5(a) tells about the effect of 0.02 M $NaBH_4$ on the degradation of ibuprofen in the absence of Dox-Ag (0) NPs. It reduces ibuprofen up to small extent (5.7%). Fig. 5(b) shows the degradation of ibuprofen (10 mg/L) using different quantities of Dox-Ag (0) NPs (0.15–0.9 mg). This demonstrates that increase in the amount of Dox-Ag (0) NPs favors to enhance the rate of reaction exponentially by providing more surface area and hence availability of more active sites for catalytic degradation of ibuprofen. The reaction was completed in 60 s under UV–vis irradiations (Fig. 5c). The kinetics of heterogeneous catalysis is best pronounced in terms of Langmuir–Hinshelwood (L–H) model (Houas et al., 2001), with following mathematical expression (Sun et al., 2002):

$$-\frac{dc}{dt}\frac{k_{L-H}k_{ad}C}{1+k_{ad}C} \quad (1)$$

where k_{L-H} denotes reaction rate constant, k_{ad} represents adsorption coefficient of pesticide on catalyst, and C is the variable concentration during any time t. Since the value of

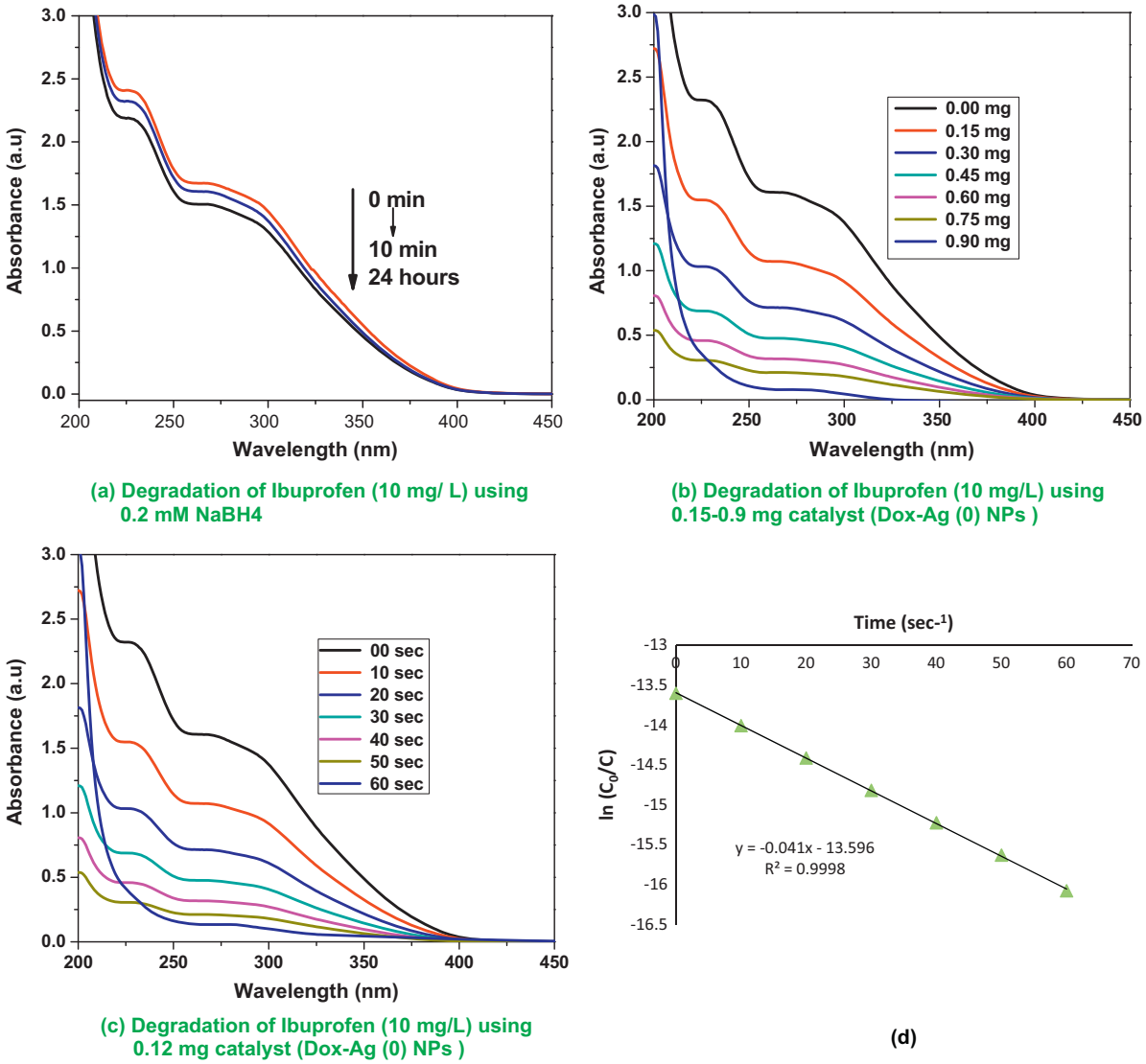

Figure 5 Degradation of ibuprofen drug; (a) degradation in the presence of $NaBH_4$ only, (b) at fixed concentration of ibuprofen drug (10 mg/L) degradation with varying amounts 0.15–0.9 mg Dox-Ag (0) NPs and 0.02 M $NaBH_4$, (c) at fixed concentration of ibuprofen drug (10 mg/L) degradation at fixed amount of Dox-Ag (0) NPs (0.9 mg) and 0.02 M $NaBH_4$ (d) linear regression for pseudo-first order kinetics for the reductive degradation of ibuprofen drug.

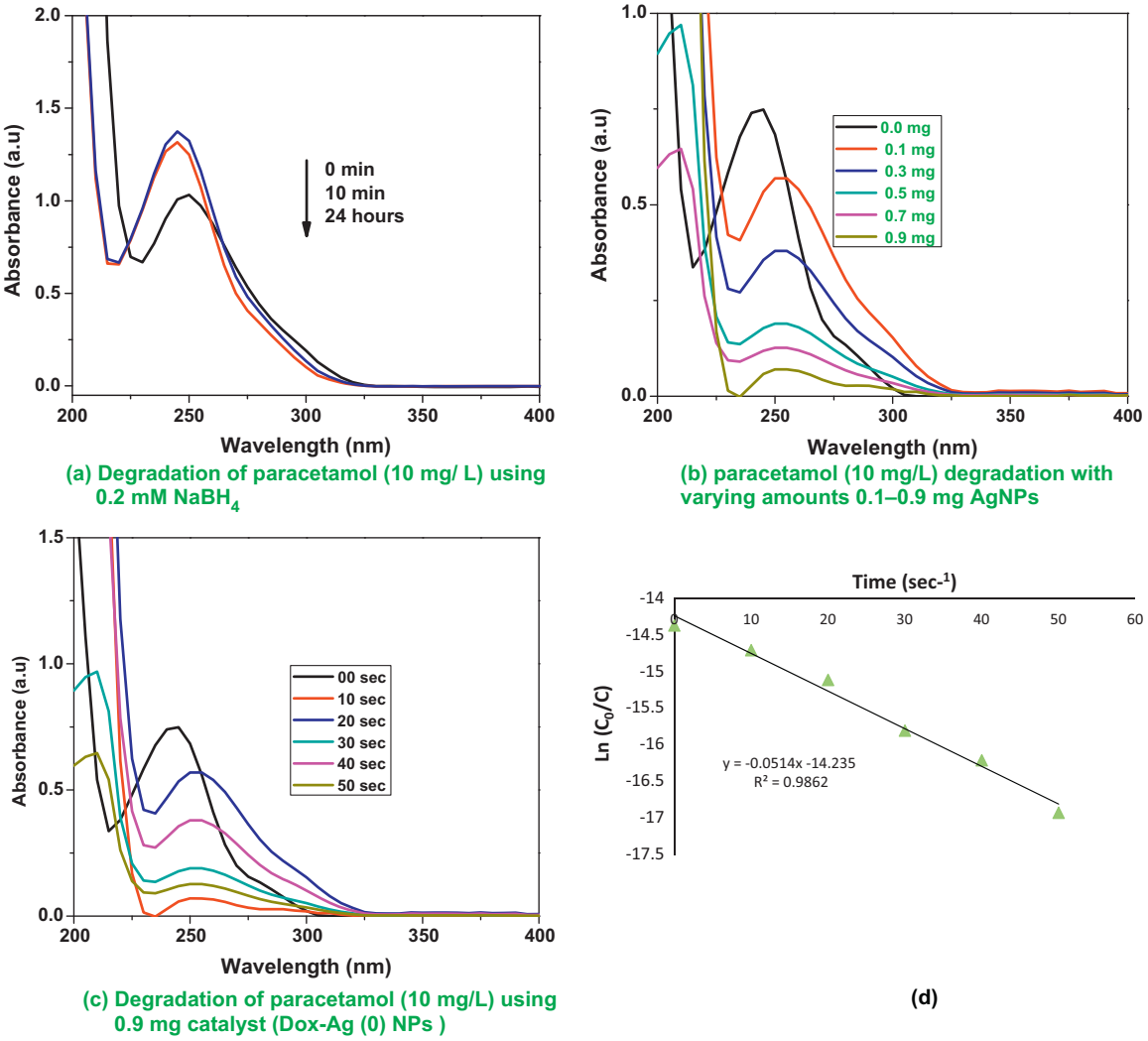

Figure 6 Degradation of paracetamol drug; (a) degradation in the presence of 0.02 M $NaBH_4$ only, (b) at fixed concentration of paracetamol drug (10 mg/L) degradation with varying amounts 0.1–0.9 mg Dox-Ag (0) NPs and 0.02 M $NaBH_4$, (c) at fixed concentration of paracetamol drug (10 mg/L) degradation at fixed amount of Dox-Ag (0) NPs (0.9 mg) and 0.02 M $NaBH_4$ (d) linear regression for pseudo-first order kinetics for the reductive degradation of paracetamol drug.

k ad C for pseudo-first order reaction is negligible compared to 1 in denominator, thus integrating Eq. (1) gives:

$$In\left(\frac{C_o}{C}\right) = k_{L-H}k_{ad}t = -kt \tag{2}$$

Here C_o denotes initial concentration and $k = k_{L-H}\,k_{ad}$ represents pseudo-first order reaction rate constant.

Fig. 5(d) shows the scatter plot between the natural logarithm of ratio of initial concentration of ibuprofen and the relative remaining concentration after degradation and the corresponding reaction time (s). Linear regression analysis depicted the reaction rate constant (k) determined as 0.10 s^{-1} and corresponding R^2 value of 0.9998 confirmed the kinetics of the degradation to be pseudo-first-order in nature.

3.5.2. Heterogeneous degradation of paracetamol

The catalytic activity of newly synthesized Dox-Ag (0) NPs was also investigated for the degradation of paracetamol (10 mg/L) that showed the surface plasmon resonance at 245 nm. Fig. 6 describes various aspects of catalytic degradation of paracetamol in the presence/absence of Dox-Ag (0) NPs and $NaBH_4$ using UV–vis spectrometry as diagnostic tool. Fig. 6 (a) tells about the effect of 0.02 M $NaBH_4$ on the degradation of paracetamol in the absence of Dox-Ag (0) NPs. It reduces ibuprofen up to small extent (5.4%). Fig. 6(b) shows the degradation of paracetamol (10 mg/L) using different quantities of Dox-Ag (0) NPs (0.1–0.9 mg). This demonstrates that increase in the amount of Dox-Ag (0) NPs favors to enhance the rate of reaction exponentially by providing more surface area and hence availability of more active sites for catalytic degradation of paracetamol. The reaction was completed in 50 s under UV–vis irradiations (Fig. 6c). Fig. 6(d) shows the scatter plot between the natural logarithm of ratio of initial concentration of paracetamol and the relative remaining concentration after degradation and the corresponding reaction time (s). Linear regression analysis depicted the reaction rate constant (k) determined as 0.10 s^{-1} and corresponding R^2 value of 0.986 confirmed the

kinetics of the degradation to be pseudo-first-order in nature. So we can comment that these nanocatalysts are highly dynamic for the mentioned degradation processes.

Generally, the degradation of ibuprofen and paracetamol using Dox-Ag (0) NPs in the presence of $NaBH_4$ is an adsorp tion–degradation–desorption phenomenon. At the initial stage, the ibuprofen and paracetamol molecules and BH_4^{-1} ions would get adsorbed onto the surface of the Dox-Ag (0) NPs where reductive degradation takes place via electron transfer process between the ibuprofen, paracetamol and BH_4^{-1}. The catalyst Dox-Ag (0) NPs is believed to serves as an electron transfer relay in this situation which concurrently accelerates the electron transfer rate and decreases the activation energy of reaction. Such rapid electron transfer sponsored by the large surface area of Dox-Ag (0) NPs leads to complete degradation of ibuprofen and paracetamol molecules simultaneously with the recovery of the catalyst as the degraded molecules leave the surface of Dox-Ag (0) NPs and diffuse into solution.

Some researchers have previously done the degradation of ibuprofen and paracetamol drugs (Machado et al., 2013; Choina et al., 2014a,b; Sheng-Peng et al., 2013; Kang et al., 2014). However, there are several attracting advantages to our nanocatalyst over earlier reported approaches. This nanocatalyst reduces target compounds in a single reaction (Figs. 5 and 6) and do not require any additional processing aids such as unique equipment or chemicals. This particular method decreases the cost drastically for performing this analysis on a large scale. The degradation time of this assay on reference samples was so less which indicated this method to be highly effective (Figs. 5 and 6). As compared to our study, researchers showed partial degradation or much more time for the degradation of ibuprofen and paracetamol drugs (Machado et al., 2013; Choina et al., 2014a,b; Sheng-Peng et al., 2013; Kang et al., 2014). Thus our method is much more attractive as compared to others due to its effectiveness. These distinctive characteristic paves way and also acts as a reference for the degradation of other toxic species, such as antibiotics, analgesics, dyes, and nitro-compounds in wastewaters. Therefore, the high effectiveness, low economy and recycling of this nanocatalyst suggested that this method is feasible and ideal for ultra-rapid degradation of ibuprofen and paracetamol drugs to control the risk of various pollutants in wastewaters.

3.6. Antimicrobial activity

Applying the disk diffusion method it was observed that standard antibiotic such as doxycycline has some inhibitory action while newly synthesized Dox-Ag (0) NPs have excellent inhibitory action on the six microorganisms used for investigation, *M. hominis* ATCC 27545, *E. coli* ATCC 25922, *P. aeruginosa* ATCC 27853, *M. flavus* ATCC 10786, *M. luteus* ATCC 53598, and *S. aureus* ATCC 25923. The experiments were done in comparison with silver ion, standard antibiotic doxycycline and Dox-Ag (0) NPs (using negative control (ddH_2O) by measuring inhibition zone diameters and the experimental results are shown in Fig. 7 and Table 1. Dox-Ag (0) NPs clearly showed antimicrobial ability against tested microorganisms (Fig. 7). The zones around the bore cavities on the agar plates were clearly observed. Therefore, our Dox-Ag (0) NPs presented the best antimicrobial activity against *M. hominis*,

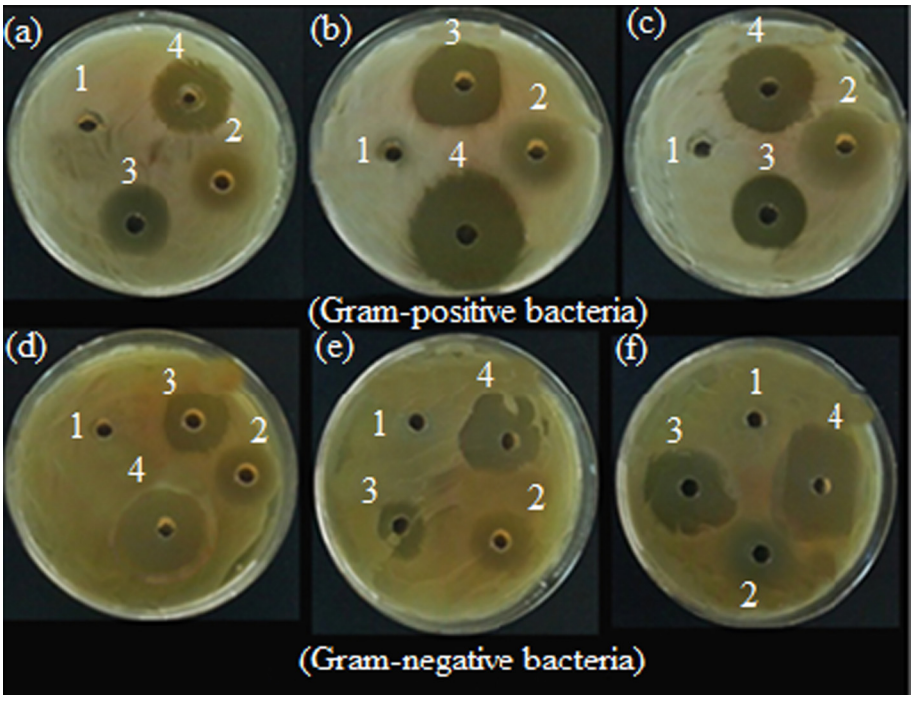

Figure 7 The antimicrobial activity of standard antibiotic (doxycycline) and Doxy-Ag (0) NPs against Gram-negative bacteria (a) *Mycoplasma hominis*, (b) *Escherichia coli*, (c) *Pseudomonas aeruginosa)* and Gram-positive bacteria (d) *Staphylococcus aureus*, (e) *Micrococcus flavus* and (f) *Micrococcus luteus)* by disk diffusion method. 1: Negative control (ddH_2O), 2: silver ion, 3: doxycycline, 4: doxycycline stabilized silver nanoparticles.

Table 1 Antimicrobial activity of the prepared samples on the microorganisms tested by disk diffusion method.

Microorganims	Diameter of zone of inhibition (mm)			
	nc	Ag+	DOXY	Doxy-AgNPs
E. coli	0	9 ± 1.3	23 ± 1.4	38 ± 1.6
M. hominis	0	10 ± 0.7	17 ± 1.7	31 ± 1.3
P. aeruginosa	0	11 ± 1.2	18 ± 0.5	33 ± 1.1
M. flavus	0	8 ± 1.7	16 ± 1.3	32 ± 0.8
M. luteus	0	7 ± 0.8	14 ± 1.4	28 ± 1.5
S. aureus	0	9 ± 00	20 ± 0.9	37 ± 1.6

Dox-AgNPs: doxycycline silver nanoparticles), DOXY: doxycycline, nc: negative control, Ag+: silver ion.

E. coli, *P. aeruginosa*, *M. flavus*, *M. luteus*, and *S. aureus* pathogens. We believe that in near future, these Ag (0) NPs could be tremendously used as anticancerious, antiviral, antiprotozoal, and antiarthropod agents due to high effectiveness, low economy and recycling characteristics.

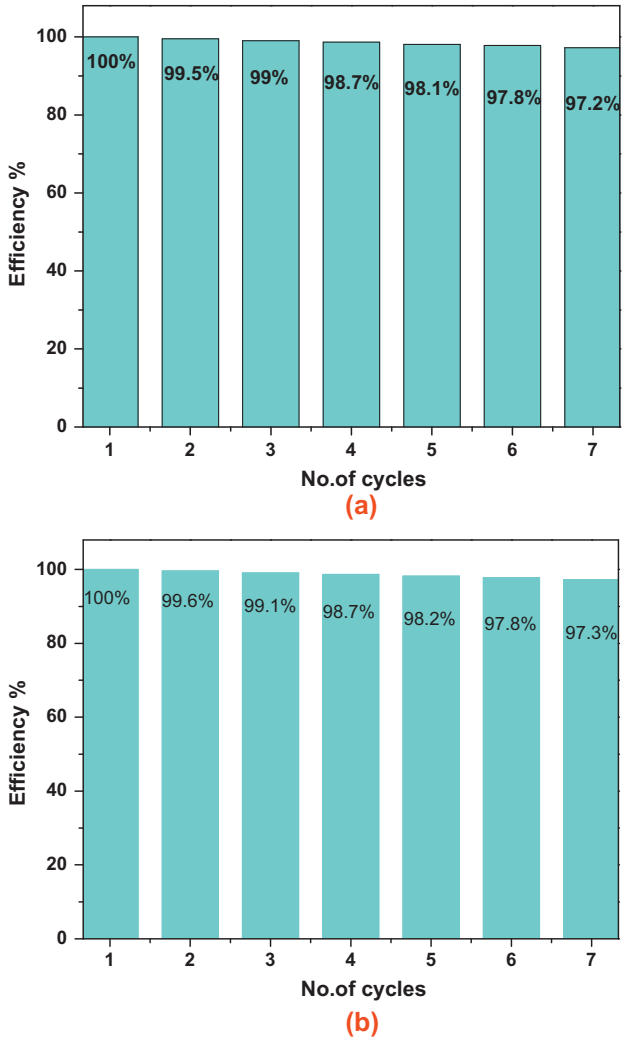

Figure 8 The efficiency of Dox-Ag (0) NPs for the degradation of (a) ibuprofen and (b) paracetamol.

3.7. Recycling and reuse of Dox-Ag (0) NPs

Glass supported Dox-Ag (0) NPs (0.9 mg) were removed washed sequentially and reused 7 times for catalytic degradation of these analgesic drugs. The reducing potential of recovered and reused Dox-Ag (0) NPs for ibuprofen and paracetamol was calculated, which is given (Fig. 8a and b). The slow deactivation of catalysts Dox-Ag (0) NPs also confirms that poisoning of catalysts is insignificant. Compared with other metal nanoparticles which are generally oxidized on the surface in alkali condition leading to activity loss (Grätzel and Frank, 1982), the Ag nanocatalyst developed in this work was stable and exhibited excellent catalytic ability. This work promises a sound environmental safety for several water based systems against analgesics pollution.

4. Conclusion

The study provides a simple, cost effective and efficient route toward small, spherical, highly dispersed Dox-Ag (0) NPs. These NPs have been synthesized by the help of antibiotic (doxycycline) as a reducing agent as well as capping and stabilizing agent for the degradation of analgesic drugs. These nanoparticles are stable in aqueous solution for a very long time more than six months without any aggregation. The synthesized nanoparticles were confirmed by many characterization techniques. UV–Vis spectrophotometer was used as first characterization. The interaction of bonding formation was confirmed by FT-IR spectrophotometer. Morphology of Dox-Ag (0) NPs was observed by HRTEM analysis and crystalline pattern was confirmed by powder XRD. The synthesized Dox-Ag (0) NPs have proved as the remarkably efficient catalysts with enhanced rate of degradation for ibuprofen and paracetamol. This study provides an economical solution to protect aquatic environment in terms of time saving and can be equally useful for the degradation of several other analgesic drugs. The present study is a first report about the use of Dox-Ag (0) NPs as degradation catalysts for different analgesic drugs and probable to open new doors for their further catalytic applications in analogous and other experiments of environmental and industrial importance.

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