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ORIGINAL ARTICLE

Biofabrication of platinum nanoparticles using *Fumariae herba* extract and their catalytic properties

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Abstract Due to the increasing popularity of using plant extract in the synthesis of nanoparticles, this study presented the synthesis of platinum nanoparticles using *Fumariae herba* extract**.** The formation of platinum nanoparticles was confirmed by UV–visible spectroscopy (UV–Vis), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with EDS profile. Transmission electron micrograph presented the hexagonal and pentagonal shape of the synthesized nanoparticles sized about 30 nm. Moreover, platinum nanoparticles presented good catalytic properties in the reduction of methylene blue and crystal violet.

1. Introduction

Nanoparticles are a special group of materials with a broad range of applications. They usually have a large surface area, which is chemically more reactive than their fine structural analogues (Ajitha et al., 2015). Metal nanoparticles have potential applications in various areas, such as electronics, cosmetics, coatings, packaging and biotechnology. Various physical and chemical processes have been used in the synthesis of nanoparticles; however, these processes generate a large amount of hazardous by-products (Thakkar et al., 2010). The use of biological organisms, such as microorganisms and plant extracts, could be an alternative to the conventional chemical and physical methods for the synthesis of nanoparticles in a clean, non-toxic, ecologically sound and environmentally friendly manner (Wang et al., 2009). Therefore, it is necessary to develop clean, biocompatible and eco-friendly methods for the synthesis of nanoparticles. Also, the synthesis of nanoparticles using plant extracts could be an alternative to the production of nanoparticles. Biological methods for the synthesis of platinum nanoparticles with the use of plant materials have not been widely exploited. According to the literature, green synthesis of platinum nanoparticles employing plants has been carried out using *Ocimum sanctum leaf extract* (Soundarrajan et al., 2012), *Diospyros kaki* (Song et al., 2010), *Cacumen platycladi* (Zheng et al., 2013) *Anacardium occidentale* (Sheny et al., 2013), *Punica granatum* (Dauthal and

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Mukhopadhyay, 2015), *Cochlospermum gossypium* (Vinod et al., 2011), *Bidens Tripartitus* (Dobrucka, 2015) and honey (Venu et al., 2011) as reducing agents.

Fumaria officinalis L is a plant that grows in Asia and Europe. In Poland, it can be found on the lowlands and in the lower parts of the mountains. *Fumariae herba*, common fumitory herb, consists of dried, above-ground parts of *Fumaria officinalis* L. (fam. *Fumariaceae*). Taking into consideration that the antioxidant property of *Fumariae herba* may be caused by alkaloids and polyphenolic compounds, which are major chemical constituents in this study, the synthesis of platinum nanoparticles was conducted using *F herba*.

2. Materials and methods

2.1. Materials

Potassium hexachloroplatinate (IV) K_2PtCl_6 98%, crystal violet and methylene blue were purchased from Sigma–Aldrich (Poland). Double-sterilized Milli-Q water was used throughout the experiments. *Fumariae herba* were collected from Lubusz region (Poland).

2.2. Synthesis of platinum nanoparticles

4 g dried and powdered herbs were put into 180 ml of double distilled water. The mix was kept at 90 °C for 45 min with vigorous magnetic stirring. Fresh extract was used immediately in all studies after filtration through Whatman's No. 1 filter paper. Then, 10 ml of the prepared extract was collected and then was added 0.004 g of K_2PtCl_6. The solution was mixed under magnetic stirring for 4 h at the temperature of 50 °C. The color changed from yellow to brown, which indicated the formation of platinum nanoparticles.

2.3. Characterization of platinum nanoparticles

The sample of green synthesized platinum nanoparticles obtained with the use of *Fumariae herba* was measured using UV–Visible spectrophotometry. The optical property of platinum nanoparticles was analyzed via ultraviolet and visible absorption spectroscopy (spectrophotometer Cary E 500) in the range 250–600 nm.

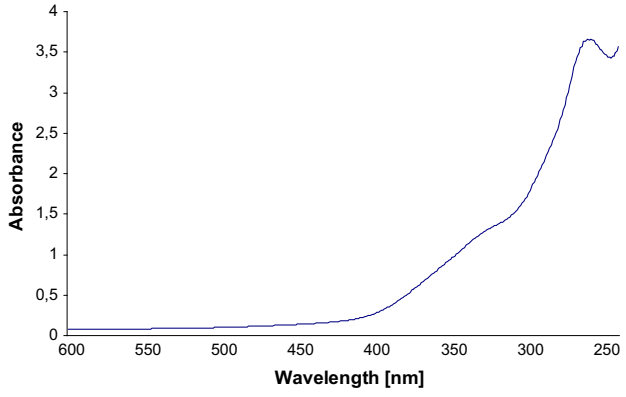

Figure 1 UV–Visible spectra of platinum nanoaprticles synthesized using *F. herba*.

FTIR spectra of the samples were measured using Perkin-Elmer Spectrum One instrument in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets. Powder samples for the FTIR were prepared similarly as for powder diffraction measurements.

The shape, size and microstructures of the synthesized platinum nanoparticles were characterized using a Transmission electron microscope JEOL JEM 1200 EXII operating at 200 kV. The morphology of the green synthesized platinum nanoparticles was examined by means of scanning electron microscopy (SU3500, Hitachi with spectral imaging system Thermo Scientific NSS (EDS), the tape of detector (BSE-3D), acceleration voltage (15 kV), working distance (11.6 mm), the pressure (40 Pa)).

2.4. Catalytic properties of platinum nanoparticles

In this study, the catalytic activity of the synthesized platinum nanoparticles was evaluated using UV–Vis spectrophotometer to monitor the absorbance peaks. For this purpose, the study used the spectrophotometer Cary E 500. The absorbance was measured in the range of 350–800 nm. The catalytic activity of the synthesized platinum nanoparticles was demonstrated by degrading methylene blue (MB) and crystal violet (CV). The two dyes were used in this study due to the fact that they are organic. Furthermore, application of the dyes can present the catalytic changes. At first, there were taken readings of samples of the aqueous solution of methylene blue (MB) and crystal violet (CV) with the volume of (1×10^{-4} M). Then, 4 ml of MB (1×10^{-4} M) or CV (1×10^{-4} M), 0.5 ml of *F. herba* water extract and 3 ml of Milli Q water were analyzed. The next stage of reaction involved preparing a mix of 4 ml of MB or CV (1×10^{-4} M), 0.5 ml of *F. herba* water extract, 1 ml of the prepared solution of Pt nanoparticles and 2 ml of Milli Q water. For this solution, the readings of absorbance were made at different time intervals: 3, 5, 7, 9, 11, 12 and 15 min. The results are presented in Section 3.5.

3. Results and discussion

3.1. UV–VIS analysis

UV–Vis spectroscopy is one of important techniques to determine the formation and stability of metal nanoparticles in aqueous solution. The absorbance was measured after the solution had been stirred magnetically for 4 h at the temperature of 50 °C. During the 4-h stirring period, the solution changed its color from light beige to brown, which suggested that Pt^{4+} ions were completely reduced to Pt^0 nanoparticles. Fig. 1 presents the UV–Vis spectra of the green synthesized platinum nanoparticles, depicting a single maximum absorption band at 259 nm. The strong peak at 259 nm indicates the complete reduction of Pt ions (Sheny et al., 2013). The further analysis included the assessment of the catalytic activity of the obtained nanoparticles (see Fig. 4).

3.2. FT IR spectra

Fourier Transform Infrared Spectroscopy was used to identify the biomolecules which are responsible for obtaining the Pt

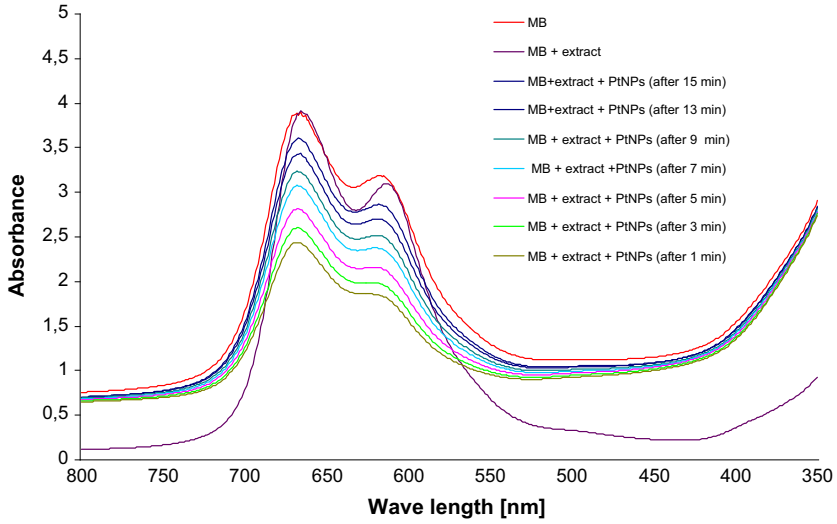

Figure 2 UV–Vis absorption spectra of methylene blue reduction by *F. herba* in the presence of platinum nanoparticles.

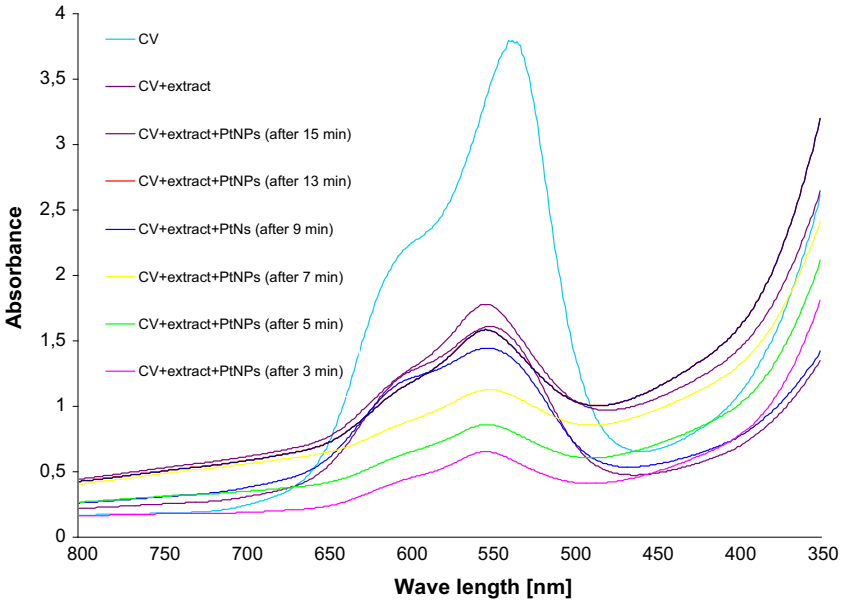

Figure 3 UV–Vis absorption spectra of crystal violet reduction by *F. herba* in the presence of platinum nanoparticles.

nanoparticles. The FTIR spectra of the sample showed the major absorption bands at 3311 cm^{-1}, 2110 cm^{-1}, 1634 cm^{-1}, 607 cm^{-1} and 387 cm^{-1}. The peak which appeared at 3311 cm^{-1} is related to O—H stretching (intramolecular hydrogen bonded OH). The band which appeared at 2110 cm^{-1} may indicate the presence of alkynes group. The most intense band at 1634 cm^{-1} represents C═O vibrations, typical for the structure of flavonoids. The peak appearing at 607 cm^{-1} is due to the presence of the alkyl halides stretching. The band at 387 cm^{-1} is attributed to the deformation vibration of C¬C in polymer chains. These findings are supported by some previous reports that evaluated the profile of compounds (such as alkaloids, flavonoid compounds and phenolic acids) present in *F. herba* extract. It has been shown that *F. herb* contains free phenolic acids such as p-coumaric acid, sinapic acid (Ivanov et al., 2014), ferulic acid (Soušek et al., 1999), caffeic acid (Bradley, 1992; Ivanov et al., 2014; Soušek et al., 1999) and chlorogenic acid (Bradley, 1992; Soušek et al., 1999). The biological activities of *Fumariae herba* are mainly associated with the presence of isoquinoline alkaloids. The dominant alkaloid is protopine (content 0.08–0.40%) (Bradley, 1992; Wichtl, 2004). In the herb of *Fumaria officinalis* L., there were also found flavonoid compounds such as quercetin-3,7-diglucoside, 3-arabinoglucoside, quercetin or rutin (Torck et al., 1971).

The presence of hydrogen and carbonyl groups in polyphenolic compound in *F. herba* extract showed stronger ability to bind metal ions (Moran et al., 1997). The strong antioxidant properties of polyphenols stem from the fact that numerous hydroxyl groups are present in their particles; the hydroxyl groups are easily oxidized and the proper O-chinons are produced. As it is known, the antioxidant properties of the

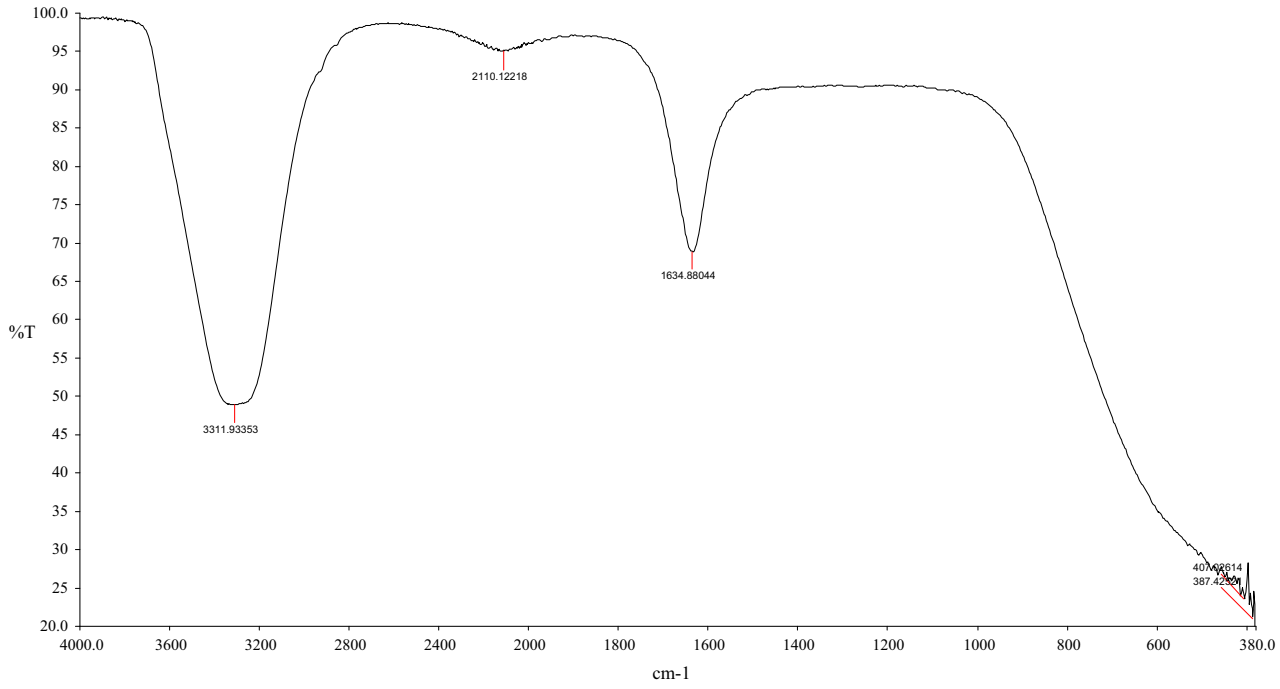

Figure 4 FTIR spectrum of platinum nanoparticles synthesized using *F. herba*.

respective flavonoid compounds increase with the number of hydroxyl groups in the aromatic ring B. Furthermore, the alkaloids present in *F. herba* extract also show antioxidant activity (Cieślińska et al., 2002).

In compounds with a hydroxy group, the antioxidant activity is increased by the presence of one or two methoxy groups in the ring. As regards the phenolic acids present in *F. herba*, sinapinic acid with two methoxy groups is more active than ferulic acid with one methoxy group, while the latter is more active than coumaric acid (one hydroxy group). According to Castellucio et al. (1995), ferulic acid is more effective than *p*-coumaric acid due to the presence of methoxy group. This group, as the electron donor, causes a greater capability to stabilize aryloxy radicals, which emerge as a result of donation of hydrogen by the hydroxy group (by means of electron delocalization). As a result of hydroxylation in lieu of methoxylation, particles having such structure become much more effective antioxidants. Also chlorogenic acid present in the *F. herba* extract shows high antioxidant activity. Fig. 5 shows the chemical structure of the dominant biologically active compounds present in *F. herba*: (A) protopine and (B) fumaricin as the representatives of alkaloids, as well as the representatives of phenolic acids, i.e. (C) sinapinic acid and (D) ferulic acid.

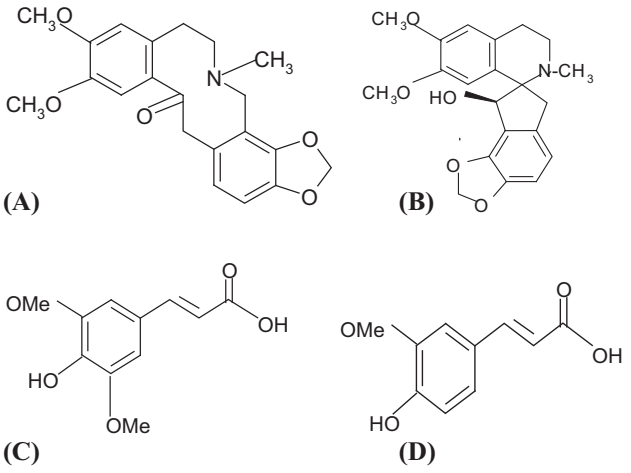

Figure 5 The chemical structure of biologically active compounds present in *F. herba* extract: (A) protopine (B) fumaricin (C) sinapic acid (D) ferulic acid.

3.3. SEM/TEM analysis

The size and shape of the prepared nanoparticles have been evaluated using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Fig. 5(A) –(C) presents the SEM images of the obtained platinum nanoparticles at different magnifications. The size of platinum nanoparticles was about 20–30 nm. Locally, the nanoparticles were agglomerated. In order to perform a more exact evaluation of the size, shape, and morphologies of the synthesized nanoparticles, Transmission Electron Microscopy (TEM) was used. Fig. 5 (D) presents the TEM image of platinum nanoparticles at 1 μm magnifications. TEM micrographs bring out the formation of platinum nanoparticles in the size range of 10–30 nm. TEM image confirmed the hexagonal and pentagonal shape of the synthesized nanoparticles. Pal et al. (2014), using microwave irradiation, obtained platinum nanoparticles of spherical shape. A similar shape of platinum nanoparticles was obtained by Dauthal and Mukhopadhyay (2013), who synthesized the nanoparticles using agro-industrial waste Punica granatum's peel extract. On the other hand, the use of dried leaf powder of *Anacardium occidentale* led to obtaining crystalline and irregular rod-shaped nanoparticles (Sheny et al., 2013). It is

known that the concentration of the extract plays the main role in the morphology of metal nanoparticles. The size and morphology of the synthesized platinum nanoparticles can be related to the interactions between biomolecules in *F. herba* extract (alkaloids, polyphenolic compounds) and the platinum atom (see Fig. 6).

3.4. SEM and EDS analysis

The morphology of platinum nanoparticles synthesized using *F. herba* was verified by SEM-EDS. Fig. 7(A) and (C) shows the SEM images of platinum nanoparticles after magnetic stirring for 4 h at the temperature of 50 °C. The size of the nanoparticles was about 20 nm. EDS profile shows additional evidence of the reduction in platinum nanoparticles. Fig. 7 (B) and (D) presents seven peaks between 0 kV and 10 kV. These results indicated that the reaction product was composed of high purity platinum nanoparticles.

3.5. Catalytic properties of synthesized platinum nanoparticles

This study evaluated the catalytic activity of the synthesized nanoparticles. The catalytic activity of platinum nanoparticles synthesized using *F. herba* was assessed using the aqueous solution of methylene blue (MB) and crystal violet (CV). Figs. 2 and 3 present UV–Vis absorption spectra of methylene blue reduction and crystal violet reduction by *F. herba* in the presence of platinum nanoparticles. The presented absorption spectra are related to the measurements conducted from minutes 3 to 15 (at 2-min intervals). Fig. 2 presents the absorption spectra of methylene blue and the mixture of methylene blue with the water extract of *F. herba* and Milli Q water at different time intervals. The maximum absorbance value of methylene blue was recorded at 660 nm. Over time (within 15 min), it was observed that the absorbance intensity peak of methylene blue decreased quickly and shifted to a higher wavelength side. Fig. 3 shows the absorption spectra of crystal violet and the mixture of crystal violet with the water extract of *F. herba* and Milli Q water at different time intervals. The maximum absorbance value of crystal violet was recorded at 538 nm. After mixing the solution of crystal violet, water and extract of *F. herba*, there was a noted decrease in absorbance. The addition of the solution of Pt nanoparticles caused further degradation of crystal violet during the study. After 15 min, the organic dye decomposed almost completely. These results confirmed the excellent catalytic activity of platinum nanoparticles synthesized using *F. herba*. As organic dyes are an important class of materials widely used in textile and many other industries (Pal et al., 2014), it is of utmost importance to find an efficient way to remove the dyes from water or to treat them in such a way so as to minimize their effects on the environment, and also to decolorize water (Alshamsi et al., 2007). The use of platinum nanoparticles may prove to be a very

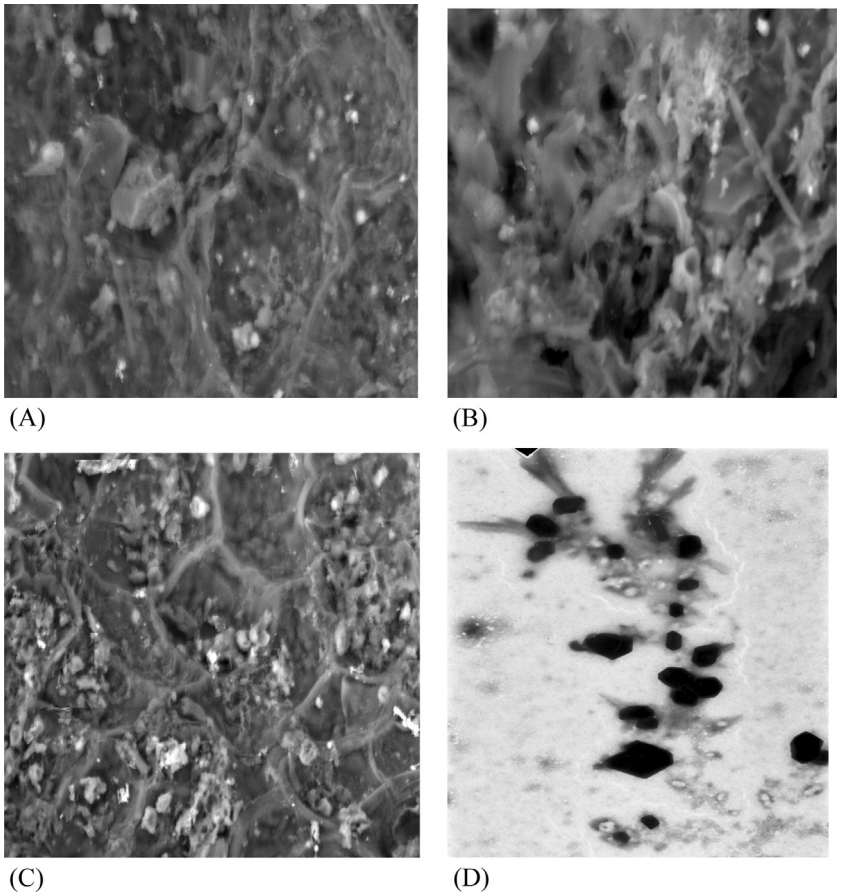

Figure 6 SEM images at different magnifications (A) 30 nm (B) 20 nm, (C) 50 nm and TEM image (D) of synthesized platinum nanoparticles at magnification 1 μm.

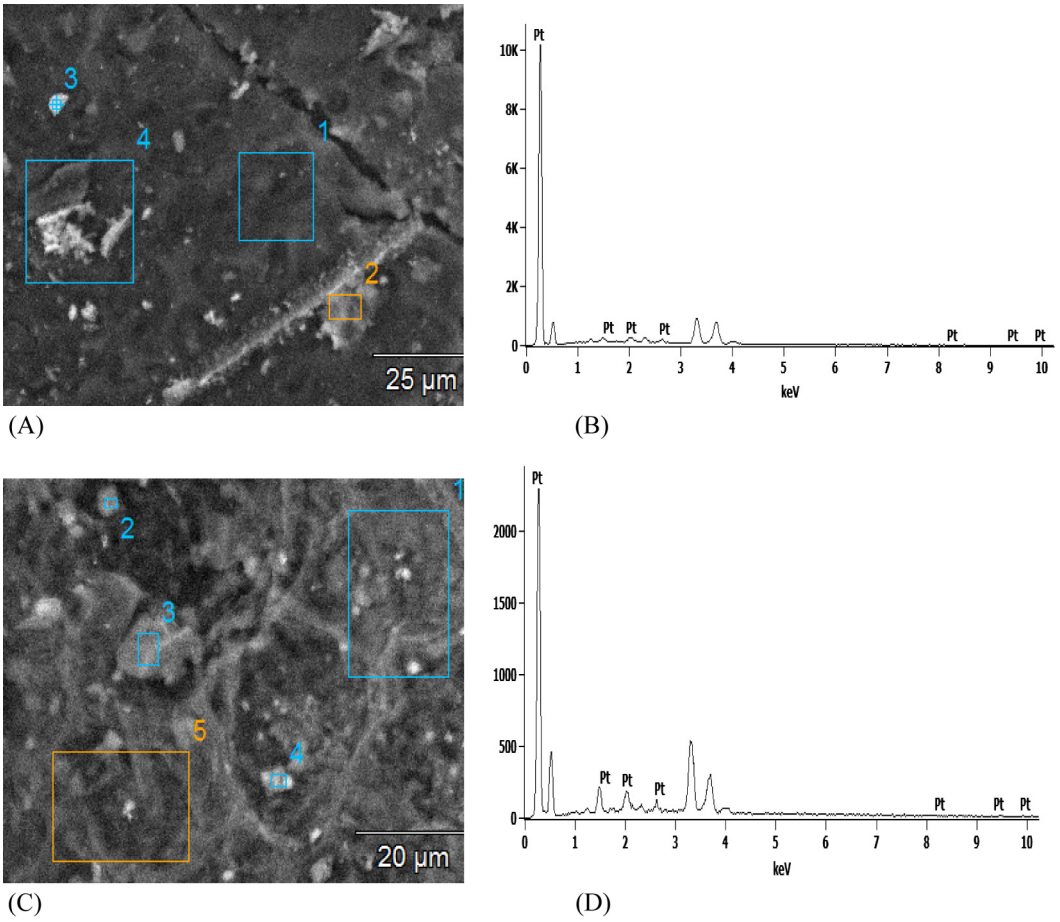

Figure 7 SEM images of synthesized platinum nanoparticles at different magnifications (A) 25 µm (C) 20 µm with EDS profile (B) and (D).

apt solution. Due to their relatively large surface-to-volume ratios, metal nanoparticles show enhanced catalytic activity for the degradation of organic dyes (Ashokkumar et al., 2014). In the literature, there are numerous examples showing the catalytic activity of metals, such as Au (Yuan et al., 2017) or Ag (Ajitha et al., 2015). As regards the catalytic properties of Pt nanoparticles, Dauthal and Mukhopadhyay (2015) conducted the reduction in anthropogenic pollutant, 3-nitrophenol, by NaBH4 using colloidal Pt nanoparticles. Gupta et al. (2011) synthesized gold, silver and platinum nanoparticles and used them for the catalytic degradation of methyl orange in the presence of $NaBH_4$. Pal et al. (2014) presented the catalytic degradation of methyl violet in aqueous solution by means of Pt nanoparticles synthesized using a microwave irradiation procedure. This work constitutes another example of the catalytic activity of synthesized Pt nanoparticles, which may be used for the purposes of degradation of organic dyes.

4. Conclusion

To summarize, Pt nanoparticles were successfully obtained using *F. herba* extract. The results obtained from UV–visible spectroscopy demonstrated the reduction of Pt^{4+} ions to Pt^0 nanoparticles. The applied techniques of TEM and SEM profile confirmed the presence of synthesized Pt nanoparticles which were hexagonal and pentagonal in shape. The EDS studies confirmed high purity of the synthesized Pt nanoparticles. FTIR confirmed the presence of active compounds responsible for the synthesis of Pt nanoparticles. The synthesized platinum nanoparticles presented catalytic activity, which was exemplified by the reduction in two organic dyes: methylene blue and crystal violet.

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