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Biosynthesis of palladium nanoparticles using *Saccharomyces cerevisiae* extract and its photocatalytic degradation behaviour

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Abstract

In this article, we have discussed the biosynthesis of palladium nanoparticles (PdNPs) using aqueous *Saccharomyces cerevisiae* extract and its photocatalytic application. The biosynthesised PdNPs were characterised by UV-Vis spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and Atomic force microscopy (AFM). The formation of PdNPs was confirmed from the disappearance of the peak at 405 nm in the UV-Vis spectrum. Agglomerated and hexagonal shaped PdNPs were noted by SEM. FTIR was performed to identify the biomolecules responsible for the synthesis of PdNPs. Bioactive compounds in the yeast extract acted as secondary metabolites which facilitated the formation of PdNPs. The yeast synthesised PdNPs degraded 98% of direct blue 71 dye photochemically within 60 min under UV light.

Keywords: biosynthesis, *Saccharomyces cerevisiae* extract, palladium nanoparticles, x-ray diffraction, photocatalytic activity, direct blue 71

Classification numbers: 2.04, 4.02, 5.07

1. Introduction

Nanoparticles (NPs) were synthesised from bacteria, fungi and plants, they have numerous applications in science and technology [1]. The reduction of metal (II) to metal (0) NPs arise by the amines, phenols, sugars, proteins, amino acids, aldehydes and carboxylic acids which are presented in the microbes and plants. Palladium is a most active metal in catalysis including reduction of hydrogen [2], dehalogenation of waste water [3], and Suzuki–Miyaura coupling [4]. Glucose determination was reported using PdNPs by amperometric sensor method [5]. NPs were established in various fields especially in catalytic application [6]. Metal and semiconductor

NPs were synthesised using biological method has gained more attention due to eco-friendly and cost effective nature [7]. This motivates the researchers to focus on biomolecules for the synthesis of metal NPs when compared to physical and chemical methods [8]. An organic-inorganic hybrid material has recently been synthesized by in situ generation of PdNPs in a hybrid gel matrix based on renewable chemicals. The xerogel of the hybrid material acted as a recyclable heterogeneous catalyst for C–C coupling and reduction reactions in aqueous media [9].

Saccharomyces cerevisiae act as probiotic microorganisms [10]. Several scientific reports showed that *Saccharomyces cerevisiae* act as biotherapeutic agent and prevent several types of diarrhoea and colitis in human beings [11]. These organisms are surviving in low pH in human intestine and make appropriate probiotic strain. It shows popular enzymatic activities and its use in pharmaceutical and food industries



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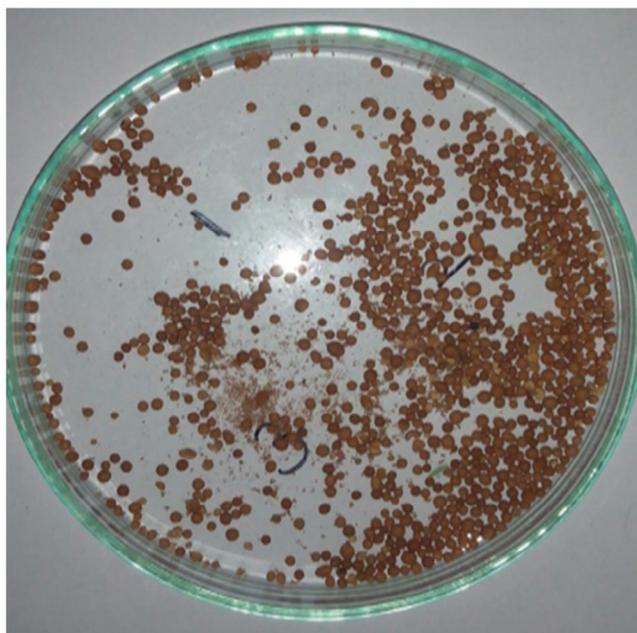


Figure 1. Dry *Saccharomyces cerevisiae*.

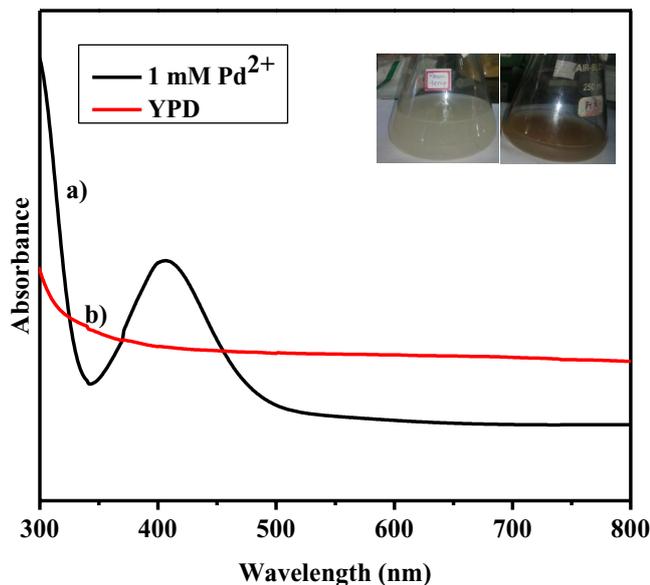


Figure 2. UV-Vis spectra of (a) 1 mM of Pd²⁺ (b) biosynthesised YPD.

[12]. The yeast is an active dietary supplement and predominant microflora for fermented food production [13]. Fernandez *et al* reported yeast such as *Cryptococcus laurentii* and *Rhodotorula glutinis* as capping and reducing agent for the synthesis of silver NPs [14]. The dry yeast is shown in figure 1.

Water pollution is a major concern in all over the world [15]. Number of synthetic colourants are used in the form of dyes in textile industries. 10% of dyes are directly released into the ecosystem and water bodies from the textile industries. Toxic dyes are contaminating the water and also act as a carcinogenic and mutagenic in marine organisms and humans [16]. It cause a number of medical disorders, intestinal cancer and affects seed germination of the plant [17]. The discharge

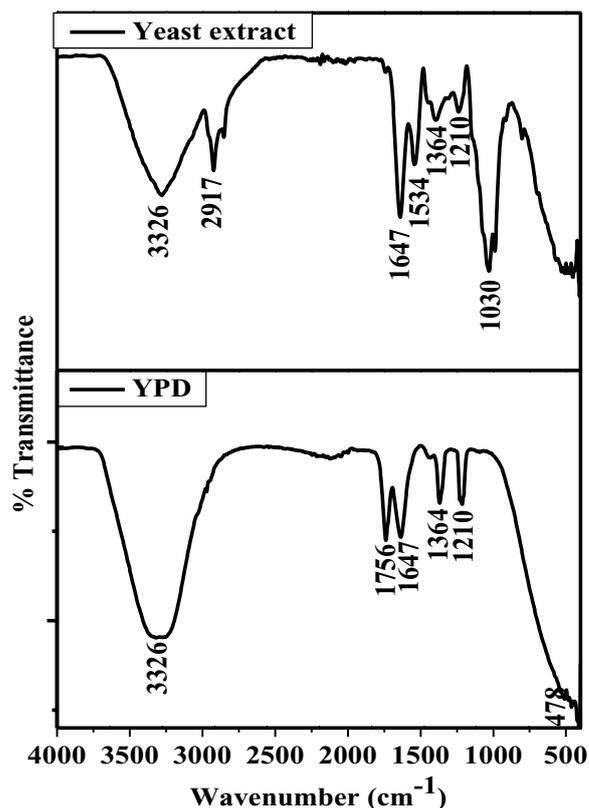


Figure 3. FTIR spectrum of YPD NPs.

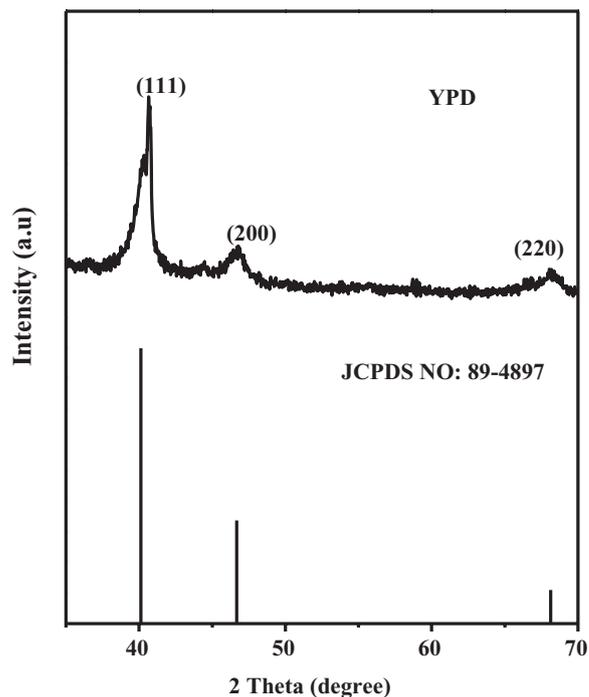


Figure 4. Powder XRD pattern of YPD NPs.

of azo dyes into the ecosystem resulted in aromatic amines and affects the aquatic life and humans [18]. Direct blue 71 dye is an azo dye, widely used in textile industry as a colouring agent and exhibit bright blue colour. In recent years, environmental pollution becomes a serious threat due to many industries such as textile, leather, and cosmetics [19].

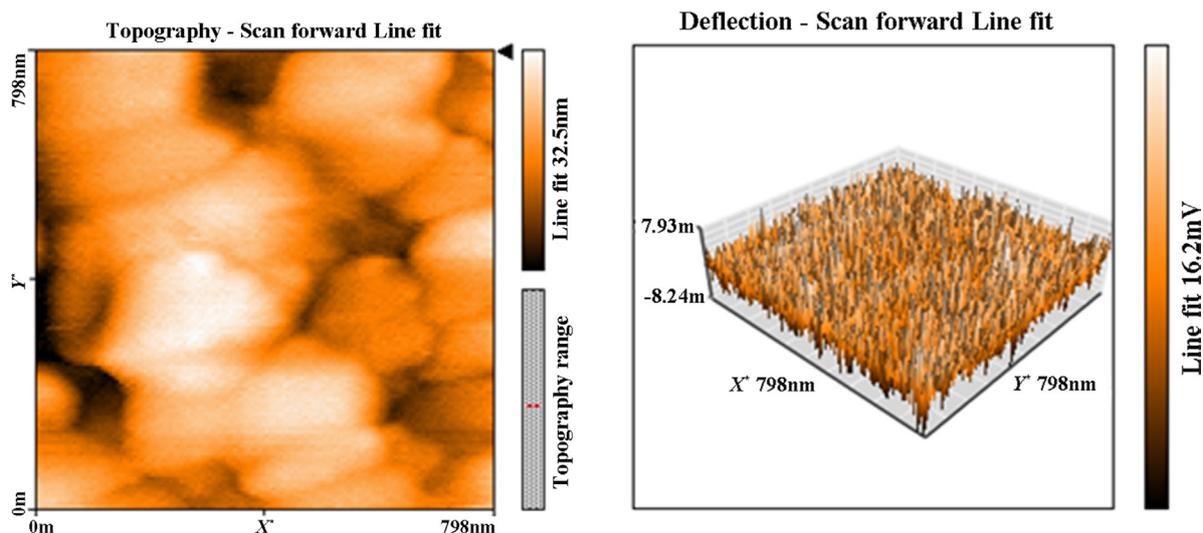


Figure 5. (a) AFM images of YPD NPs (b) 3D topography of the surface of YPD NPs.

Currently, researchers are focused on different wastewater treatment methods for the degradation of the toxic hazardous chemical compound to simple nontoxic compounds. More quantities of dyes are released without proper treatment and the resulting effluents are hazardous to the environment. Removal of dyes from wastewater was studied using different methods such as biodegradation [20], electrocoagulation [21], adsorption [22], chemical oxidation [23] and photodegradation [24]. Nowadays scientists focused on the photodegradation of dyes using nanotechnology and nanomaterials.

In this research paper, we studied the photocatalytic activity of PdNPs synthesized using *Saccharomyces cerevisiae* organisms. *Saccharomyces cerevisiae* organisms are non-pathogenic, readily available and found to possess many bioactive molecules which can assist in the synthesis of PdNPs from palladium precursors. The aim of our work is to synthesize PdNPs using aqueous yeast extract solution (YPD) from palladium acetate solution (as the precursor for palladium) and to investigate the degradation of textile dye direct blue 71.

2. Materials and methods

2.1. Materials

Dry *Saccharomyces cerevisiae* (Active dry yeast, Kwality brand, Pagariya food products (P) Ltd) was purchased from Vellore, Tamil Nadu, India. Pure Palladium acetate ($C_4H_6O_4Pd$) was purchased from Sigma-Aldrich. The azo dye, direct blue 71 was purchased from Thirupur.

2.2. Synthesis of PdNPs

5g of dry yeast granules was added to the 100ml of water and stirred at room temperature for 30 min. From this 10ml of the aqueous solution was taken and added to 90ml of 1mM of palladium acetate solution. The entire mixture was kept at room temperature for 24h. The reduction of Pd(II) to Pd(0)

was indicated by a colour change from transparent to dark brownish colour. The PdNPs were separated by centrifugation at 5000rpm for 15 min.

2.3. Characterization of PdNPs

The synthesised NPs were confirmed using UV-Vis spectroscopy (Jasco V670 spectrophotometer). The absorbance ranges from 300nm to 800nm and the distilled water was used as a reference. The bio-functional group of the secondary metabolites was identified using FTIR spectroscopy (FTIR SHIMADZU model IR affinity.1) in the range between 4000 and 450 cm^{-1} by attenuated total reflection (ATR) method. The phase purity and structure of synthesised PdNPs was authenticated by XRD analysis (D8 advance BRUKER Germany). XRD patterns of the biosynthesised PdNPs were studied at 30kV ($CuK\alpha$) with scan rate of 0.03° s^{-1} . A thin smear of biosynthesised PdNPs was prepared on the clean glass slide to analyse the surface morphology. The prepared thin smear was used for AFM analysis (NanoSurf Easy scan 2, version 1.3) in the tapping mode. The shape and morphology of the PdNPs were examined using SEM. EDX analysis of PdNPs was performed using SEM equipped with an EDX attachment (SEM-EDX ZEISS EVO18).

2.4. Photocatalytic activity

The photocatalytic activity of biosynthesised PdNPs were tested for the reduction of direct blue 71 dye. 50 ml of 10ppm direct blue 71 solution was taken in 100ml beaker, and then 10mg of PdNPs were added and stirred for 60 min in dark conditions to attain the equilibrium. Direct blue 71 dye photodegradation was carried out using photoreactor under (365 nm) UV light. 3 ml of dye solution was withdrawn at regular intervals of time (10 min) for the UV analysis. The percentage of degradation was calculated from the formula mentioned below [25]

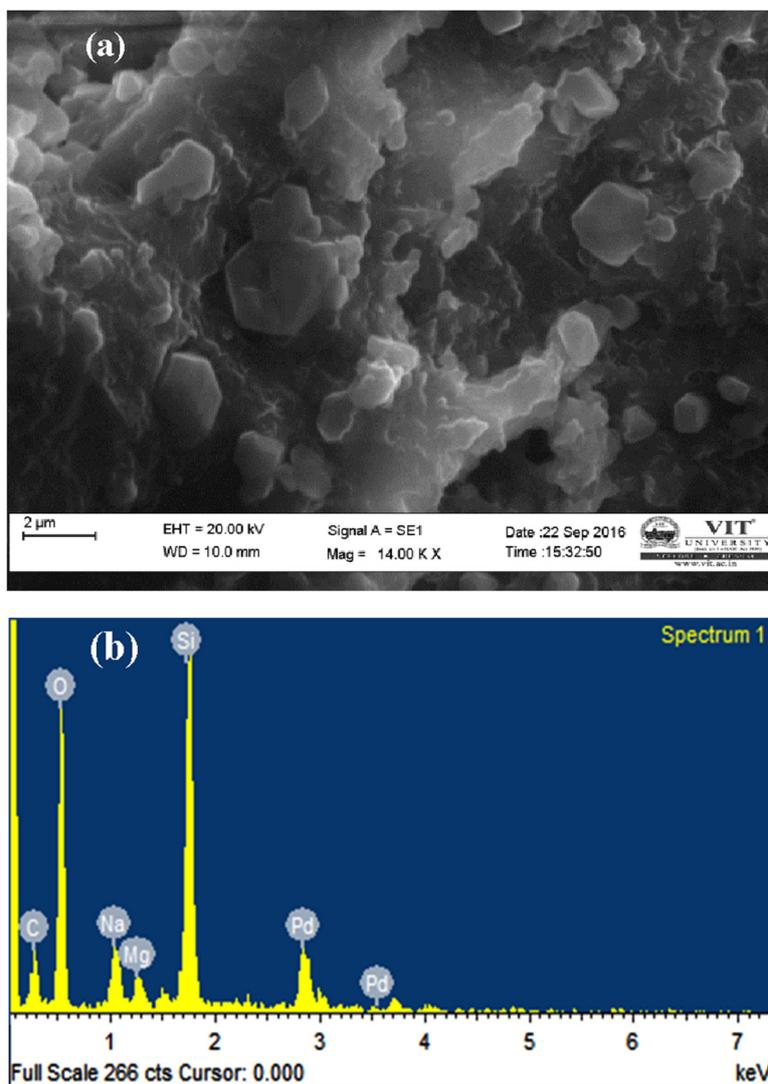


Figure 6. (a) SEM (b) EDAX of biosynthesized YPD NPs.

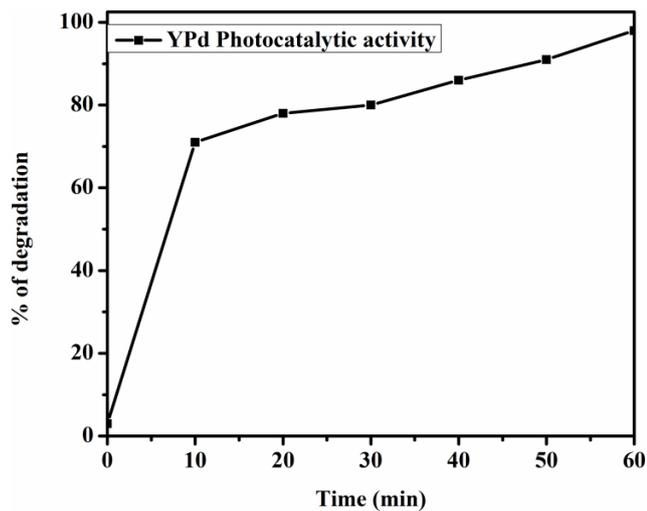


Figure 7. UV-visible analysis of % dye degradation.

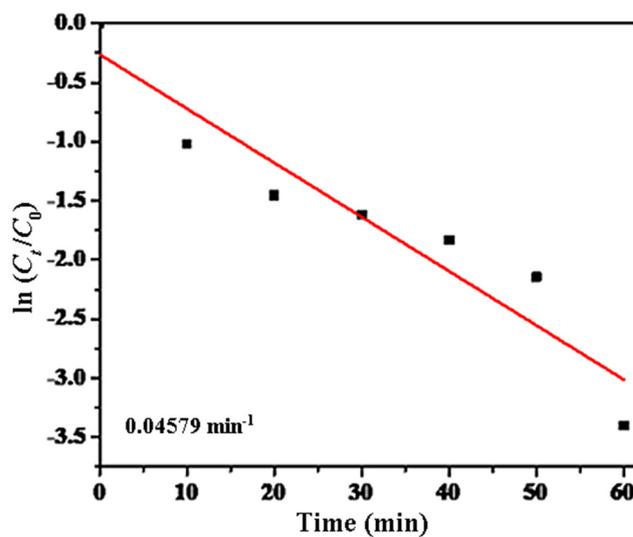


Figure 8. Photo degradation kinetics of direct blue 71.

Table 1. Photocatalytic degradation of PdNPs using other sources.

Source of PdNPs	Photocatalytic activity	Reference
<i>C. spinosa</i> root bark extract	83% of congo red dye degradation in 20 min	[42]
Andean blackberry leaf extract	72.16% of methylene blue dye degradation in 420 min	[43]
<i>Pimpinella tirupatiensis</i> plant extract	94% of Congo red dye degradation in 60 min	[44]
<i>Sapium sebiferum</i> leaf extract	90% of Methylene blue dye degradation in 70 min	[45]
<i>Saccharomyces cerevisiae</i>	98% of Direct blue 71 textile dye degrade within 60 min	Current work

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100.$$

here C_0 is the initial dye concentration and C_t is the concentration of dye after degradation at various time t . The concentration was calculated based on the absorbance measured using UV-Vis spectrometer by considering that the absorbance is directly proportional to concentration.

3. Results and discussion

3.1. UV-Vis spectroscopy analysis

The formation of PdNPs was examined by UV-Vis spectroscopy. The absorbance was recorded in the wavelength range 300–800 nm. After 24 h incubation, the colour changed from transparent to brown colour which is a preliminary evidence for the formation of PdNPs from aqueous solution of the yeast and 1 mM of palladium acetate. The aqueous 1 mM of palladium acetate solution showed a broad peak at 405 nm. The formation of YPD NPs were identified by the disappearance of the peak at 405 nm which indicates the reduction of Pd (II) to Pd (0) (figure 2). Veisi *et al* also reported the peak at 400 nm corresponds to palladium (II) disappeared after the reduction to Pd (0) [26]. Similar observations are also found using *Anacardium occidentale* plant extracts [27]. Anand *et al* [28] also observed the similar change for PdNPs synthesized using *Moringa oleifera* flower extract.

3.2. Fourier transform infrared spectroscopy (FTIR)

FTIR spectrum was recorded to detect the various functional groups which were used for the reduction of Pd (II) to YPD nanoparticles. FTIR spectra of yeast extract and the YPD NPs are shown in figure 3 that demonstrates the presence of functional groups responsible for the reduction of palladium in the mixture. The absorption at 3293 cm^{-1} is due to the presence of $-\text{OH}$ group in phenolic compound [4]. The absorption peak at 1745 cm^{-1} and 1633 cm^{-1} are associated with $\text{C}=\text{O}$ and $\text{C}=\text{C}$ stretching respectively [29]. The band observed at 1369 cm^{-1} assigned to a CH_3 bending. 1215 cm^{-1} band assigned to the $\text{C}-\text{O}$ group stretching vibration in phenolic compounds [30]. This result clearly indicates that the bioactive functional group such as hydroxyl and other functional groups have participated and stabilized the PdNPs in the mixture [31]. The small peak at lower wavenumber 478 cm^{-1} could be due to the presence of palladium in the synthesized NPs [32].

3.3. Powder x-ray diffraction (XRD)

The XRD pattern of YPD NPs is shown in figure 4. The phase formation of the synthesized YPD was confirmed using the XRD analysis. XRD pattern of YPD showed 2θ values at 40.66° , 46.76° and which corresponds to the (111), (200), (220) planes. The structure of PdNPs (face-centred cubic) are confirmed from the JCPDS NO: 89-4897. A similar result was reported for PdNPs using *Chlorella vulgaris* aqueous extract [33]. The average crystalline size of PdNPs was calculated using Scherrer's equation [34] and it was found to be 32 nm.

$$D = \frac{k\lambda}{\beta \cos \theta}.$$

where, D is the average crystalline size, $k = 0.89$ is a constant. λ , β and θ is the x-ray wavelength, full width at half maximum value and Bragg's angle, respectively.

3.4. Atomic force microscopy (AFM)

AFM is one of the advanced scanning probe technique used for the characterization of NPs. The morphology of the YPD is highly variable and having a rough surface. Figure 5(a) shows a mixture of spherical and triangular shapes of YPD NPs. Size distribution and roughness image of the NPs' surface was shown in figure 5(b). A similar type of observation is reported for biosynthesized PdNPs using watermelon rind [35].

3.5. Scanning electron microscopy (SEM) and energy dispersion x-ray spectroscopy (EDX)

The surface morphology and shape of the YPD NPs were confirmed by SEM as shown in figure 6(a). The particles are found to be small and hexagonal in shape. The presence of palladium was confirmed using the EDX analysis (figure 6(b)).

3.6. Photocatalytic activity

The photocatalytic activity of synthesised PdNPs are tested for the degradation of direct blue 71 textile dye under UV light. The characteristic absorption peak of direct blue 71 dye was noticed at 591 nm and degradation of dye in the presence of YPD NPs was confirmed by the decrease in the peak intensity. 98% of the textile dye was degraded in 60 min using YPD. The UV-Vis spectrum and the images of the dye degradation after every 10 min were shown in figure 7. The decrease in the absorbance represents the ability of YPD to

degrade textile dye. Nashwa *et al* [36] synthesised iron NPs using aqueous *Saccharomyces cerevisiae* extract and reported 100% direct blue 71 dye degradation in 72h. However, in the current work, PdNPs have shown 98% dye degradation in 60 min. Meenakshi Agarwal *et al* synthesised copper nano-flowers using *F. benghalensis* leaf extracts for the degradation of methylene blue and sodium borohydride complex solution [2]. In addition, from muskmelon, *Trichoderma harzianum* extracts and *Ficus panda* leaf extracts synthesised carbon dots, cadmium sulphide and silver NPs respectively also reported as a photocatalyst for methylene blue dye degradation [37–39]. The rate of the reaction (figure 8) was calculated by plotting $\ln(C_t/C_0)$ against the time of the reaction and it was found to be 0.04579 min^{-1} under UV light. It is noted that the degradation reaction followed the pseudo-first-order kinetics [37, 40, 41]. Photocatalytic degradation of PdNPs using other sources is shown in table 1.

4. Conclusion

In conclusion, PdNPs were synthesized using aqueous solution of the yeast without adding any chemical reducing agent. The XRD analysis established the cubic structure of YPD NPs with an average size of 32 nm. The synthesized PdNPs were found to be active towards the photocatalytic degradation of the azo dye direct blue 71. These PdNPs have remarkable application in textile industries by degrading 98% of direct blue 71 dye associated water in 60 min.

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