Effective and reproducible biosynthesis of nanogold-composite catalyst for paracetamol oxidation

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Abstract
Pharmaceutical products are some of the most serious emergent pollutants in the environment, especially nowadays of the COVID-19 pandemic. In this study, nanogold-composite was prepared, and its catalytic activity for paracetamol degradation was investigated. Moreover, for the first time, recycled waste diatomite earth (WDE) from beer filtration was used for reproducible gold nanoparticle (Au NPs) preparation. We studied Au NPs by various physical-chemical and analytical methods. Transmission and scanning electron microscopy were used for nanogold-composite morphology, size and shape characterization. Total element concentrations were determined using inductively coupled plasma mass and X-ray fluorescence spectrometry. X-ray powder diffraction analysis was used for crystal structure characterization of samples. Fourier transform infrared spectrometer was used to study the chemical changes before and after Au NP formation. The results revealed that the WDE served as both a reducing and a stabilizing agent for crystalline spherical 30 nm Au NPs as well as acting as a direct support matrix. The kinetics of paracetamol degradation was studied by high-performance liquid chromatography with a photodiode array detector. The conversion of paracetamol was 62% and 67% after 72 h in the absence or presence of light irradiation, respectively, with 0.0126 h⁻¹ and 0.0148 h⁻¹ reaction rate constants. The presented study demonstrates the successful use of waste material from the food industry for nanogold-composite preparation and its application as a promising catalyst in paracetamol removal.

Keywords
Biosynthesis · Nanogold-composite · Nanoparticles · Reproducibility · Catalyst · Paracetamol

Introduction
Pharmaceutical compounds are some of the most serious environmental pollutants in aquatic systems (Varma et al. 2020). Pharmaceutical products (PhPs) such as antibiotics, antiseptics, anti-inflammatory drugs and disinfectants are widely used in human and veterinary medicine (Shakir et al. 2016), and their metabolites and residues can contaminate surface or groundwater and/or accumulate in the topsoil (Martins et al. 2017). In addition, just low concentrations of some PhPs can have a negative effect on living organisms, with estrogens, clofibric acid, sulfamethoxazole, ciprofloxacin, ibuprofen and paracetamol (PCTM) being important examples (Jarošová et al. 2015; Lee and Lee 2017; Martins et al. 2017).

N-acetyl-para-aminophenol (PCTM) is a widely used analgesic and antipyretic drug. Especially nowadays, PCTM is used frequently (Pandolfi et al. 2021). Scientists recommend that people showing symptoms of COVID-19 should use PCTM rather than ibuprofen, which can exacerbate the condition (Day 2020). In the study, Leal and colleagues showed that PCTM is associated with a lower risk of COVID-19 infectivity (Leal et al. 2021).
concentrations of 0.01–0.03 mg·L⁻¹ which may be harmful. This drug causes liver failure, hepatic necrosis or nephrotoxicity (Jarošová et al. 2015; Lee and Lee 2017; Martins et al. 2017). It is therefore important to develop an efficient treatment method to eliminate PCTM from the environment (Shakir et al. 2016; Tiwari et al. 2017).

Many studies showed that PhPs are not completely degraded during the usual wastewater treatment process. PhPs can be degraded by advanced chemical or physical methods such as oxidative processes including photolysis, sonolysis, sonocatalysis and Fenton and photo-Fenton oxidation (Hama Aziz et al. 2017). Degradation processes based on the use of metal nanoparticles (NPs) as catalysts are very promising approaches for wastewater treatment. Moreover, their biosynthetic formation is considered to be a non-toxic and environmentally friendly approach for metal nanocatalyst preparation (Kratošová et al. 2019; Samadi et al. 2021).

Among synthetic metal NPs, Au/Ag/AgCl NPs prepared using Momordica charantia extracts have been tested for ibuprofen (IBP) and clofibric acid degradation (Devi and Ahmaruzzaman 2017). In another publication, Martins et al. (2017) focused on the degradation of sulfamethoxazole, ciprofloxacin, 17β-estradiol and IBP by Pd and Pt bio-NPs. Bio Pd NPs showed catalytic activity in the degradation of sulfamethoxazole in the presence of H₂. In the case of Pt NPs, catalytic activity was observed for sulfamethoxazole, ciprofloxacin and 17β-estradiol degradation also in the presence of H₂ (Martins et al. 2017). Another work focused on the synthesis of Fe NPs from grapefruit extract, black tea and grape leaves, and these NPs were then used for IBP degradation in an aqueous medium (Machado et al. 2013). Zia and Riaz reported the preparation of Ag–Ag₂O NPs using Osmium sanctum plant extracts and their modification with polythiophene (PTh). The catalytic activity of Ag–Ag₂O/PTh was then investigated in the degradation of PCTM under microwave irradiation (Zia and Riaz 2020).

Nanogold is one of the most catalytic active elements due to its thermodynamic stability, inertness, quantum size and generation of surface plasmon resonance (SPR) (Aleshammari and Kalevaru 2016). Generally, a local enhanced electromagnetic field formed on the surface of metal NPs enhances the generation of reactive oxygen species (ROS) (Cuenya 2010; Zhao et al. 2017). Also, Au NPs behave as peroxidase-like agents for H₂O₂ decomposition and enhanced production of hydroxyl radicals (·OH). These ROS and ·OH radicals can be used as intermediates for PhP oxidation (Liu et al. 2019). There are proposed several possible ways for PCTM oxidation by hydroxyl radicals. Degradation by-products are 1,4-benzoquinone and oxamic acid. The final product can be oxalic acid (Fig. 1) (Skolotneva et al. 2020).

Inspired by the reported biosynthesized NPs, we used recycled waste diatomite earth (WDE) from beer filtration for Au NP biosynthesis for the first time. WDE is a low-cost and eco-friendly material with unique chemical composition, availability, renewability and efficiency for nanostructure biosynthesis. The WDE from beer filtration is composed mainly of diatomite earth which is covered with yeast cell debris (Anders and Alwaedi 2015). The residual yeast presence is beneficial for biosynthesis and stabilization of Au NPs, and the porous surface of diatomaceous earth is excellent for their attachment by electrostatic interactions (Lupa et al. 2019). The combination of Au NP properties with chemically stable silica support creates a functional nanocomposite for heterogenous catalysis (Sosa et al. 2019). Silica algae themselves were also widely used for Au NP-SiO₂ and other NP preparation (Li et al. 2021). Our previous results demonstrated CO oxidation on biosynthesized Au NPs with Diadesmis gallica (Holišová et al. 2019a), while Au NPs synthesized with Mallomonas kalinae were used for soman hydrolysis (Holišová et al. 2019b).

These results prompted us to conduct Au NP biosynthesis using waste biomaterial such as the WDE from beer filtration.

![Fig. 1 Possible ways for PCTM oxidation by hydroxyl radicals (Skolotneva et al. 2020)](image-url)
The main goals of this study are as follows: (i) the preparation and characterization of unique nanogold-composite, (ii) the verification of preparation method reproducibility, (iii) the study of the Au NP biosynthesis mechanism, and (iv) the evaluation of PCTM oxidation in the presence of H₂O₂ and the nanogold-composite with and without light irradiation.

Materials and methods

Nanogold-composite preparation

The WDE supplied by Radegast a.s. Brewery (Nošovice, Czech Republic) was dried at 36 °C for 24 h. Then, 2.5 g of the dried WDE powder was mixed with 400 mL of 0.5 mmol·L⁻¹ HAuCl₄·3 H₂O (≥ 99.5%, Carl Roth, Germany) aqueous solution. The suspension was continuously mixed at 400 rpm for 24 h at 24 °C. The WDE with Au NPs was dried at 36 °C for a further 24 h.

One gram of prepared WDE sample with Au NPs was removed and mixed with 200 mL of DEMI water at pH 7 and stirred continuously at 450 rpm at 24 °C for 24 h for the removal of residual Au ions. After 24 h, the mixture was centrifuged at 3500 rpm for 3 min. The excess supernatant solution was removed, and the nanogold-composite was dried at 36 °C for 24 h.

The nanogold-composite preparation was repeated five times, and the final samples were labelled as 1Au/WDE, 2Au/WDE, 3Au/WDE, 4Au/WDE and 5Au/WDE. Dried WDEs as controls were stored at laboratory conditions and tested in pentaplicates (1WDE–5WDE).

Size, surface and morphology characterization

Scanning electron microscopy (SEM) with EDS analysis was performed using a Quanta FEG 450 (Thermo Fisher Scientific, USA). Samples were put on carbon tape, and an Au thin layer was then spread. Transmission electron microscopy (TEM, 1200 EX, Japan, JEOL, accelerating voltage 80 kV) was used to evaluate the Au NP shapes and sizes and their dispersion on the WDE surface. Small amounts of samples were suspended in ethanol and fixed on formvar/copper grids. The Au NP size distribution and pore size were evaluated using the JMicroVision software (www.jmicrovision.com) from 150 Au NP TEM and SEM images. The specific surface area was estimated by the Brunauer–Emmett–Teller method (BET) on a Surfer Gas adsorption porosimeter (Thermo Fisher, USA).

Spectroscopy characterization

The crystal structure of the samples was characterized by X-ray powder diffraction analysis (XRD) using a Bruker D8 Advance X-ray diffractometer (Bruker AXS, Germany) with the Co lamp (CoKα, λ = 1.7889 Å). Analyses were performed in the range of 30–80° 2θ. The phase composition was evaluated using the PDF 2 Release 2014 database (International Centre for Diffraction Data). The total gold content was determined by Ciros Vision inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPECTRO Analytical Instruments Inc., Kleve, Germany). The energy dispersive X-ray fluorescence spectrometer (XRFS) SPECTRO XEPoS new (SPECTRO A. I., Kleve Germany) was used for the overall qualitative and quantitative element determination in all samples. A NICOLET 6700 FT-IR spectrometer (Thermo Scientific, USA) was used to study the chemical changes before and after Au NP formation by the ATR technique with diamond crystal in the range 400–4000 cm⁻¹. The UV–VIS spectra of Au/WDE and WDE samples were measured in the range of 250–800 nm using a UV-2600 spectrophotometer (IRS-2600Plus, Shimadzu, Japan). All graphs and plots were created using MATLAB software (Mathworks, USA).

Study of nanogold biosynthesis

Nanogold biosynthesis using yeast and diatomaceous earth

The yeasts Saccharomyces cerevisiae were supplied by Radegast a.s. Brewery (Nošovice, Czech Republic) and were collected from beer filtration. The yeasts were used to verify their bioreductive properties during Au NP biosynthesis. One millilitre of yeast was mixed with 15 mL of 1 mmol·L⁻¹ HAuCl₄·3 H₂O (≥ 99.5%, Carl Roth, Germany) at 24 °C under static conditions for 24 h.

Pure diatomaceous earth (DE) consists of 65% large DE named as L_DE (fraction size > 20 µm, EP Minerals, USA) and 35% medium DE named as M_DE (fraction size 7–20 µm, EP Minerals, USA). DE was used for the synthesis of Au NPs as a parallel experiment. 2.5 g of filtration DE was mixed with 400 mL of 0.5 mmol·L⁻¹ HAuCl₄·3 H₂O (≥ 99.5%, Carl Roth, Germany), and the mixture was stirred at 24 °C for 24 h. Then, the excess solution was removed, and the final Au-doped DE suspension was dried at 36 °C for 24 h.

Determination of inorganic and organic substances

The nitrogenous substances of the pure DE and the WDE were determined using the Kjeldahl method. The analyses were performed at the workplace of the Research Institute of Brewing and Malting a.s. (Brno, Czech Republic). The organic carbon in the samples was determined using a
Multiphase Carbon analyser (RC612, LECO, USA) to determine the amount of organic matter expressed.

**Oxidation of paracetamol**

**Experimental design**

0.06 g of a nanogold-composite or the WDE as a control sample was mixed with 13.9 mL DEMI water at pH 2, 1 mL H₂O₂ (Mach chemicals spol. s r.o., Czech Republic) and 1034 mg·L⁻¹ PCTM (98%, Alfa Aesar, USA) to total volume 15 mL. The mixtures without silica-based samples were prepared as controls (blank) in a total volume of 15 mL for PCTM. PCTM mixtures with the WDE and Au/WDE samples were shaken and analysed at 1, 4, 8, 16, 24, 48 and 72 h in the dark and light (λ = 525–530 nm) at 25 °C.

**Analytical methods**

The concentration of PCTM after the catalytic reaction was analysed by high-performance liquid chromatography (HPLC Waters Alliance e2695, USA) with a photodiode array (PDA) detector (2998 Waters, USA). A XBridge® C18 column (3.5 µm; 4.6 × 100 mm) was used for the separation of PCTM. Isocratic condition and an injection of 5 µL were used for the quantification of PCTM. The total analysis took 3 min. The mobile phase was a mixture of 0.2% formic acid (≥ 99%, VWR, USA) in DEMI water as solvent A and acetonitrile (Honeywell, USA) as solvent B. The ratio of solvents A:B was 85:15 for the PCTM sample. The flow rate through the column was 0.8 mL·min⁻¹. The column temperature was maintained at 30 °C. 25 °C was the temperature of the samples. The wavelength is 249 nm for PCTM detection.

Prior to the chromatographic analysis, solid-phase extraction (SPE) columns (Oasis HLB 3 cc, Waters, USA) were used to extract and concentrate PCTM from aqueous solutions. At first, the solutions from the catalytic processes were centrifuged (2000 rpm) to separate the solid (catalysts) and liquid (supernatant) phases. The SPE columns were activated with 2 mL of methanol (Honeywell, USA) and 2 mL of DEMI water. After activation, 10 mL of supernatant was percolated through the columns, which were then washed with 2 mL of DEMI water and dried in a N₂ flow. Finally, PCTM were eluted from the columns with 2 mL of methanol. The prepared samples were used for HPLC analysis.

**Pharmaceutical products removal kinetics**

Residual concentrations of PhP after degradation were fitted using pseudo-first-order kinetics, and the rate constant (k) was calculated by Eq. (1):

\[
\ln \left( \frac{c_t}{c_0} \right) = -kt, \tag{1}
\]

where \(c_t\) and \(c_0\) describe the percentage content of PhP at a given time \(t\) and initial time (\(t = 0\), respectively, and \(t\) is reaction time (h). PhP conversion was then calculated by Eq. (2).

\[
X_{PhP} = c_0 - c_t, \tag{2}
\]

where \(X_{PhP}\) is the percentage of the conversion.

**Results and discussion**

**Waste diatomite earth characterization**

Since this is a new use of WDE for the reproducible biosynthesis of Au NPs, their chemical and physical properties were analysed.

![Fig. 2 FTIR spectra of A the WDE and B the WDE with Au NPs in pentaplicates](image-url)
The main functional groups were determined by FTIR analysis (Fig. 2A). The main spectral peaks were detected at 3271, 1636, 1518, 1453, 1408, 1070, 792, 615 and 463 cm⁻¹. The signals generated at 3271 cm⁻¹ and 1636 cm⁻¹ correspond to symmetric and bending vibration of the O–H group. The bands at 1518, 1453 and 1408 cm⁻¹ are very weak and probably belong to C–N and C=O bonds (Socrates 2004). These peaks can indicate the presence of enzymes, proteins, and lipids, which may come from yeast cell debris from the filtration process, but their identity cannot be exactly determined. The intensity of the absorption band centred at 1070 cm⁻¹ is due to Si–O–Si stretching (de Jesús Ruiz-Baltazar 2018). The band at 792 cm⁻¹ belongs to the allotropic phase of SiO₂, and the band at 463 cm⁻¹ corresponds to the vibration of the Si–O bond. The band at 615 cm⁻¹ corresponds to the vibration of Si–O–Al (Anbalagan et al. 2010). This result is in accordance with the XRFS analysis, which confirmed the presence of SiO₂ in the pure WDE (Mishra et al. 2017). Figure 2B will be discussed in the “Spectroscopic analysis” section.

The XRFS revealed that the main component of the WDE samples (1WDE-5WDE) is SiO₂ with average 81.2 ± 0.2 wt.%, and other components in the range 0.008–1.800 wt.% are MnO, Fe₂O₃, TiO₂, SO₃, P₂O₅, CaO, K₂O and Al₂O₃ (see Supplementary Information (SI), Table S1). These inorganic substances are commonly in the algae’s natural environment and are necessary for their frustule formation (de Jesús Ruiz-Baltazar 2018).

The WDE structure, size and morphology were studied by SEM and shown in SI (Fig. S1A and S1B). The WDE microstructure after beer filtration contains numerous frustules of diatomaceous algae with pores of about 400 nm. The predominant morphology matches the Fragilariophyceae type with silica shells and fragments in the range of 7–20 µm (Pytlik and Brunner 2018).

The data suggest that the WDE from beer filtration is a suitable material for NP biosynthesis. The WDE contains a homogeneous composition of both organic and inorganic substances and we assume that the organic component would reduce Au ions to Au⁰, stabilize Au NPs, while the porous silica surface would serve as a perfect matrix for their anchoring (Konvičková et al. 2016; Kratošová et al. 2016; Lupa et al. 2019). Generally, anchored NPs are more suitable for certain applications than colloidal systems. For example, separation of catalytically active nanomaterials (by filtration or sedimentation) when used for environmental decontamination will be easier as a nanocomposite than as unanchored NPs.

The WDE can be supplied by the food industry and stored in dried form in unlimited amounts. In contrast, with algae-based biosynthesis, the algae cells must be aseptically cultivated and continuously maintained for long time periods to provide suitable cell cultures for NP biosynthesis (Kratošová et al. 2019). Moreover, because of the varying organic substances, the final NPs differ in size and shape and the final yields are often low after drying. Despite these limitations for silica algae-based NP biosynthesis, frustules are commonly used for NP fixation. A major benefit for using WDE materials is their low price and high availability because of their industrial use.

Characterization of nanogold-composite

Surface analysis

Au NPs were successfully synthesized in five replicates (1Au/WDE-5Au/WDE). A suspension colour change from brown to red was observed after 24 h, and this with the SEM and TEM results confirmed that Au(III) ions were reduced to Au⁰ and then anchored on the WDE surface (Fig. 3).

The specific surface area of the WDE before biosynthesis was 23 m²·g⁻¹. After biosynthesis and anchoring of NPs on the WDE surface, the surface area of the sample increased to 32 m²·g⁻¹. Figure 3A and B show the anchored Au NPs on the porous silica surface for the 1Au/WDE sample, and Au NPs were also synthesized on the frustule fragments (Fig. 3C, D). The WDE morphology did not change after Au NP formation. Samples 1Au/WDE-5Au/WDE contained mostly spherical NPs with a minority of triangular and hexagonal NPs.

The average size of all nanogold-based samples is 31 ± 2 nm (SI, Table S2). The most common size of
nanogold is in the range of 20–40 nm. In SI, Fig. S2 shows the histograms of the size distribution of Au NPs for all samples; the histograms are interpolated by an asymmetric distribution function describing a slight NP size polydispersity. In comparison with the similar silica-based nanocomposites, Au NPs biosynthesized using *Diadesmis gallica* showed a mean particle size around 22 nm, whereas Au NPs synthesized by *Navicula atomus* had a smaller mean particle size (9 nm) (Schröfel et al. 2011). Spherical nanogold biosynthesized using *Eolimna minima* had a size distribution of 5–80 nm (Feurtet-Mazel et al. 2016). Finally, the WDE nanogold-composites show similar features as algal-based biosynthesis, and therefore, the WDE nanogold-composite is suitable for use as a nanocatalyst in heterogenous reactions.

**Spectroscopic analysis**

XRD analysis of samples 1Au/WDE-5Au/WDE confirmed a crystalline structure for the biosynthesized Au NPs. The XRD pattern in Fig. 4A shows three characteristic diffraction peaks at 2Theta values 45°, 52° and 77° corresponding to (1 1 1), (2 0 0) and (2 2 0) planes of cubic crystal structure gold (PDF number 04–0784), respectively. Figure 4A, B also confirmed the crystalline nature of the WDE in which the cristobalite phase was observed at characteristic angles of 25°, 37° and 42° of 2Theta. During the calcination process, diatomite earth (DE) for beer filtration crystallized to cristobalite (Cruickshanks-Boyd and Stevens 1983); thus, specific peaks were observed. Surface oxygen vacancies of crystalline SiO$_2$ might play an important role in nucleation of Au NPs (Ishida et al. 2020).

Table S3 in SI shows the results of the AES-ICP analysis, which confirmed a similar content of Au in all Au/WDE samples before and after washing with DEMI water. The Au content of the nanogold-composite was 1.16±0.05 wt.% and 1.13±0.03 wt.% respectively before and after washing, confirming that the NPs were stable and tightly anchored on the silica surface. The loss of Au after washing of Au/WDE samples is around 3.4%, and efficiency of Au NP biosynthesis and anchoring on the frustule surface after washing was around 73±2% (Table S3).

The homogeneity of Au/WDE and the content of the chemical compounds in the samples were verified and confirmed by XRF analysis (SI, Table S4). In all samples, minor amounts of MnO, Fe$_2$O$_3$, TiO$_2$, SO$_3$, P$_2$O$_5$, K$_2$O, CaO and Al$_2$O$_3$ were found, and the major component was SiO$_2$. The biosynthesis process did not influence the basic elemental composition, which was the same as the WDE.

Figure 2B shows the FTIR spectra of the WDE with nanogold. A comparison of the absorption bands of all samples shows that there are no significant differences in the spectra. There are the same infrared bands discussed in section Waste diatomite earth characterization, except for the band at 1408 cm$^{-1}$ for C=O, which disappeared after biosynthesis and will be discussed in the “Bioreduction properties” section.

The biosynthesis of Au NPs using the WDE from beer filtration was confirmed to be reproducible. The chemical properties of the five Au/WDE replicate samples were very similar. Beer production and filtration is a well-established biotechnological process and will produce waste material with similar properties beneficial for further manipulation.
and experiments (Mussatto 2009). Therefore, the WDE from various beer productions will have similar reduction properties for Au NP biosynthesis. In addition, the use of waste material from biotechnological processes for the preparation of nanomaterial is currently very desirable green technology (Jouyandeh et al. 2022).

**Bioreduction properties**

To evaluate which component of the WDE has the highest bioreduction activity, the biosynthesis of Au NPs was performed with beer yeast *Saccharomyces cerevisiae* and pure filter DE. The ability of brewer’s yeast and yeast in general to reduce Au, Ag and Pd metal ions to the nanoform have already been experimentally verified in several publications (Hulkoti and Taranath 2014; Kratošová et al. 2019). A colour change of the beer yeast suspension after adding Au precursor due to the presence of spherical Au NPs was observed in our experiments (Holišová et al. 2021). Figure 5A illustrates a suspension of yeast before and after exposure to the gold precursor.

Nanogold particles were further characterized by TEM (Fig. 5B), and the size of NPs was around 30–46 nm correlated with the size of Au NPs on the WDE surface.

The absorption bands (SI, Fig. S3) in the yeast infrared spectrum were mainly composed of the characteristic peaks for proteins, carbohydrates and hydroxyl groups. The contributions of O–H and N–H vibrations of proteins can be observed in a broad band at 3750–3000 cm\(^{-1}\) in the spectra. Bands in the region 3050–2700 cm\(^{-1}\) indicate the lipid composition of the yeast cell debris (Salari et al. 2013). The band at 1636 cm\(^{-1}\) is due to the bending vibration of the O–H group (Socrates 2004), while that at 1076 cm\(^{-1}\) may be attributed to the absorption of C–O–C from the RNA and DNA in the yeast or the C–O stretching from carbohydrates or alcohols in the yeast cell walls (Xie et al. 2019). Bands with shoulders at 1200–900 cm\(^{-1}\) may be connected to polysaccharides and those in the region of 900–700 cm\(^{-1}\) to nucleic acid (Taha et al. 2013).

FTIR spectra of the yeast with the Au NPs show two new peaks at 1520 and 1456 cm\(^{-1}\) as well as the loss of some bands (1406, 928, 848, 678 and 575 cm\(^{-1}\)). The absent band at 1406 cm\(^{-1}\) could be related to the missing band at 1408 cm\(^{-1}\) in the FTIR spectra of the 1-5Au/WDE samples after Au NP biosynthesis. It was suggested that the formation of the metallic NPs involves trapping of the metallic ions on the surface of the cells via electrostatic interaction with negatively charged groups (e.g. carboxylate, hydroxyl) in enzymes or in amino acids of polypeptides present in the cell wall (Hulkoti and Taranath 2014).

Table 1 shows the content of substances in the DE before and after beer filtration. The WDE contains a higher amount of soluble nitrogen, nitrogenous substances and organic carbon than pure DE. The nitrogen in the WDE may be partly due to the amino acids in the yeast enzymes. This result corresponds with the FTIR analysis of the WDE.

In the case of the synthesis of Au NPs using pure filter DE, the colour change of the suspension did not occur after 24 h, and it can be assumed Au NPs were not formed. ICP-AES analysis confirmed the low gold content (<0.018 wt. %) in the dried sample of pure DE after the addition of tetrachloroauric acid, in contrast to that in the Au/WDE sample (approximately 1.2 wt. %).

The FTIR spectrum of the DE (SI, Fig. S4) corresponds to the spectrum of L_DE. The spectrum of M_DE has a more amorphous character (the main Si–O–Si band is wider) and the band at 615 cm\(^{-1}\) (Si–O–Al) is missing (Anbalagan et al. 2010). In the spectrum of pure DE after Au precursor exposure (Au/DE), there are only bands corresponding to the presence of Si–O bonds with no change after the addition of the Au precursor. In addition, the spectrum of pure DE has no band at 1408 cm\(^{-1}\), which is present in the WDE spectrum due to the organic components after beer filtration but disappears after biosynthesis of Au NPs. In conclusion, we predict that DE does not have reducing properties for Au(III) cations and that the

| Table 1 | The content of compounds in the DE and the WDE |
|---------|---------------------------------------------|
|         | DE              | WDE               |
| Nitrogenous substances [%] | <0.50 | 9.75 ± 8.00 |
| Soluble nitrogen [mg·mL\(^{-1}\)] | <0.05 | 0.977 ± 0.058 |
| Organic carbon [wt.%] | <5.0 | 6.0–6.5 |
yeast cell debris in the WDE are responsible for Au NP biosynthesis.

**Paracetamol oxidation**

**Paracetamol removal kinetics**

The catalytic activity of nanogold-composite was investigated using PCTM in the presence of H₂O₂ without and with light irradiation. H₂O₂ served as a source of -OH radicals for PCTM oxidation, and irradiation would enable the photocatalytic activity of the Au NPs (Rabiee et al. 2022). The WDE without Au NPs in the presence of H₂O₂ was also tested for PCTM removal. Degradation of PCTM in the absence WDE was included as a blank.

The removal of the drug in the presence H₂O₂ activated by Au/WDE samples is shown in Fig. 6. After 72 h of reaction in the dark, approximately 62% of PCTM was removed in the presence of Au/WDE, with a removal rate constant of 0.0126 h⁻¹. No degradation of PCTM and in control mixtures without Au NPs was observed in the dark (Fig. 6A).

Furthermore, the tested mixtures with PCTM were studied under the light in the range of 525–530 nm to boost Au NPs’ catalytic activity. Sixty-seven per cent of PCTM was removed, and the rate constant was slightly higher at 0.0148 h⁻¹ (Fig. 6B). Surface plasmon resonance (SPR) was generated at 532 nm for the Au/WDE samples (Fig. 6C), but light irradiation did not have a significant influence on PCTM oxidation.

Degradation of PCTM has been reported by various kinds of catalysts which are given in Table 2. It is problematic to compare the catalytic efficiency of the nanogold-composite with other nanomaterials because the input conditions like PCTM and nanocatalyst concentration and its size are different. However, we used a higher concentration of PCTM solution in comparison with mentioned studies in Table 2 and despite that our nanogold-composite proved good catalytic

![Graph A](image1)

![Graph B](image2)

![Graph C](image3)

Fig. 6 A Degradation of PCTM in the presence WDE and Au/WDE. B The curves of PCTM degradation using Au/WDE under the light (525–530 nm) are shown with the comparison of PCTM degradation using Au/WDE without light. C UV–VIS diffuse reflectance spectrum confirmed the characteristic SPR peak of Au/WDE at 532 nm.
activity. Further research will be focused on increasing the nanogold-composite catalytic activity of PCTM degradation. One of the way how the unique catalytic properties of Au NPs can be further enhanced is the combination of the nanogold with other nanomaterials, such as ferrofluid (Holišová et al. 2019a).

Principle of nanogold-composite catalytic effect

We propose that Au NPs have peroxidase-like activity for H₂O₂ reduction and production of hydroxyl radicals (·OH), which bring about PhP oxidation (Liu et al. 2019). The ·OH radicals can abstract hydrogen atoms from other molecules to form water (Zhang et al. 2018). Concurrently, Au NPs act as catalysts, which is influenced by their quantum size. It was indicated that the bilayer morphology of the electron-laden Au cluster is responsible for the dissociation of O₂ and that these effects are crucial for enhanced catalytic reactivity. The electron structure resulting from Au–Au bond contraction in NPs could also explain the observed enhanced reactivity. Recent research suggested that correlations may exist between the active site and the low-coordinated Au atoms, particularly at corner sites (Alshammari and Kalevaru 2016).

Generally, NPs are more reactive than microparticles, due to the highly curved surfaces and thus the larger number of exposed surface atoms. The edges of the triangular NPs are highly curved with locations of increased reactivity. We assume that the combined effects of NPs size, shape and peroxidase-like activity contribute to the PCTM degradation (Wen et al. 2016). The possible by-products of the reaction could be 1,4-benzoquinone or oxamic acid in acidic condition. The final product of PCTM degradation may be oxalic acid (Fig. 1) (Skolotneva et al. 2020).

Further, the degradation of PCTM with Au/WDE was studied under light at 525–530 nm. Our hypothesis was that light would generate SPR and promote oxidation of the PCTM in the presence of H₂O₂. Generally, a local enhanced electromagnetic field forms on the surface of metal NPs promoting the generation of reactive oxygen species (ROS) including ·OH, O₂⁻, and O₂ (He et al. 2014). The generation of hydroxyl radicals is strongly dependent on the chemical environment and more ·OH is formed at a lower pH (Okawa et al. 2015). In our case, this hypothesis was not confirmed, and the catalytic activity of Au/WDE was not increased under light. This may have been due to insufficient energy and intensity of the light, and/or inappropriate size or concentration of Au NPs anchored on the WDE. An important parameter in photocatalysis efficiency is the catalyst dosage. At higher catalyst dosages, a screening effect due to prevention of light penetration could occur resulting in decreased photocatalytic efficiency (Padilla Villavicencio et al. 2020).

Conclusion

We report a novel use of WDE for the biosynthesis of Au NPs, in which WDE served as both a reducing agent for Au ions and a stabilizer for the Au NPs. It was verified that the yeast cell debris from beer filtration enabled nanogold biosynthesis. Moreover, diatomite earth, the inorganic component of the WDE, served as a support for their efficient anchoring. The nanogold-composite contained spherical, crystalline Au NPs with an average size of 31 nm. We demonstrated that this biosynthesis method is reproducible and is therefore promising for future use. The nanogold-composite was tested as a catalyst for PCTM decomposition in the presence of H₂O₂ under dark and light conditions. The Au NPs anchored on WDE were shown to catalyze the degradation of PCTM in the dark and under light irradiation, with respectively 62% and 67% degradation after 72 h, corresponding to rate constants of 0.0126 h⁻¹ and 0.0148 h⁻¹, respectively. The performance of Au NPs supported on the silica matrix demonstrates their potential as novel nanocatalysts for use in innovative water treatment processes for the removal of problematic PhPs.
Further research will be focused on increasing their catalytic activity and identifying degradation products during PCTM decompositions. The unique catalytic properties of Au NPs can be further enhanced by combining the nanogold with other nanomaterials, such as ferrofluid.

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**Author contribution** All authors contributed to the study of conception and design. Material preparation, TEM and SEM analysis and data collection were performed by Veronika Krbečková and Zuzana Šimonová. Šárka Tomisová was responsible for the ICP-AES analysis. Karla Čech Barabaszová focused on the BET analysis. Pavlína Peikertová arranged the FTIR analysis and measurement and his kind help. Many thanks to Ladislav Svoboda, Ph.D., for the spectrophotometry measurement and his kind help.

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