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FULL PAPER

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Novel marine-based gold nanocatalyst in solvent-free synthesis of polyhydroquinoline derivatives: Green and sustainable protocol

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We report an ecofriendly synthetic approach for the fabrication of biogenic gold nanoparticles (AuNPs) using electron-rich sea cucumber extract as a bio-reductant and stabilizing agent in reducing gold cations into AuNPs at the optimal conditions. The produced AuNPs are spherical in shape with an average particle size of 11 ± 1.5 nm in transmission electron microscopy (TEM) and exhibited a crystal structure of face-centered cubic in X-ray diffraction (XRD) analyses. Our results indicated that bioinspired AuNPs demonstrate superior catalytic activity in the safe and facile one-pot synthesis of polyhydroquinoline derivatives under solvent-free reaction conditions. This green route encompasses multiple benefits including highly recyclable bioinspired catalyst (5 cycles), short reaction times, convenient workout, high to excellent product yields (82%–97%), and nonhazardous conditions.

KEYWORDS

biosynthesis, gold nanocatalyst, polyhydroquinoline, sea cucumber extract

1 | INTRODUCTION

Green synthesis is a developing area in the field of chemistry, which aims to design clean products and sustainable processes through whether curtailing or eliminating the implementation of unsafe solvents as well as toxic reagents.[1,2] Because the growing innovative green processing and synthesis utilizes nontoxic precursors and mild reaction conditions, they are considered as a valuable alternative option for promoting environmental sustainability.[3] Moreover, ecofriendly synthesis reactions essentially comply with 12 principals of green chemistry, providing cost-effective, facile, stable, and relatively reproducible nanomaterial. Hence, over the past decade, diverse biological methods have been developed in the biosynthesis of nanoparticles (NPs) including plants,[4,5] microorganisms (bacteria, yeast, and fungi),[6] and marine algae extracts[7–9] among many others. Both marine and land sources are applicable in the biosynthesis of a wide range of NP. In fact, there are plenty of publications, for example, articles, books, and reviews, that have been reported in the literature using those methodologies. They present green downstream processing in NP production; nevertheless, it is premature to demonstrate which one is more preferential.[10] Compared with the fairly complicated and harsh operational conditions of physical and chemical synthetic procedures, the biocompatible peers are environmentally friendly and fiscal substitutes for scaling up to large production of NPs.

Over the past years, noble metal NPs have gained popularity from researchers owing to their considerably physicochemical and biological properties. In particular, gold NPs (AuNPs) extensively preferred and synthesized via green synthesis[11,12] because of its unique intrinsic properties[13] and broad-spectrum application scopes in areas such as biomedicine,[14] environmental remediation,[15] organic photovoltaics,[16] sensors,[17]

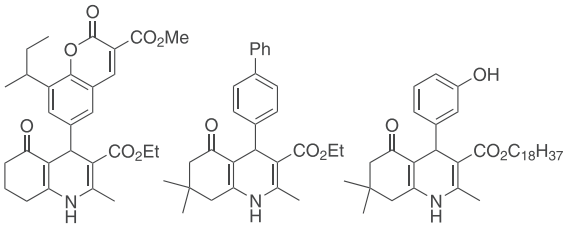
optical imaging,[18] and therapeutic agents.[19] In addition, they are widely used as a catalyst in a number of chemical reactions.[20]

Multicomponent reactions (MCRs) as powerful synthetic methodology have attracted a surge of interest in modern organic synthesis and medicinal chemistry because they create strategic organic molecules and variation of structures in a one-pot single fashion.[21] They not only reduce the amount of energy and solvent required for separation and purification of intermediates but also generate highly selective products that maintain large quantities of the starting material. Owing to multiple benefits of MCRs process including atom-economy, efficiency, diversity, and environmental sustainability, the development of new NP-catalyzed MCRs based on eco-friendly procedures has been established as an area of growing interest in organic chemistry.[22]

The ocean covers more than 70% of the surface of our planet. Hence, the surging popularity of marine routes in synthesis of NPs mainly relies on their abundance, reasonable costs, sustainability, and less contamination. However, the large-scale production of green NPs from lab scale to pilot-plant level using an eco-friendly and biocompatible process still at its early stage in comparison with conventional methods.[23] In this connection, sea cucumbers are a high value of nutrients marine animals that widely used as food and traditional medicine especially in Asia. These edible sea cucumbers are rich sources of nutritional ingredients such as high-quality proteins, vitamins, minerals, and fatty acids. It is also home of broad spectrum of isolated electron-rich bioactive compounds including alkaloid, sulfated polysaccharides, terpenoids, phenols, flavonoids, saponins, carbohydrates, glycosides, tannins, and steroids.[24]

Polyhydroquinoline (PHQ) compounds are considered as a privileged skeleton for various N-heterocyclic derivatives, and because of their promising pharmacological and biological activities, they were broadly investigated as neurotropic, anticancer, antitubercular, and antidiabetic activities[25] (Scheme 1). Owing to these distinct features, PHQ nucleus unites have received considerable attention in medicinal chemistry such as antitumor and vasodilator[26,27]; hence, significant attempts have been devoted to innovating straightforward synthetic methods targeting compounds possessing the PHQ core.

Therefore, in the present research, we illustrate an innovative biogenic procedure to fabricate Au NPs using the natural extract of sea cucumber[28] under optimized reaction conditions. Then, the bioprepared AuNPs were utilized as a novel biogenic catalyst in the solvent-free synthesis of environmentally benign PHQ derivatives by one-pot four-component designed in time-efficient MCRs manner. Apart from full compliance with green chemistry rules, solvent-free reactions manifest ample benefits in industrial applications mainly due to facile workout technique, low cost, and pollution reduction.[26]



SCHEME 1 Selected biologically active polyhydroquinoline products[25]

2 | EXPERIMENTAL

All chemicals used in this study were purchased from Sigma-Aldrich and utilized as received. Produced NPs were analyzed using a UV–vis (Analytic Jena-Germany) spectrophotometer covered the spectral range 200–700 nm. X-ray diffraction (XRD) diffractometer (Cu Ka, radiation, $\lambda = 1.5405$ Å) was operated at a scanning speed of 2/min from 10 to 80 (2θ). Fourier transform infrared (FTIR) spectra of the compounds were recorded on Nicolet MAGNA-IR 550 spectrometer (Madison, WI, USA) by a KBr pellet. To explore the surface of the NPs, thermogravimetric analysis (TGA; PerkinElmer, Pyris 1, USA) experiment was run under inert argon gas flow. Transmission electron microscopy (TEM) was performed with a Leo 912 AB at an accelerating voltage 200 kV. For organic product characterization, melting points were recorded using the electrothermal IA9200 apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker (Rheinstetten, Germany) NMR spectrometer at 250 and 63 MHz using tetramethylsilane (TMS) as the internal standard. The progress of the reactions and determination of the purity of the substrates were monitored using thin-layer chromatography (TLC) on silica gel SILG/UV 254 and 365 plates. Sea cucumber (*Holothuria parva*) was collected during low tide from the coasts of the Bushehr Province, Iran.

2.1 | Preparation of sea cucumber extract

The organic extract was obtained by mixing 3 g of thoroughly washed air-dried powder of body wall of sea cucumber organ sample with 10 ml of extraction solvent mixtures of methanol and distilled water (3:1, v:v) and 97 m; of distilled water in a 150-ml Erlenmeyer flask under vigorous stirring with a magnetic stirrer. The

combination was heated for 20 min, then cooled and filtered using standard Whatman Grade 1 filter paper. The resultant was stored in the refrigerator for fulfilling the additional experiments demand.

2.2 | Biosynthesis of AuNPs

AuNPs were synthesized by adding 30 ml of an aqueous solution of $HAuCl_4{\cdot}3H_2O$ (1 mM) to 10 ml of sea cucumber extract. The reaction mixture containing sea cucumber extract and tetrachloroauric acid solution was incubated at 70°C for 24 h on a shaker at 600 rpm. The purification of obtained solution accomplished by reiterated centrifugation at 15,000 rpm for 15 min followed by decanting and dried at 70°C in an oven overnight.

2.3 | Synthesis of PHQ derivatives in the presence of Au nanocatalyst

A mixture of 4-hydroxy coumarin (**1**, 1 mmol) and ammonium acetate (**4**, 2 mmol) was heated with stirring at 100°C for half an hour. Then, dimedone (**2**, 1 mmol), aldehyde (**3**, 1 mmol), and Au nanocatalyst (1.5 mg) were added, and the reaction was continued for 20 min under solvent-free conditions (Scheme 2). After completion of the reaction indicated via TLC monitoring, the solution was cooled down to room temperature, and then the precipitated product was diluted with cold H_2O and filtered. The crude precipitate dissolved in DMF (5 ml), and the catalyst was then separated by simple centrifugation, washed with large amounts of anhydrous ethanol, dried at 60°C overnight, and recycled. After the separation of Au nanocatalyst, 12 ml of water was added to the mixture of reaction to precipitate of the product. Then, the precipitate was filtered, washed with water, and recrystallized by ethanol to afford pure products.

2.4 | 7-(4-Chlorophenyl)-10,10-dimethyl-7,10,11,12-tetrahydro-6*H*-chromeno[4,3-*b*]quinoline-6,8(9*H*)-dione (5k)

MP: (256–258°C); FTIR (KBr, ν, cm^{-1}): 3,308, 2,959, 2,933, 1,682, 1,670, 1,464, 1,363, 1,225, 1,194, 1,147, 1,042, 830, 733, 620. ^{1}H NMR (250 MHz, DMSO-d_6) (Figure S1): δ 9.70 (s, 1H, NH), 8.27 (d, J = 7.5 Hz, 1H, Ar–H), 7.58 (m, 1H, Ar–H), 7.22–7.40 (m, 6H, Ar–H), 4.90 (s, 1H, CH), 2.48 (s, 2H, CH_2), 2.24 (d, J = 16 Hz, 1H, CH_2), 2.04 (d, J = 16 Hz, 1H, CH_2),1.03 (s, 3H, CH_3), 0.90. (s, 3H, CH_3), ^{13}C NMR (63 MHz, DMSO-d_6) (Figure S2): δ 196.1, 161.7, 153.5, 151.3, 146.2, 143.7, 133.5, 132.2, 131.0, 129.4, 125.5, 124.5, 118.3, 114.4, 111.9, 102.8, 51.5, 35.6, 33.6, 30.4, 28.0. Anal. calcd for $C_{24}H_{20}NO_3Cl$: C 71.02, H 4.97, N 3.45. Found: C 71.04, H 4.92, N 3.47.

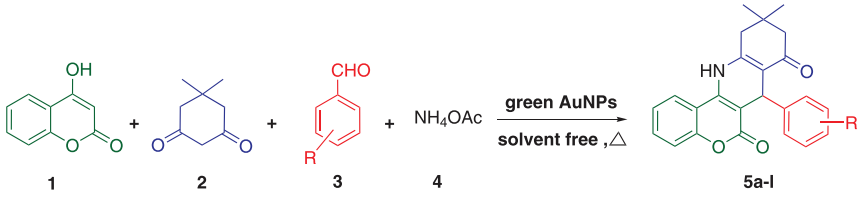
2.5 | 7-(4-Bromophenyl)-10,10-dimethyl-7,10,11,12-tetrahydro-6*H*-chromeno[4,3-*b*]quinoline-6,8(9*H*)-dione (5l)

MP: 283–285°C; FTIR (KBr, ν, cm^{-1}): 3,309, 2,949, 2,939, 2,876, 1,669, 1,462, 1,362, 1,235, 1,192, 1,145, 1,041, 851, 758, 621. ^{1}H NMR (250 MHz, DMSO-d_6) (Figure S3): δ 9.70 (s, 1H, NH), 8.28 (d, J = 7.5 Hz, 1H, Ar–H), 7.60 (t, J = 7.5 Hz, 1H, Ar–H), 7.32–7.43 (m, 4H, Ar–H), 7.15–7.18 (m, 2H, Ar–H), 4.88 (s, 1H, CH), 2.62 (s, 2H, CH_2), 2.24 (d, J = 16 Hz, 1H, CH_2), 2.04 (d, J = 16 Hz, 1H, CH_2),1.04 (s, 3H,CH_3), 0.90. (s, 3H, CH_3), ^{13}C NMR (63 MHz, DMSO-d_6) (Figure S4): δ 196.1, 161.6, 153.5, 151.2, 146.6, 143.7, 133.5, 132.3, 131.5, 125.5, 124.5, 120.7, 118.3, 114.3, 111.8, 102.7, 51.5, 35.7, 33.6, 30.4, 28.0. Anal. calcd for $C_{24}H_{20}NO_3Br$: C 64.01, H 4.48, N 3.11. Found: C 64.04, H 4.45, N 3.14.

3 | RESULTS AND DISCUSSION

3.1 | UV–visible spectroscopy analysis

The preliminary visual confirmation of AuNPs formation was observed when the solution color turned from light yellow to dark brown. Further, in contrast to pristine sea cucumber extract, the generated biogenic AuNPs were determined spectrophotometrically in the UV–vis spectrum, which appears distinctive plasmon peak at 550 nm (Figure 1a,b). Monitoring the reaction kinetics of $AuCl_4^-$ reduction by UV–vis absorption spectrum as a function of time (5 min, 15 min, 45 min, 1 h, and 4 h) revealed the completion of the reaction after 1 h and the stability of the absorbance peak, with no significant change beyond



SCHEME 2 The synthesis of polyhydroquinoline derivatives catalyzed by a novel sea cucumber extract-mediated biosynthesized gold nanoparticles (AuNPs)

this time, as shown in Figure 1b. These results are in accordance with earlier reports showing absorption peak around 525–540 which is attributed to the noble AuNPs.[29]

3.2 | XRD analysis

The XRD pattern of gold NPs fabricated by sea cucumber extract is depicted in Figure 2. The XRD spectrum reveals four characteristic Bragg diffraction peaks including 38.10°, 45.15°, 65.37°, and 78.24°, which related to the (111), (200), (220), and (311) lattice planes, respectively[30] (Figure 2). As a result, the produced green AuNPs are highly crystalline in nature with the face center cubic (FCC) crystal structure. Moreover, the obtained results of bio-assisted AuNPs are in good agreement with XRD reference pattern of the Joint Committee on Powder Diffraction Standards (JCPDS) for the bulk gold (card no: 04-0784)[31] as well as biological AuNPs synthesized utilizing other eco-friendly synthetic procedures.[11,32] According to the line width of the intensive peak at 38.10° (111), the average crystallite size of biogenic AuNPs calculated by Debye–Scherrer's equation is found to be 10 nm.[33]

3.3 | TEM characterization

The morphology and particle size of AuNPs were analyzed using the TEM technique. As can be seen in Figure 3, the morphology of the NPs is spherical in nature, with the slight aggregation of particles occurred haphazardly due to inappropriate preparation of the sample. Additionally, the TEM image demonstrated that the AuNPs have a mean diameter of about 11 ± 1.5 nm

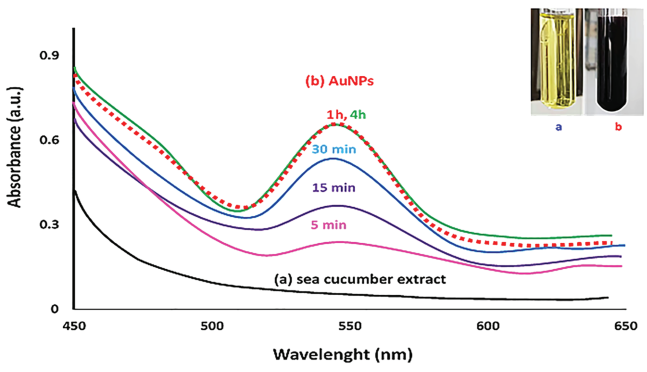


FIGURE 1 UV–visible spectra of (a) ethanolic sea cucumber extract, (b) biogenic gold nanoparticles (AuNPs), and impact of different time intervals on AuNPs absorbance peak; inset illustrates photographic images of visual color changes upon the formation of AuNPs

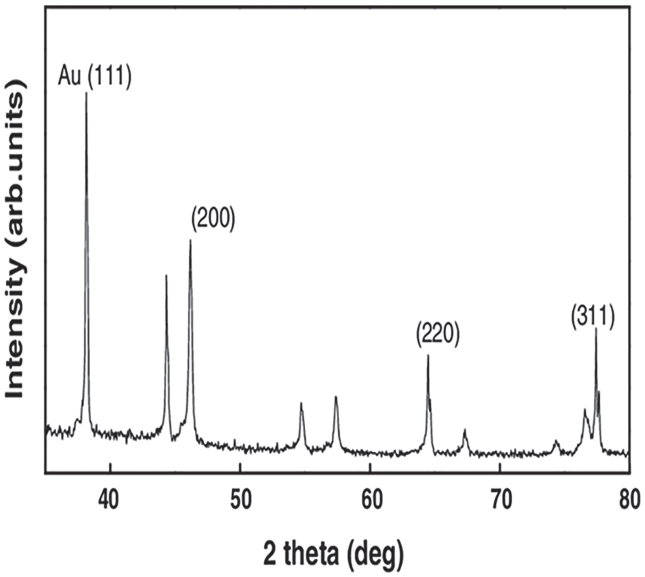


FIGURE 2 X-ray diffraction (XRD) pattern of marine-based gold nanoparticles (AuNPs) arranged in crystalline face center cubic (FCC) lattice structure

achieved through counting 300 particles by ImageJ software.[34]

After characterizations, we examined the catalytic efficiency of the AuNPs in the one-pot synthesis of novel PHQ derivatives using a four-component condensation reaction of aldehyde **1a,** 4-hydroxy coumarin **2b,** dimedone **3c**, and ammonium acetate **4d** as a model reaction under solvent-free condition (Scheme 2). To the best of our knowledge, this is the first report on the application of biosynthesized AuNPs as an efficient catalyst in this type of organic reactions.

3.4 | FTIR analysis

FTIR spectrum of the pristine sea cucumber extract and bio-mediated AuNPs is depicted in Figure 4. The results demonstrate the availability of various sea cucumber-derived functional groups on the surface of NPs, which involved in bioreduction and proficient stabilization of fresh AuNPs (Figure 4b). This postulation can be fortified because the position and intensity of some peaks, in particular, carbonyl and phenolic hydroxy groups, have changed in the biological AuNPs spectrum rather than corresponding raw sea cucumber extract. The noticeably abroad peak appeared in the range of 3,423 cm^{-1} is associated with O—H and/or N—H stretching, resulting from the multiple intramolecular hydrogen-bonding interactions. The presence of an aliphatic symmetric C—H stretching mode of the methylene and methyl groups can be assigned at 2,945 and 2,885 cm^{-1}. The vibrational

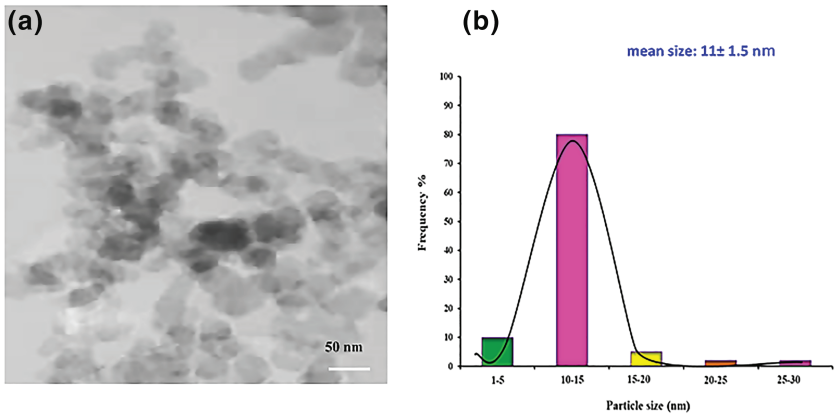


FIGURE 3 (a) The transmission electron microscopy (TEM) image and (b) the histogram demonstrating particle size distribution of gold nanoparticles (AuNPs) biosynthesized using sea cucumber extract

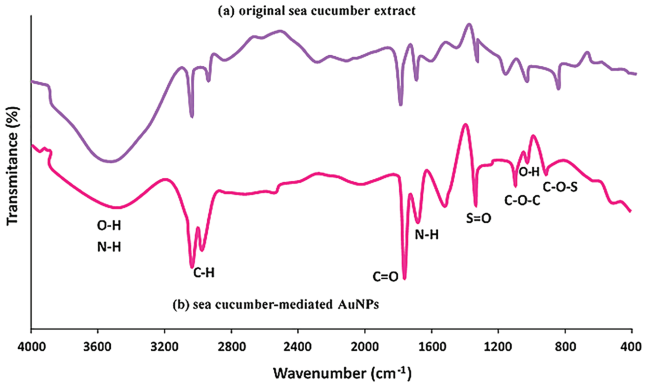


FIGURE 4 Fourier transform infrared (FTIR) spectra of (a) original sea cucumber extract and (b) bio-mediated gold nanoparticles

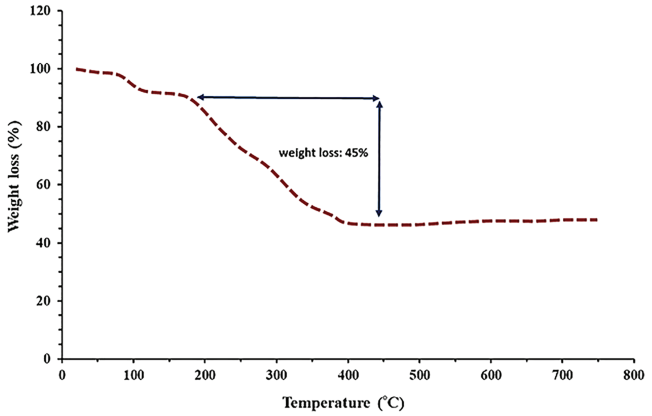


FIGURE 5 Thermogravimetric analysis (TGA) plot of biocapped gold nanoparticle (AuNPs) fabricated using sea cucumber extract

band observed at 1,731 cm^{-1} is corresponded to the stretching vibration of the carbonyl group (C═O). The absorption band centered at 1,639 cm^{-1} is attributed to N—H bending vibrations of residual amide. The quite distinctive absorption band at 1,336 cm^{-1} is corresponded to C—N stretching of amino and/or amid entity. The characteristic absorption peaks at 1,246 and 823 cm^{-1} can be assigned to S═O and C—O—S stretching modes of sulfated polysaccharide. Finally, carbohydrates etheric and phenolic O—H vibration bands appear at 1,132 and 1,048 cm^{-1}, respectively.[35]

3.5 | TGA examination of biocapped AuNPs

In order to determine the proportional amount of the biofunctional groups adsorbed on the surface of NPs, the TGA technique was used. Figure 5 shows two steps of steady weight loss in the TGA curve of the freshly bioproduced AuNPs. First, an initial weight loss rate of 10% occurs in the temperature range of 80–110°C high likely due to the evaporation of the absorbed water. The second weight loss with a proximate proportion of 45% is mainly attributed to the decomposition of bioorganic compounds that were compassed the AuNPs. As a result, TGA analysis reveals that copious bioactive phytochemicals present in the marine cucumber extract such as phenolic and polysaccharides could coat the surface of the nanoparticles and function as steric and/or electrostatic stabilizing agent.[36] This result is in accordance with FTIR findings and other reports of green synthesized AuNPs,[37] exhibiting multiple functions of marine-derived biomolecules in reduction gold cations, shielding fresh AuNPs, and curb aggregation/agglomeration of biocompatible NPs.

3.6 | Biogenic AuNPs catalytic activity

Our investigation commenced with an optimization study of the different catalytic concentrations for the solvent-free synthesis of PHQ derivatives in the presence of AuNPs as a robust catalyst at 60°C. The practicability

TABLE 1 Impact of catalytic concentration of green gold nanoparticle (AuNPs) in the solvent-free synthesis of polyhydroquinoline **5a**

Entry	Catalytic conc. (mg)	Time (min)	Yield (%)
1	0.5	50	68
2	1	50	79
3	1.5	50	95
4	2	50	91
5	2.5	50	80

TABLE 2 Comparison of various catalysts in the synthesis of **5a**

Entry	Catalyst	Time (min)	Yield (%)
1	Bulk gold	160	53
2	Chemical AuNPs	120	75
3	Acetic acid	140	≤60
4	Biogenic AuNPs	50	95
5	None	24 h	15

Abbreviation: AuNPs, gold nanoparticles.

of the various catalytic concentrations is depicted in Table 1. It is found that 1.5-mg loading of AuNPs (Entry 3) is the optimal amount of choice in the model reaction of four components according to yield as presented in Table 1. It can be noted that sensible changes in the yield were observed using larger quantities of green Au nanocatalyst.

Afterward, in order to compare the catalytic activity of biprepared AuNPs with other catalysts, different types of catalysts have addressed in the model reaction under free solvent conditions as a function of end reaction time. As can be shown from Table 2, the biological AuNPs relatively afford higher yield (Entry 4) of the related PHQ products in record time rather than counterparts including chemical-based AuNPs. In addition, in the absence of catalyst and after even lengthy reaction time only neglectable yield of product was produced. Apart from using bioinspired methods in the biogenic synthesis of NPs, this type of green nanomaterial genuinely takes advantage of controllable, well-defined size, shape, and particle distribution because they are encompassed by a diverse range of biomolecules during both reduction and stabilization process. As a result, in nano-catalyzed organic reactions, it would remarkably enhance their catalysis efficiency rather than corresponding chemical ones.[38] According to these results, it can be noted that the use of eco-friendly AuNPs would offer substantial benefits for the sake of environmental sustainability when compared with commercial ones.

During the green synthetic reactions, the recyclability of the catalyst is of paramount importance. Hence, for the recovery of bioinspired AuNPs-based catalyst, it was filtered off from the reaction mixture via centrifugation and washed with a mixture of water and ethanol to eliminate the residual product. Once dried, it was devoted to another reaction. We examined the reusability of the AuNPs in subsequent experiments up to 5 cycles without appreciable loss in its catalytic activity as illustrated in Figure 6.

To scrutinize the scope and limits of bioproduced gold nanocatalyst activities, more functionalized PHQ derivatives were prepared, and experiments were accomplished by creating an array of arylaldehydes holding a collection of different functional groups (Table 3). All products were produced in high to excellent yields and high purity. Based on results, both electron-withdrawing and electron-donating substituents increase the yield of products, advocating the great potency of designed reaction in this study. Furthermore, 4-nitrobenzaldehyde (Table 3, Entry 6) afforded the target product (**5e**) in the higher

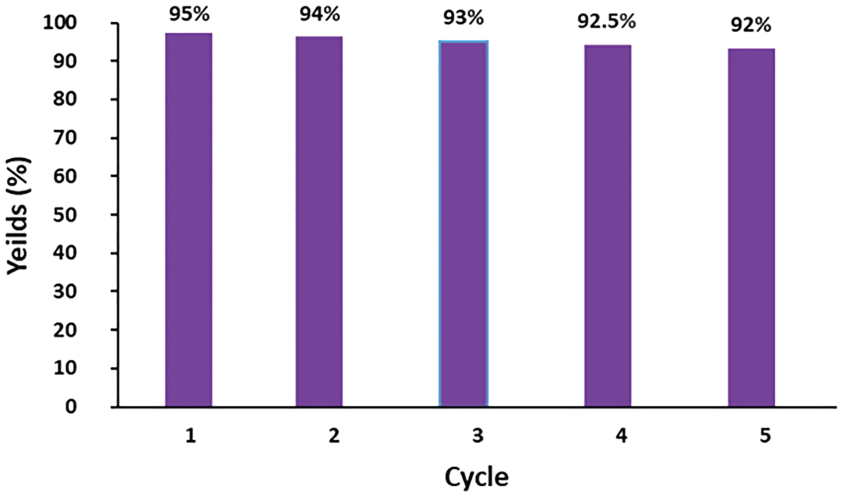
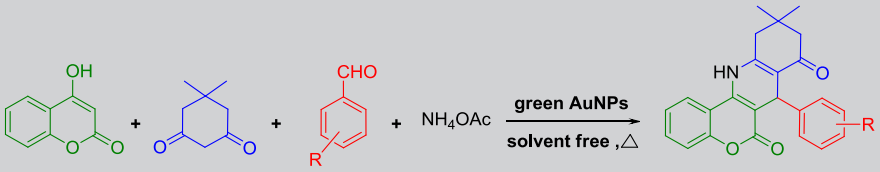
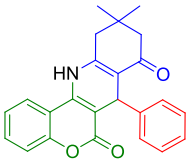
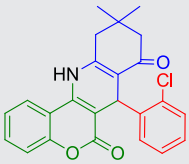
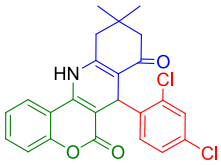
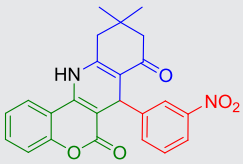
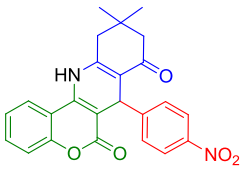


FIGURE 6 Recyclability of biosynthesized gold nanocatalyst for the synthesis of **5a**

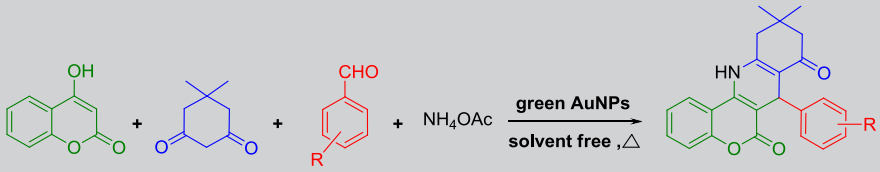
TABLE 3 polyhydroquinoline derivatives synthesized in the presence of biological gold nanocatalyst

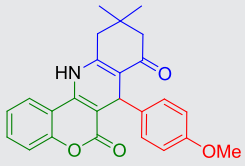
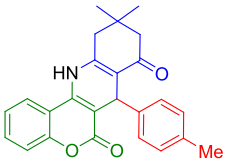
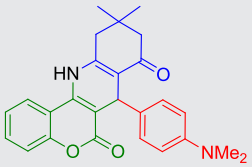
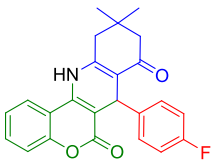
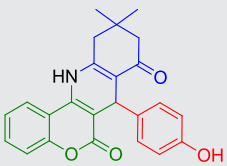


Entry	R	Product		Yield (%)[a]	Mp (°C)	Reported Mp (°C)
1	H		**5a**	95	271–273	272[41]
2	2-Cl		**5b**	89	300–302	300[41]
3	2,4-DiCl		**5c**	90	330–332	333–334[42]
4	3-NO_2		**5d**	95	283–285	282–284[42]
5	4-NO_2		**5e**	97	277–279	279[41]

(Continues)

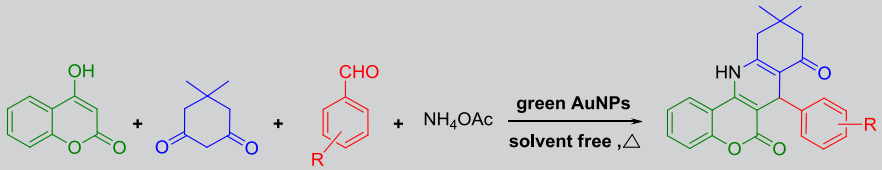
TABLE 3 (Continued)

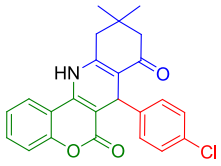
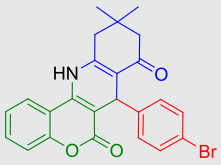


Entry	R	Product		Yield (%)[a]	Mp (°C)	Reported Mp (°C)
6	4-OCH_3		**5f**	82	243–245	242[41]
7	4-Me		**5 g**	94	251–253	250[41]
8	4-$N(CH_3)_2$		**5 h**	95	159–161	160–161[42]
9	4-F		**5i**	83	219–220	220[41]
10	4-OH		**5j**	95	295–297	295[41]

(Continues)

TABLE 3 (Continued)



Entry	R	Product		Yield (%)[a]	Mp (°C)	Reported Mp (°C)
11	4-Cl		**5 k**	91	256–258	—
12	4-Br		**5 l**	93	283–285	—

Note: Reaction conditions: 4-hydroxy coumarin (1 mmol), ammonium acetate (2 mmol), dimedone (1 mmol), aldehyde (1 mmol), and AuNPs (1.5 mg).

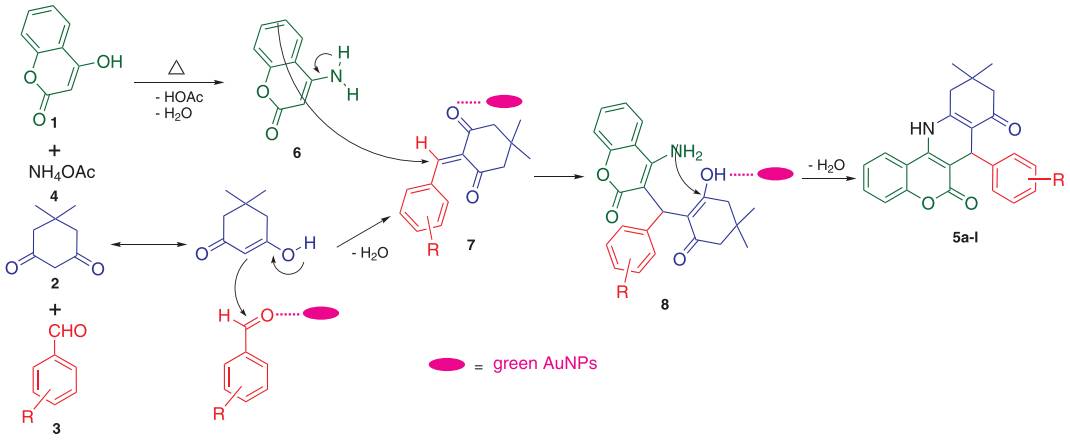
Abbreviation: AuNPs, gold nanoparticles.

[a]Isolated yeild.

yield (97%) rather than counterpart products under the same reaction conditions. Experimentally, aliphatic aldehydes were presented products with a lower yield than corresponding aromatic peers in the multicomponent synthesis of PHQ. Furthermore, a significant proportion of the by-products also were obtained along with target compounds when aliphatic aldehydes were involved in the synthesis reaction.

3.7 | PHQ synthesis mechanism

Whereas no experimental proof established concerning the mechanistic pathway of four-component reaction, a reasonable mechanism could be elucidated by the reaction sequence in Scheme 3 according to literature precedent of alike MCRs. First, the reaction perhaps proceeds via a reaction between the in situ generated NH_3 from ammonium acetate (**4**) and 4-hydroxy coumarin (**4**) to yield 4-amino coumarin (**6**) at 100°C. Second, based on Knoevenagel condensation, the enolic form of dimedone (**2**) reacts with the catalyst-activated carbonyl of arylaldehyde (**3**) to produce the α,β-unsaturated compound **7**. Third, compound **7** converts to intermediate **8** via Michael addition of enamine (**6**). Lastly, products **5a–l** were achieved through an intramolecular ring cyclization process from compound **8**, followed by the elimination of a molecule of water. The Lewis acidic character of bioinspired AuNPs catalyst could act an essential role in both enhancing the electrophilicity of the reactants as well as intermediates stability. These results are consistent with the concept that indicates that in Lewis acid-catalyzed organic reaction, a metal-based Lewis acid serves as an electron pair acceptor that in turn increases the reactivity of an organic substrate toward nucleophilic attack.[39,40] Moreover, it is presumably expected that electron-withdrawing groups afford products with better yields than electron-donating ones; however, because of the appropriate effect of biogenic Au nanocatalyst in the synthesis of PHQ derivatives, interestingly both electron-donating and withdrawing groups of benzaldehyde lead to an approximately excellent yield of products.



SCHEME 3 A putative mechanism route for the synthesis of polyhydroquinolines using marine-mediated Au nanocatalyst

4 | CONCLUSION

In summary, we have established a novel marine-based biocompatible and a straight forward synthetic route for the biofabrication of AuNPs via the direct interaction of gold nitrate with extract of the sea cucumber body wall. In the aqueous reaction mixture, the extract-derived electron-rich biomolecules not only reduced the Au ions to zero-valent metallic atoms but also stabilized and protected the freshly formed NPs from agglomeration. Our results indicated that highly recyclable biogenic AuNPs demonstrated superior catalytic activity in the one-pot synthesis of polyhyroquinline derivatives, producing higher yields of desired products in record time under solvent-free conditions. Owing to compliance with green chemistry principles, this novel sea cucumber-mediated biosynthesized AuNPs could consider as a sustainable and environmentally friendly protocol in broad-spectrum applications such as organic synthesis, medicinal chemistry, and environmental remediation. In the context of NP biofabrication following future prospects should be addressed: (a) comparison of viable marine organisms as sources of electron-rich molecules advantageous in the synthetic processes of NPs, (b) recognizing controlled and optimized conditions for large-scale production of green NPs, and (c) investigation of the various parts of marine creature for highly efficient synthesis of NPs including organ, tissue, leaves, stem, and cell.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable; no new data are generated.

AUTHOR CONTRIBUTIONS

Mahsa Sepahvand: Investigation; project administration; software; visualization. **Foad Buazar:** Methodology; supervision; visualization. **Mohammad Hosein Sayahi:** Formal analysis; methodology; project administration; validation.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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