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Research article

Synthesis and chemosensing of nitrofurazone using olive oil based silver nanoparticles (O-AgNPs)

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ABSTRACT

Silver nanoparticles were synthesized using Olive oil (O-AgNPs) as reducing as well as capping agent and extensively characterized by UV–vis spectroscopy, fourier transform infrared, energy disperse spectroscopy, dynamic light scattering and atomic force microscopy. The chrome yellow color solution of O-AgNPs show the typical absorption maximum at 430 nm. FTIR analysis revealed that the carbonyl (C=O) groups of Olive oil plays the most vital role in reduction of Ag^+ and the nanoparticles synthesis. The morphology of O-AgNPs were found spherical in nature, while the size of O-AgNPs ranges between 35 to 65 nm as established by AFM and DLS studies, respectively. Stability of O-AgNPs studied by varying storage period, temperature, salt and pH of the medium were found quite stable probably because of oil suspension nature. Despite potent antimicrobial, anti-biofilm and biofilm eradicating activities, O-AgNPs were found to be non-toxic on cell lines. Moreover, chemosensing properties of the O-AgNPs were also tested against different drugs. The O-AgNPs showed high selectivity towards nitrofurazone (NFZ) with the lowest detection limit of 1.88 μM as was monitored by UV–vis spectroscopy. The mechanism of O-AgNPs interaction with drug was followed by DLS suggest that NFZ induces a time dependent nanoparticles aggregation.

1. Introduction

Environmental pollution has become an alarming issue in the developing as well as advanced countries. Pharmaceutical drugs released in the environment is one of the most emerging issue and which need to be consistently monitored. A large amount of spurn drugs were reported frighteningly in high concentrations ($\mu g\ ml^{-1}$) range in shallow, drainage, and sewage water system of Karachi, Pakistan [1,2] which finally reaches in trace amount in drinking water mainly because of poor drainage and/or water supplying system.

Nitrofurazone (NFZ; 2-[(5-nitro-2-furanyl) methylene] hydrazine carboxamide) was first introduced in mid 40s. NFZ as a synthetic broad-spectrum antibiotic, has been extensively applied in the prevention and treatment of several protozoan infections (e.g. trypanosomiasis) and bacterial diseases particularly caused by *Escherichia coli* and *Salmonella* species [3,4]. NFZ belongs to the nitroufuran group of antibiotics, primly including nitrofurazone, furazolidone, nitrofurantoin and furaltadone. Besides antimicrobial function, NFZ also used for wound healing of burns as well as to increase the productivity of aquatic and farm animals [5]. It is also very well established fact that NFZ causes chronic toxicity by lifelong or high dose uses, with major symptom of insanity, thrombocytopenia, hemolytic anemia, blood eosinophilia and other allergic reactions [6,7]. Because of their potential mutagenic and carcinogenic effects on human health, European Union, United States and China have already banned the use of NFZ since many years and set up strict monitoring standards for their residues in aquatic, poultry and other animal products [8,9].

A number of analytical methods have been described in literature for the detection of NFZ including; spectrometric, electrochemical [10,11], chromatographic [12–15], polarographic [16,17], as well as highly selective florescent [18] and chemiluminescence [19] probe based techniques. Very recently [5] designed a very sen-

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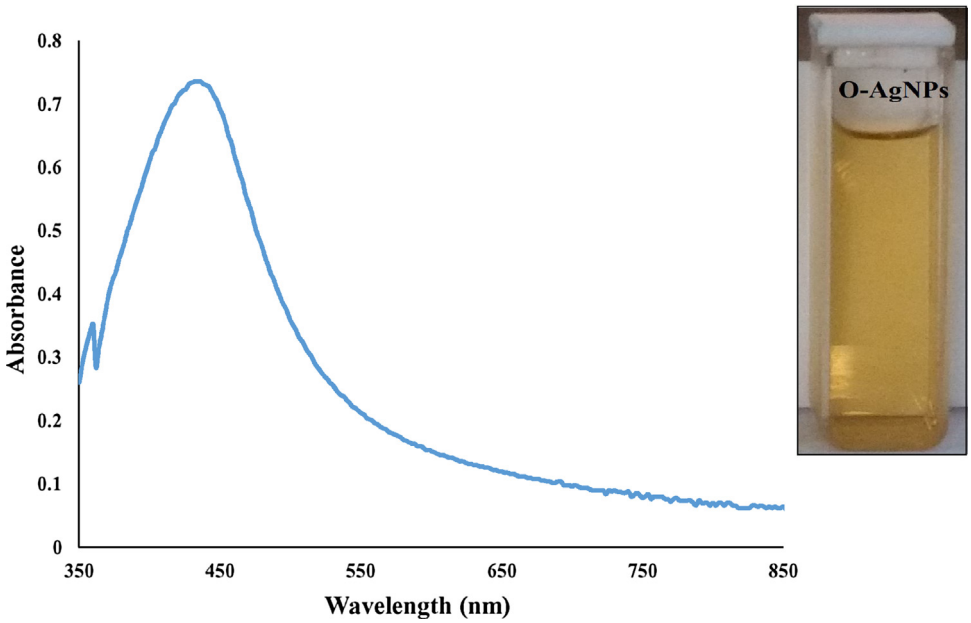

Fig. 1. Spectroscopic characterization of the synthesize O-AgNPs. *Inset*: Suspension of O-AgNPs.

sitive electrochemical sensor utilizing a glassy carbon electrode (modified with graphene and Fe_3O_4 nanoparticles) for the detection of NFZ and its metabolite semicarbazide hydrochloride.

In the recent past, gold and silver nanoparticles have generated a great interest as a research tool spanning all states of matter. Particularly silver nanoparticles (AgNPs) have various significant applications in exclusive fields. It is widely used as an antibacterial and antifungal agent and have strong optical features which makes them suitable for biological sensing and imaging [20–22]. The highly conductive natures of silver also make nanoparticles useful for numerous electronic devices, adhesives, conductive inks and many others [23]. These nanoparticles are also used in organic synthesis as catalysts [24]. Many methods have been proposed for the synthesis of Ag and AuNPs such as; thermal reduction [25,26], thermal decomposition [27], microwave assisted [28], laser mediated [29] and biological reduction [30] sodium borohydride reduction [31] techniques. The smooth availability, biological importance and non-toxic nature of Olive oil has been extensively recognized. Olive oil contains phenolic constituents such as flavonoids, lignans (pinoresinol, steganacin and podophyllotoxin) and fatty acids e.g. oleic, stearic, linolenic and palmitic acids [32,33]. Olive oil contains polar carboxylic groups and long non-polar carbon chains [34]. Thus these compounds can act as both reducing and capping agent for silver nanoparticles synthesis. Edible oils have also been reported as stabilizing and capping agents in nanoparticles synthesis through wet chemical reactions [35–37].

It is the simplicity of AgNPs synthesis (into diverse shape and size) that support the investigators to discover the ultimate prospective of these nanoparticles for various purposes; in particular for drug loading, controlled release, imaging and drug sensing etc. [38–41]. Hence, the present study was designed to synthesize the Olive oil based nanoparticles (O-AgNPs), extensively characterized and subjected for their possible role as chemosensor. Studies were conducted utilizing different spectroscopic (UV/Vis, and FTIR), morphology and size (AFM and DLS) and energy disperse spectroscopic (EDS) techniques. Furthermore, the same techniques were also used to establish the interaction of O-AgNPs with some frequently in use drugs (e.g. nitrofurazone and Zuclopenthixol) for their possible chemosensing applications. The synthesized O-AgNPs was found to be quite selective and highly sensitive towards NFZ, and a time dependent NFZ induced agglomeration and/or aggregation mechanism of O-AgNPs were illustrated by DLS. Despite potent antimicrobial, anti-biofilm and biofilm eradicating activities, O-AgNPs were found to be non-toxic on both normal as well as cancer cell lines.

2. Experimental section

2.1. Reagents and materials

Aspirin, amoxicillin, atenolol, diclofenac sodium, gabapentin, levetiracetam, metronidazole, nitrofurazone, paracetamol, secnidazole, topiramate and Zuclopenthixol were kindly provided by Nabi Qasim Pharma, Karachi Pakistan. Silver nitrate and acetone, were purchased from Sigma-Aldrich (USA) and Merck (Germany), respectively. Pure Olive oil 100% (SASSO, Italy) was purchased from Karachi local market. Throughout the experiment, de-ionized (DI) water (18.0 mΩ, Millipore, USA) was used.

2.2. Instrumentations

UV–visible spectra of O-AgNPs were recorded with a resolution of 2 nm in a quartz cell using a UV-6310 spectrophotometer (Jenway, Staffordshire, UK). In order to establish the relationship between localized surface plasmon resonance (LSPR) signal and O-AgNPs concentration, absorption spectra were recorded after dilution (if required) in DI water.

FTIR data was collected from IR Prestige-21 spectrophotometer (Shimadzu, Japan) using a bright ceramic light source. Olive oil was recorded as such, while O-AgNPs were first centrifuged at 14,000 rpm for 15 min at 4 °C (Biofuge Primo R, Heraeus, USA) and then the concentrated O-AgNPs was used for analysis.

Elemental characterization was performed by energy dispersive X-ray spectroscopy (EDS) mode of scanning electron microscope (SEM, JSM-6380A Jeol, Japan) at the Centralized Science Laboratory (CSL, University of Karachi), which can count emission peaks to 9335 counts per second. Sample was prepared by depositing a drop of O-AgNPs solution on aluminum grid sample holder and dried at room temperature. Analysis was performed under high