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Studies on interaction of ribonucleotides with zinc ferrite nanoparticles using spectroscopic and microscopic techniques

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Abstract

Interaction of ribonucleotides with zinc ferrite nanoparticles (~15 nm) prepared by the sol-gel method was studied at physiological pH (~7.0). Ultra-violet (UV-Vis), Fourier transform infrared (FT-IR), Raman spectroscopy and field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) were employed to investigate the interaction of ribonucleotides with zinc ferrite surface. Langmuir and Freundlich adsorption models were used to describe the equilibrium isotherms in the concentration range of 1.0×10^{-4} M- 4.0×10^{-4} M of ribonucleotides. The maximum adsorption capacity determined for 5'-GMP, 5'-AMP, 5'-UMP, 5'-CMP was 22.37 mg/g, 17.42 mg/g, 16.03 mg/g and 14.03 mg/g, respectively. Langmuir model was found to show the best fit for experimental data. Adsorption kinetics were studied by pseudo-first order and pseudo-second order kinetic models, and the adsorption process was best described by the pseudo-second order kinetic model. FE-SEM images clearly showed that ribonucleotide adheres onto the zinc ferrite nanoparticles surface. AFM analysis demonstrated that the root mean square roughness (Rms, S_q) and average roughness (S_a) increased from 0.98 nm to 1.80 and 0.67 nm–1.38 nm, respectively following exposure to ribonucleotide. FT-IR spectroscopy revealed that the zinc ferrite nanoparticles interact strongly with the phosphate, carbonyl and amino groups of ribonucleotides. Raman spectra of 5'-AMP-zinc ferrite adduct showed the participation of amino and a phosphate group with zinc ferrite nanoparticles surface.

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Keywords: Ribonucleotides; Adsorption; AFM; FT-IR; FE-SEM

1. Introduction

Adsorption of nucleic acids and their components on mineral matrices are especially interesting in respect of several scientific issues. After the death of organism and subsequent cell lysis a significant amount of nucleic acids is released in natural environment, mainly in soil [1-3]. The released nucleic acids are adsorbed onto mineral surfaces and preserved in the natural environment. Mineral surface protects them from UV-mediated or enzymatic degradation [4-8]. This preserved nucleic acid further can be taken up by the microorganisms for horizontal gene transfer or transfection [9-11]. Several important biomedical experiments involving nucleic acid—mineral interaction have been carried out in recent past [12-17]. Apart from this the adsorption of nucleic acids and

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their components on mineral surfaces may have important rule on the origin of life issue, where mineral surfaces concentrate the nucleic acid components from dilute oceans [18–21]. Several minerals such as olivine, pyrite, calcite, hematite and rutile [22], zinc oxide [23], alumina [24,25], manganese oxides [26], metal octacyanomolybdates [27], natural zeolite [28], clays [29–34] have been employed to study the adsorption of nucleic acid and their components.

Spinel ferrites a group of minerals having the general formula $M^{II}Fe_2^{III}O_4$ where M may be Zn, Ni, Co, Cu, etc., are a special class of compounds having high magnetic properties. Ferrite nanoparticles are particularly useful in biomedicine for nucleic acid separation, gene detection, as contrast agent and biosensors [35,36]. Zinc ferrite mineral (ZnFe₂O₄) has attracted an increasing attention due to possessing excellent electrical, optical and magnetic properties. This important material can be used in areas devoted to hyperthermia [37], MRI contrast agent [38], gas sensors [39], catalyst [40], etc. Although several minerals have been tested for the adsorption of nucleic acid, only a few literature are available involving metal ferrite-nucleic acid interactions. Magnetite, cobalt ferrite and silica-magnetite composite have been used as an effective adsorbent for the isolation of genomic DNA molecules [41,42]. Pershina et al., (2009) studied the interaction between DNA and cobalt nano ferrite particles using FTIR spectroscopy [43]. Recent work involving adsorption of DNA on Fe₃O₄ nanoparticles has been carried out by Ghaemi and Absalan (2014) [44]. To the best of our knowledge spinel metal ferrites has not been tested to study the adsorption of nucleotides (monomeric unit of nucleic acid) that prompted us to investigate the interaction between nucleotides and zinc ferrite nanoparticles.

In the present work we report the interaction between ribonucleotides (5'-AMP, 5'-GMP, 5'-UMP and 5'-CMP) and zinc ferrite nanoparticles under physiological pH (~7.0) using spectroscopic and microscopic techniques. This study involving magnetic nanoparticle—nucleic acid interaction may be of high importance because of the influence of nano materials on biosystems and further the mechanism of interaction can be used to develop bio-nano composites.

2. Experimental

2.1. Materials

Zinc(II) nitrate $(Zn(NO_3)_2.6H_2O)$ was purchased from E. Merck, Citric acid $(C_6H_8O_7.H_2O)$ from

RANKEM, Ethylene glycol $(C_2H_6O_2)$ from Sisco Research Laboratory, India, Iron(III) nitrate (Fe(NO₃)₃.9H₂O) and disodium salts of ribonucleotides were purchased from Sigma–Aldrich. The reagents were used without further purification. Millipore water was used throughout the studies. Graphs are plotted and smoothened in Origin Pro 8.1 software.

2.2. Apparatus and measurements

X-ray powder diffraction analysis of samples was carried out using a Brucker AXS D8 advanced X-ray diffractometer (Cu-K α , $\lambda = 0.1540$ nm). Ultraviolet-visible (UV-Vis) absorption spectra of the samples were recorded in the wavelength range of 200-800 nm with a resolution of 0.1 nm in a quartz cuvette by using a Shimadzu UV-16001 spectrophotometer. The infrared spectra of samples were recorded using a KBr pressed disk technique by a Fourier transform infrared spectrometer (Perkin-Elmer), operating in the range of $400-4000 \text{ cm}^{-1}$. About 10 mg of sample with 200 mg of KBr were ground in an agate mortar until a homogenous mixture was obtained. Then this mixture was hydraulic pressed to form disc pellets. Spectra were recorded with a scanning speed of 2 mm/s with resolution of 2 cm^{-1} . Raman spectra of the samples were recorded using a RENISHAW in Via Raman spectrophotometer with 4 cm⁻¹ resolution. An argon ion laser operating at 514.5 nm was used as the excitation source having laser power of 1 mW an and acquisition time of 30 s. The zeta potential of the zinc ferrites nanoparticles was measured at different pH (*i.e.*, pH = 3, 5, 7, 9, 11) using Malvern Zeta Sizer Nano ZS90. The pH of the solutions was adjusted by adding dilute hydrochloric acid (0.01 M) or sodium hydroxide (0.01 M). The experiments were carried out by dispersing 5 mg of zinc ferrite in 50 mL of 10 mM NaCl solution and sonicated for 10 min. Surface morphological images of the samples were carried out using a FEI Quanta 200F scanning electron microscope operating at 20 kV. The sample is first made conductive for current by smearing the sample on a conducting carbon tape and then gold sputtered for 100 s in a high vacuum chamber. Elemental compositions of the samples were also analyzed using an energy dispersive X-ray analysis (EDX) facility attached with the FE-SEM. Surface topography of the samples was analyzed by recording 2D images on a NTEGRE (NT-MDT) atomic force microscope (AFM) equipped with NOVA software. The textural characteristics of the samples were

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