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Phosphate Removal from Aqueous Solutions by A Nano-Structured Ag–Chitosan Film

V. Durga Praveena[1], K. Vijaya Kumar[2,*], K. Venkataratnam[3]

[1]*Department of Chemistry, SASJ GDC, Narayanapuram – 534 406, Andhra Pradesh, India.*
[2]*Department of Physics, Dayananda Sagar Academy of Technology and Management, Bangalore – 560 082, Karnataka, India.*
[3]*Department of Physics, Malaviya National Institute of Technology, Jaipur – 302 017, Rajasthan, India.*

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ABSTRACT

The present study investigates the effective removal of phosphate in sewage wastewater using silver nano-cs films (Ag NP's-CS). The ecofriendly prepared silver nanoparticles (Ag NP's) embedded in chitosan of around 8–10 nm was synthesized using non-toxic-green method. The interaction of Ag NP's-CS film and phosphate was studied using UV-Vis technique. Ag NP's-CS film exhibit more than 95% phosphate reduction in 5 min and close to 100% in 10 min. High-resolution scanning electron microscopy, X-ray diffraction, UV-Vis and Fourier transform spectrometry were used to characterize the AgNP's-CS film. The film has been shown to be effective for the detection and the removal of phosphates from natural wastes and wastewaters within the response time of 2-3 seconds.

1. Introduction

The quality of water was analyzed on the basis of colour, odour, and taste. People exploit water from ponds, lakes and rivers for drinking. Owing to the augment in population and pollution of the environment, the quantity of surface water [1] i.e., available dwindle with time and most of it capitulate to severe pollution.

Phosphates are chemical compounds made from the elements phosphorous and oxygen. Phosphorus is a nutrient required by all organisms for the basic processes of life. It is a natural element found in rocks, soils and organic material. Phosphorus clings tightly to soil particles and is used by plants, its concentrations in clean water is generally very low [2]. Phosphorous is usually present in water in the form of phosphate (PO_4^{-3}) at low concentrations, which limits plant growth. High phosphate levels can come from man-made sources such as septic systems, animal waste, wastes from laundries, industrial discharge, fertilizer runoff and improperly treated waste-water [3]. Many seemingly harmless activities added together can cause phosphorus overloads.

As phosphates increase, there will be an excess of plant growth (eutrophication) and decomposition [4]. Large growths of algae are called algal blooms and they can severely reduce or eliminate oxygen in the water, leading to illnesses in fish and the death of large numbers of fish. Some algal blooms are harmful to humans because they produce elevated toxins and bacterial growth that can make people sick if they come into contact with polluted water.

According to the EPA total phosphate should not exceed 0.05 mg L^{-1} in a stream where it enters a lake or reservoir, and should not exceed 0.1 mg L^{-1} in streams that do not discharge directly into lakes or reservoirs [5]. Phosphate levels greater than 1.0 mg L^{-1} may interfere with coagulation in water treatment plants. Addison's disease, severe heart and lung disease, kidney disease, thyroid problems and liver disease were the effects of excess phosphates present in the water [6-8].

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Nanotechnology plays an important role for the sensing and removal of pollutants. Nano materials shown to be excellent candidates for the purification of water [10-15]. Due to their unusual reactivity, surface-volume ratio as well as size dependent physical, optical and chemical properties [16]. Many nano systems such as nano scale grapheme [17], grapheme oxide, metal oxide composites, carbon nanotubes, zerovalent iron, Al, Ti, Mg, Ce, Mn, Zn, noble metals (Ag, Au, Cu) for the treatment of water [18-20]. Application of Noble metals, even though not in nano form, they were damaging the DNA of bacteria. AgNp's have also been widely used in sensing applications for a variety of inorganic pollutants.

In the present study we employed a spectrophotometric method for the detection and deduction of phosphate ions using nano silver coated chitosan biofilm (AgNp's/CS) [21, 23].

2. Experimental Methods

2.1 Materials

Chitosan (degree of deacetylation: 79%, molecular mass: 500,000 g/mol) was purchased from sea foods (Cochin), India. $AgNO_3$ was purchased from Aldrich and used without farther purification. The other chemicals were analytical grade from Fischer Scientific without further treatment. All aqueous solutions were made using ultrahigh purity water purified using a Mill-Q Plus system (resistivity = 18 MΩcm) (Millipore Co.).

2.2 Preparation of Plant Extract

The fresh leaves of *Achyranthes aspera* were collected from the surrounding areas of West Godavari district and were washed several times with millipore water to remove dust then it was cut into small pieces. 5 g of thoroughly washed leaves were heated in 250 mL of millipore water for 15 min in an Erlenmeyer flask using a water bath then the solution is filtered using Whatman no.40 filter paper. The filtered leaf extract was stored in a cooled atmosphere for further use.

2.3 Preparation of Silver Nano particles

The Silver nitrate solution was reduced using plant extract at room temperature, resulting in a light yellow colour solution indicating the formation silver nano particles.

*Corresponding Author
Email Address: kvk64nano@kluniversity.in (K. Vijaya Kumar)

2.4 Characterization of Synthesized Silver Nanoparticles

The characterization of AgNp/CS thin film has been evaluated by FESEM, EDS, FTIR, UV-VIS and XRD. Field Emission Scanning Electron Microscope (Nova Nano FE-SEM 450 Model) was used to obtain SEM images at an accelerating voltage of 200 kV. The presence of Ag has been confirmed by ED's spectrum. Absorption spectra of the samples were taken on a UV-VIS double beam spectrophotometer (JASCO model V-670) with a range of 300-580 nm. X-Ray Diffractometer (PAN Analytical X'Pert Pro) was used to analyze the crystallographic studies of Ag-CS thin film. FTIR spectra were recorded in a Perkin Elmer Version 10.03.06.

2.5 Deposition of Silver Nanoparticles in Chitosan Matrix

The CS was prepared by the method described below: 2 g CS was dissolved in 200 mL 2% (V/V) acetic acid solution under magnetic stirring. When the solution became clear, silver nanoparticles, Chitosan solutions were mixed in 2:3 ratio. Finally, films were made by casting the solution on the glass slides, dried at room temperature. A range of AgNP/CS concentrations were used to treat the bacteria and for other experiments in this study.

2.6 Sensing Study of Phosphate Ions

For the sensing study $1X10^{-3}$ M of Sodium phosphate solution is used. Phosphate concentration is varied by diluting phosphate , solutions of different concentrations (1 to 100 ppm in deionised distilled water) were prepared right before experiment.

3. Results and Discussion

3.1 UV-VIS Spectroscopy

UV-visible spectroscopic data of Each sample was analyzed by UV-visible spectrophotometer (Jasco V-670) in the range 250-750 nm and the wavelength corresponding to maximum absorption (λ_{max}) was recorded which are identical to the characteristics UV-visible spectrum of metallic silver nanoparticles. Chitosan in 1% (V/V) acetic acid is used as blank.

Silver nanoparticles absorb radiation in the visible region of the electromagnetic spectrum (380–450 nm) due to the excitation of Surface plasmon vibrations, and this is responsible for the striking yellow–brown color of silver nanoparticles.

Silver nanoparticles stability was checked up to six months and it was found that stability is nearly constant even up to six months. Due to Vander Waals forces or Coulomb's forces of attraction the individual particles have a tendency to form large sized agglomerates during the preparation of silver nanoparticle suspension. Chitosan is used as a stabilizer in order to prevent the agglomeration of small particles which can form a protective layer on the particle's surface. A strong physical adsorption of the CS onto the surface of the silver nanoparticles is also an indication of better stabilization. The evolution of UV–VIS absorption spectrum of silver nanoparticles embedded in chitosan film is shown in Fig. 1b. A plasmon absorbance of the film was observed between 410–450 nm.

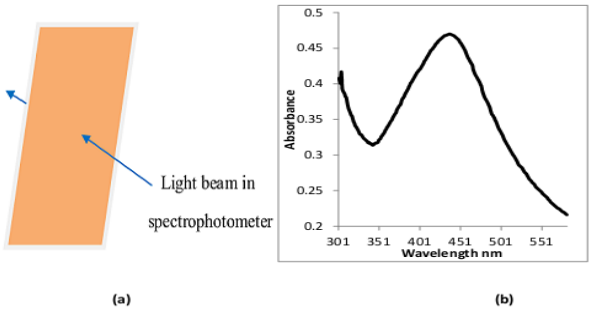


Fig. 1 (a) Schematic diagram of the AgNp's/CS thin film sensor; path of the light beam in the spectrometer is shown. (b) Surface Plasmon Resonance (SPR) spectrum, of the AgNps/CS.

3.1.1. Effect of Reaction Duration

The formation of silver nanoparticles was evidenced with the change in colour of the solution from colourless to light yellowish colour. The formation of silver nanoparticles was monitored through UV–Vis spectrophotometer at different time intervals (Fig. 2) the spectrum obtained at 90 min shows the absorption maximum at 454 nm. The intensity of the peak with respect to the height increases gradually with increase of time. There was no change in peak position for 10 hrs to 24 hrs. Now these nanoparticles can be embedded in chitosan for further application.

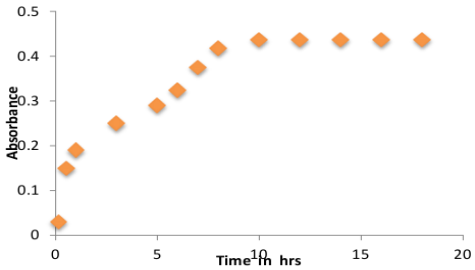


Fig. 2 Changes in the SPR band of the AgNp's at various time intervals using UV–VIS spectrophotometer

3.2 FTIR Spectra of Chitosan and Its Derivative

FTIR spectra were recorded in a Perkin Elmer version 10.03.06, Spectrophotometer. The spectral band for chitosan appear at 3,526 cm^{-1} (axial OH group), 3,337 cm^{-1} (N-H stretching), 2,364 cm^{-1} (CN asymmetric band stretching), 1,754 cm^{-1} (amide linkage), 1,673 cm^{-1} (CO band stretching), 1,523 cm^{-1} (NH angular deformation in CONH plane), 1,320 cm^{-1} (CN band stretching ,axial deformation of amino group) and 1,140-1,026 cm^{-1} (ether linkage, C-O-C band stretching).

In AgNp/CS, (Fig. 3) shows bands are shifted to higher frequencies i.e., 3353.51 cm^{-1} (overlap of O– H and N– H stretching vibrations), 2922.34 cm^{-1} (C – H stretching), 1744.89 cm^{-1}, 1728.74 cm^{-1} (–NH_2 bending ,amide linkage), 1569.07 cm^{-1}, 1411.41 cm^{-1}, 1070.14 cm^{-1}, 649.17 cm^{-1} [C-C, C-O(esters and ethers) and C-O (polyols)] more pronounced shift in the FTIR spectrum could be observed in the complexes (Fig. 3(b) inside). The major differences are: the peak at 3,526 cm^{-1} corresponding to the stretching vibration of amino group (-NH_2) and hydroxyl group (-OH), shifted to lower frequency (3339 cm^{-1}), and the peak of 3339 cm^{-1} becomes wider, which indicates hydrogen bonding is enhanced and may be explained as that the additive effect of water absorbed on the surface of Ag nanoparticles and the –OH group of CS. This suggests that NPs were capped by the polymer.

The polar groups O- H of polysaccharide have the good ability of coordination reaction with metal ions (e.g., with silver ions). When O-H groups and silver ions form coordination bonds, the interactions among the resultant Ag particles and oxygen atoms of O-H groups become stronger with increasing amount of Ag. This can lead to corresponding changes both in the positions and in the strengths of IR spectra of CS.

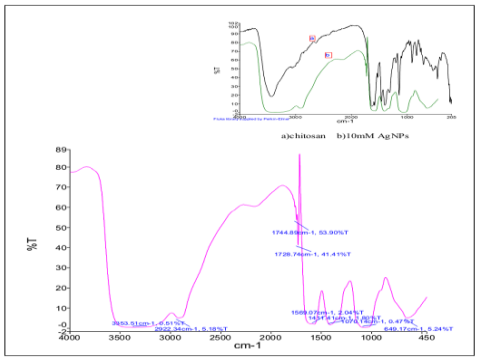
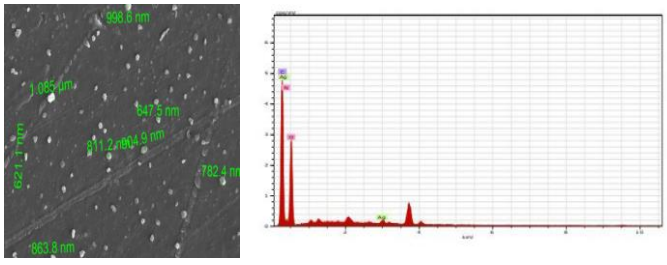


Fig. 3 FT-IR Spectra of AgNps/CS film



(a) (b)

Fig. 4 (a) SEM image of the AgNPs/CS using *Achyranthes aspera* L, extracts (b) EDS spectra of silver nanoparticles

Fig. 4(a) shows the SEM images of CS/AgNP Thin film prepared from 1mM $AgNO_3$ as precursor. It is clear from these images that a common characteristic of the particles is their spherical shape. EDS spectra confirms the presence of silver nano particles.

3.3 XRD

The XRD pattern was recorded by X-ray diffractometer (PAN Analytical X ' Pert, Almelo, The Netherlands) equipped with Ni filter and CuKα (l = 1. 54056 A^0) radiation source.

Fig. 5 shows the XRD pattern for silver nanoparticles synthesized using natural plants extract and the diffraction peaks were found to be broad around their bases indicating that the silver particles are in nanosizes. The mean particle diameter of silver nanoparticles was calculated from the XRD pattern according to the line width of the plane, refraction peak using the following Scherer's equation: The equation uses the reference peak width at angle h, where k is the X-ray wavelength (1.5418 Å), $\beta^{1/2}$ is the width of the XRD peak at half height and K is a shape factor. The particle sizes of the samples in our study have been estimated by using the above Scherer's equation and were found to be ~17nm for the strongest peak.

$$D = \frac{K\lambda}{\beta^{1/2}\cos\Theta}$$

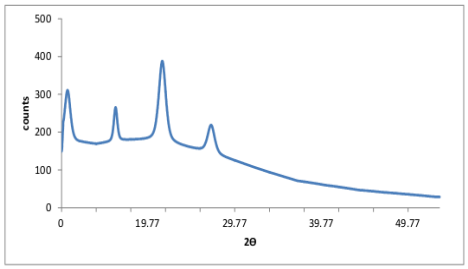


Fig. 5 XRD Spectra of AgNps/CS film

3.4 Dissolution and Swelling Test of Chitosan Based Silver Nano Particles

The swelling studies of chitosan based silver nano particles were carried out in distilled water at room temperature for a period of 24 hrs the percentage of swelling of these films were calculated by using the Eq.(1):

$$\text{Percentage of swelling} = \frac{WS-W}{W} \times 100\% \qquad (1)$$

where, Ws is the weight of swollen chitosan film (g) and W is the weight of dry chitosan film. It was observed that chitosan film had 37.5% swelling when allowed to remain in distilled water for 24 hrs at room temperature

3.4.1 Sensing Experiments

All experiments (except those related to the temperature dependence) were carried out at the ambient temperature of 25 °C. The sensor film was immersed in ultra-pure water (Millipore Milli -Q, resistivity = 18 MΩcm) then placed in a spectrometer; the SPR spectrum of the film was monitored at first time. The water was removed and replaced with the analyte solution. The SPR spectrum of the film was recorded. A fresh film was used for each new experiment. The reproducibility of the sensing process was examined by running repeated batches of selected experiments.

3.5 Phosphate Sensing of Green AgNp's/CS Film

To investigate the sensitivity effect of the AgNp toward PO_4^{-3} ion, PO_4^{-3} ions with the concentrations of 0.01 mgL^{-1} to 50 mgL^{-1} was added to the AgNp's solution. The sensing ability and selectivity of the prepared AgNp's were studied by using UV-VIS spectroscopy. On interaction of PO_4^{-3} ions with AgNps, PO_4^{-3} undergoes diffusion into the polymer matrix during which the metal changes into metal salt. A clear blue shift of the peak is observed at higher concentrations of PO_4^{-3}. This aspect can be exploited by including the peak shift, ΔA= [Amax (0) -Amax (t)] in the sensor response. This is due to the fact that, degradation of PO_4^{-3} takes place with the formation of AgNp-PO_4^{-3} surface complex.

The absorbance spectra for a set of selected concentrations are shown in Fig. 6; for each measurement, fresh film of AgNPs/CS is taken. The spectra show small but definite and reproducible decrease in intensity within a few minutes. In addition to the decrease in intensity, the peak undergoes a blue shift which becomes prominent at higher concentrations and the LSPR peak intensity at 437 nm decreases and another peak appears at 409 nm as the PO_4^{-3} content is increased. Change in absorbance at two different wavelength as a function of PO_4^{-3} concentration are provided in Fig. 7a. We have plotted absorbance ratio (Abs 409/Abs437) as a function of PO_4^{-3} concentration in Fig. 7b. Within the range of 2 to16 mgL^{-1} the absorbance ratio is almost linear, which indicates that the AgNP's/CS film is active for detection and removal of PO_4^{-3} content in the solution.

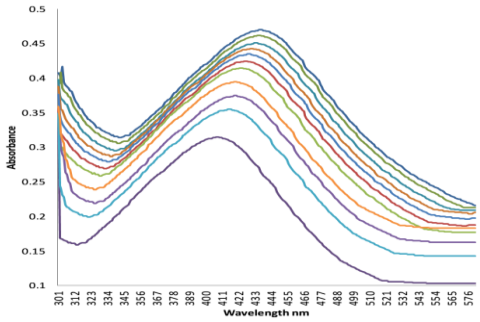


Fig. 6 UV–Vis absorbtion response of green AgNP-CS film upon addition of different concentration of PO_4^{-3} ions.

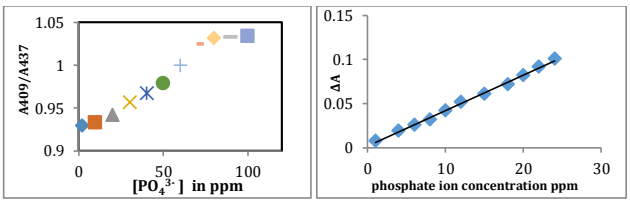


Fig. 7 (a) Plot of absorbance intensity at 409 nm versus PO_4^{-3} concentration. (b) Ratio of the absorbance peak (Abs409/Abs437) for a silver nanoparticles solution exposed to increasing PO_4^{-3} content

Conclusion

The silver NPs dispersion in a chitosan bio polymer matrix played a more important role in colorimetric sensing applications. In this study we have shown the feasibility of forming silver nanoparticles from silver nitrate through green process using aqueous extract of *Achyranthes* aspera L,. Based on the unique LSPR properties of metallic nanoparticles, Colorimetric assays have showed to be very useful due to their simplicity, high sensitivity, low detection limit, low cost, fast response time and great reproducibility. The present study reports the application of nanoparticles for the removal of phosphate ions using AgNPs-CS film with high selectivity and sensitivity over Mn^{+2}, Fe^{+3}, CO^{+2}, Ni^{+2}, Zn^{+2}, K^{+}, Mg^{+2}, Ba^{+2} ions. Keeping these significance properties in mind, in the near future we can use this thin film as a filter to remove inorganic pollutants for the water purification at room temperature.

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