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# Preparation of Silver Nanoparticles from Synthetic and Natural Sources: Remediation Model for PAHs

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**Abstract.** The emergence of nanoscience and technology is gaining popularity with an increasing demand for metal nanoparticles applicability in various areas such as electronics, catalysis, chemistry, energy and medicine. Metallic nanoparticles are traditionally synthesized by wet chemical techniques, where the chemicals used are quite often toxic and flammable. In this work, an attempt is made to compare the efficiency of two different synthesis methods and application of each for the remediation of poly aromatic hydrocarbons (PAHs). In this regard, silver nanoparticles are prepared by green and wet chemical method using plant extract of garlic (*Allium sativum*). The extract is known to reduce the metal during synthesis and acts as stabilizing ligand. These synthesized silver nanoparticles (Agp) and (AgW) were applied as adsorbents in synthetic batch mode experiments at varying parameters of pH and temperature. A concentration of 0.01mg/L of Phenanthrene, Anthracene, and Pyrene were induced at fixed dosage of 1mg/Kg of adsorbent. Residual concentration of each PAH was analyzed on UV-Visible spectrophotometer. The results indicated that both adsorbents follow the sequence of Phenanthrene>Pyrene>Anthracene with optimal removal of higher than 85% in each case. A distinguishing privilege is attained by Agp adsorbent showing 3, 3 and 11 orders of magnitude higher efficiency than Agw. It may be attributed to more functional groups in the plant extract participating in binding of PAH to the surface. Each synthesized adsorbents was characterized by FTIR, SEM and EDX. The average particle size was determined to be of the order of 13-26 nm. The study concludes the use of alternate economical and green adsorbents for control of poly aromatic hydrocarbons (PAHs).

## 1. Introduction

Toxic organic pollutants are released to water with the rapid industrialization of human society. Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds present in the environment with adverse impacts on ecosystems and human health. PAHs are among the most carcinogenic, teratogenic, mutagenic and toxic contaminants [1] and are classified among persistent organic pollutants. PAHs are known to pose, even at very low concentrations, a threat to environment due to their benzene structures [2].

PAHs have received immense attention because of their omnipresence in industrial and municipal wastewater and can be generated from both natural processes and anthropogenic activities [3]. PAHs are by-products of incomplete combustion (pyrolysis) of wood, oil, coal, garbage or hydrolysis of organic materials [4].

Removal of PAHs is of considerable interest in environmental analysis. Several methods including immunoassay [5], gas chromatography [6] and high performance liquid chromatography (HPLC) with UV-Vis absorbance or fluorescence detection [7] and capillary electrophoresis (CE) equipped with



laser-induced fluorescence [8] have been used for the determination of PAHs. These methods are expensive, time consuming, require large sample volumes as well as large amount of organic solvent with separation and extraction procedures [9].

Adsorption technology is regarded as the most promising one due to its low cost, high efficiency and simple to operate for removing trace levels of effluents. Traditional sorbents could remove effluents from wastewater but the low sorption capacities and efficiencies limit their application. Nanoparticles have exhibited much higher efficiency and faster rates in water treatment [10] due to high specific surface area and occupy a large number of unsaturated atoms on the surfaces [11]. These specific advantages enhance adsorption capacity for the removal of organic and inorganic pollutants [12].

Recently metal based nanoparticles have been successfully applied for removal of various toxic materials due to high ordered structure, high mechanical and thermal strength. Sumesh et al., [13] applied synthesized silver nanoparticles for the removal of mercuric ions present in contaminated water. Removal of methyl orange (MO) from aqueous solutions was achieved by silver nanoparticles loaded on activated carbon [14]. Liu *et al.*, [15] removed trace Cr (VI) ions from aqueous solution by titanium oxide–Ag composite adsorbents.

The present investigation is step forward to prepare Silver based nanoparticles from plant extract (*Allium Sativum*) following slight modification of method reported by White et al., [16] and extend its application for the removal of persistent organic pollutants. Use of plants in synthesis of nanoparticles provide advancement over chemical and physical method as it is cost effective and environment friendly that do not require any special culture preparation and isolation techniques [17].

For comparison, Ag particles are also synthesized from wet chemical co-precipitation method to determine the efficiency of both as adsorbents in removing selected PAHs.

## 2. Experimental

### 2.1. Synthesis of Silver nanoparticles

Silver nanoparticles were synthesized separately from plant extract (*Allium sativum*) and wet chemical method. The products obtained are coded as Ag<sub>p</sub> and Ag<sub>w</sub>, respectively.

A procedure adapted from White et al., [16] has been used for the preparation of garlic extract from *Allium sativum*. The extract obtained was then subjected to silver particles synthesis using the following protocol.

*Allium sativum* (2.5 ml) extract solution was added to 50ml of 0.98mM of AgNO<sub>3</sub> in distilled water. After standing of two hours, change in color to light orange was observed. The solution was allowed to age for one week to yield a deep orange-brown color and monitored on UV-Visible spectrophotometer (full scan range 190-1100 cm<sup>-1</sup>) to indicate the formation of silver nanoparticles. 10 ml of 2M NaOH solution was added to facilitate the precipitate formation. Grayish silver nanoparticles were obtained and dried under vacuum.

Silver particles were also synthesized by wet chemical co-precipitation method adapted from Moghaddam et al, [18]. The beaker containing 0.9 M aqueous solution of sodium hydroxide was heated at 55°C followed by drop wise addition of 0.45 M aqueous solution of silver nitrate (Ag(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) under speed stirring. The precipitates of Ag nanoparticles were collected after 2 hours standing, cleaned with distilled water, ethanol and finally air dried at 60 °C.

### 2.2. Characterization

Each synthesized silver nanoparticle was subjected to characterization by standardized spectroscopic tools of Fourier Transform Infrared (FTIR) and UV-Visible spectroscopy. FTIR spectra of pressed pellet were recorded from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> on FTIR-8400, Shimadzu, Japan. The dried mass of garlic extract (reducing agent) was also pressed into pellet for observation under FTIR. UV-VIS spectra were fit with Gaussian curves for measurement of  $\lambda_{\text{max}}$  keeping distilled water for background correction. The samples surface morphology and size was determined with Scanning Electron Microscopy (SEM) coupled with EDX. Sample was sonicated and analyzed at different magnifications

on 6490(LA) JEOL machine with gold sputtering at a potential of 20 kV prior to recording SEM. EDX analysis was done on JED-2300 analysis station.

### 2.3. Batch Experiment for Adsorption

The synthesized silver nanoparticles ( $Ag_p$  and  $Ag_w$ ) were applied as adsorbents in time-dependent batch experiment to evaluate the removal of poly aromatic hydrocarbons. Each batch was investigated at variable temperature and pH to determine the optimal removal efficiency. The following general protocol is adopted for batch experiment.

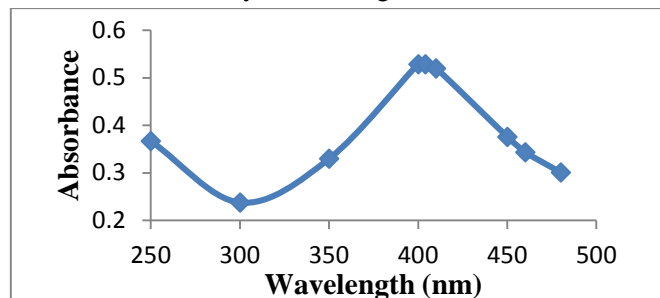
Synthetic solution of known concentration (0.01 mg/L) of each poly aromatic hydrocarbon was prepared and a known volume (5ml) of it was added in test tubes containing 1mg of each adsorbent. The aliquot was drawn after 5 minutes, filtered and analyzed on UV-visible spectrophotometer at wavelengths of 250 nm, 260 nm and 241 nm for phenanthrene, anthracene, and pyrene, in respective order.

## 3. Results and Discussion

### 3.1. UV-Visible analysis

The process of synthesis of silver nanoparticles ( $Ag_p$ ) was followed on UV-Vis spectrophotometer by recording the spectra of dark brown colored mixture of garlic extract and silver nitrate. Reduction of silver ions can easily be observed by UV-vis spectra presented in Figure 1. It is clearly visible that optimum absorbance is obtained at 400 nm, depicts the characteristic of surface plasmon absorption band [19]. This band is attributed to silver nanoparticles free electrons [20]. Saha et al., [21] reported absorption band for synthesized silver particles at 420 nm due to colloidal silver.

A broadening of peak in the range from 400-410 nm is also observed indicating that the particles are polydispersed [22], further confirmed by SEM images.



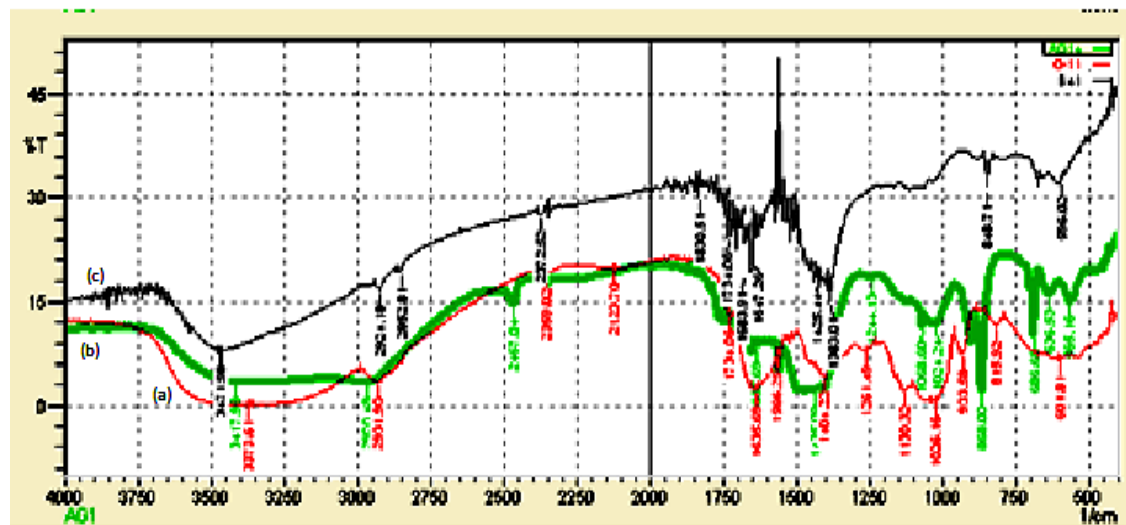
**Figure 1.** UV-visible spectra of silver nanoparticles synthesized from *Allium sativum* extract ( $Ag_p$ ).

### 3.2. FTIR characterization of silver nanoparticles

The important frequencies (in  $cm^{-1}$ ) recorded under FTIR for *Allium sativum* and two synthesized silver particles ( $Ag_p$  and  $Ag_w$ ) are presented in Figure 2.

FTIR spectra of garlic extract consist of S=O (at  $1026\text{ cm}^{-1}$ ) and S group (at  $1261\text{ cm}^{-1}$ ) indicates the presence of allicin as major component [23]. Further elucidation of FTIR spectra of garlic extract alone shows large –OH and –CH stretches at  $3373\text{ cm}^{-1}$  and  $2931\text{ cm}^{-1}$ , characteristic of nonstructural sucrose and fructose [16]. On the other hand, the synthesized silver nanoparticles ( $Ag_p$ ) represent a peak shift of  $41\text{ cm}^{-1}$  in –OH and –CH stretches confirming its complete formation.

FTIR spectra of silver nanoparticles ( $Ag_w$ ) synthesized by wet chemical method presents two peaks of absorption bands at  $596\text{ cm}^{-1}$  and  $848\text{ cm}^{-1}$  representing presence of Ag-O bond [24].



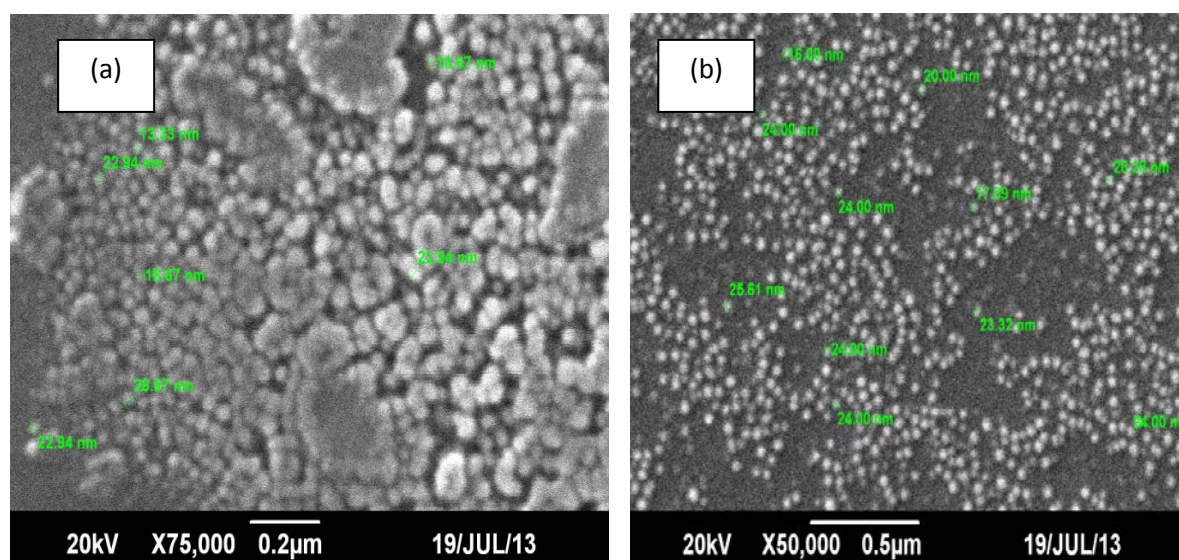
**Figure 2.** (a) FTIR spectra of dried powder of *Allium sativum* extract. (b) silver nanoparticles synthesized from *Allium sativum* extract ( $Ag_p$ ). (c) silver nanoparticles synthesized by wet chemical method ( $Ag_w$ ).

### 3.3. SEM & EDX analysis of silver nanoparticles

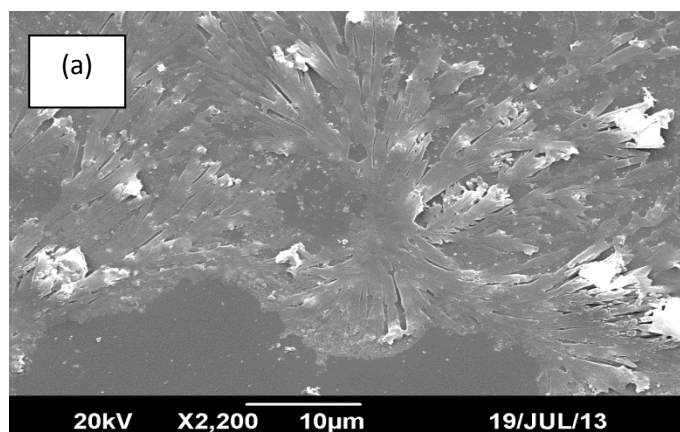
SEM images of synthesized silver nanoparticles  $Ag_p$  and  $Ag_w$  are shown in Figure 3 (a and b), respectively, whereas Figure 3(c) image presents the garlic extract loaded with silver particles.

It is evident that silver particles synthesized by two routes can safely be regarded as nanoparticles showing particle diameter range of 13 to 26 nm for  $Ag_p$  and 16 to 28 nm for  $Ag_w$ .

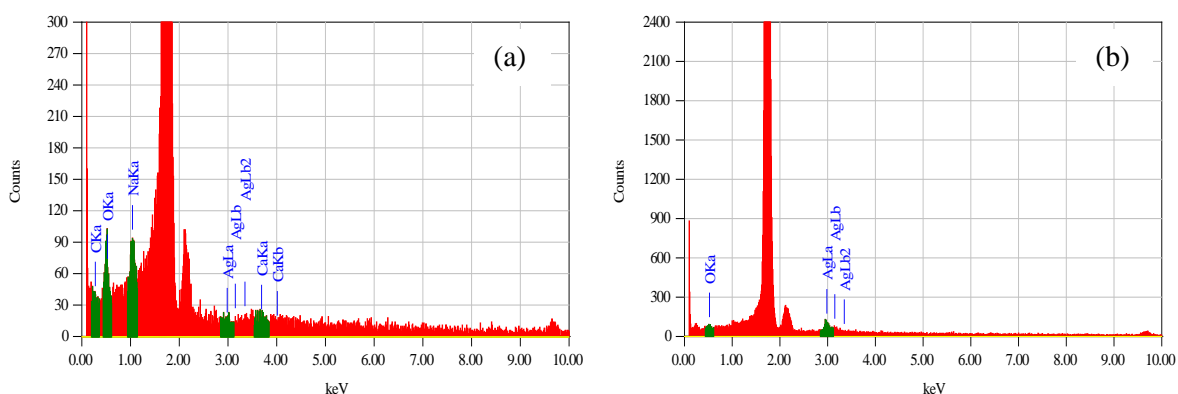
EDX spectra and quantitative data is reported in Figure 4(a and b), showing signals having 4.97 and 59.57 mass % of silver in  $Ag_p$  and  $Ag_w$ , respectively. Higher mass percentage of silver in  $Ag_w$  may be assigned to higher molar ratio of reagents used in the synthesis protocol in comparison to  $Ag_p$ . The presence of oxygen, carbon, sodium and calcium signals in  $Ag_p$  indicates their origin from biomolecules bound to the surface [25].







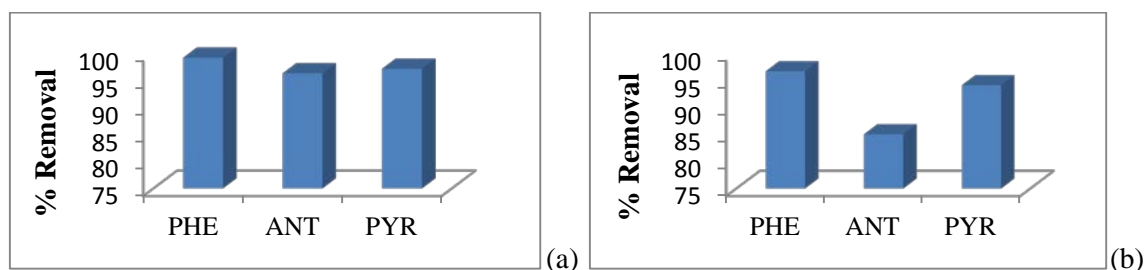
**Figure 3.** SEM images of synthesized silver nanoparticles (a) silver nanoparticles ( $Ag_p$ ) at 75,000 magnification. (b) silver nanoparticles ( $Ag_w$ ) at 50,000 magnification. (c) *Allium sativum* extract loaded with silver nanoparticles ( $Ag_p$ ).



**Figure 4.** EDX image of synthesized silver nanoparticles. (a). Silver nanoparticles synthesized from *Allium sativum* extract ( $Ag_p$ ). (b) Silver nanoparticles synthesized by wet chemical method ( $Ag_w$ ).

### 3.4. Adsorption experiments

The synthesized silver nanoparticles ( $Ag_w$  and  $Ag_p$ ) were applied as adsorbents to evaluate the removal of selected poly aromatic hydrocarbons.



**Figure 5:** Removal (in %age) of phenanthrene, anthracene and pyrene on (a)  $Ag_p$  and (b)  $Ag_w$  adsorbents.

The results are graphically presented in Figure 4 (a and b), respectively. It is clearly evident that both silver particles are good adsorbent for the removal of PAHs. PAHs are optimally removed

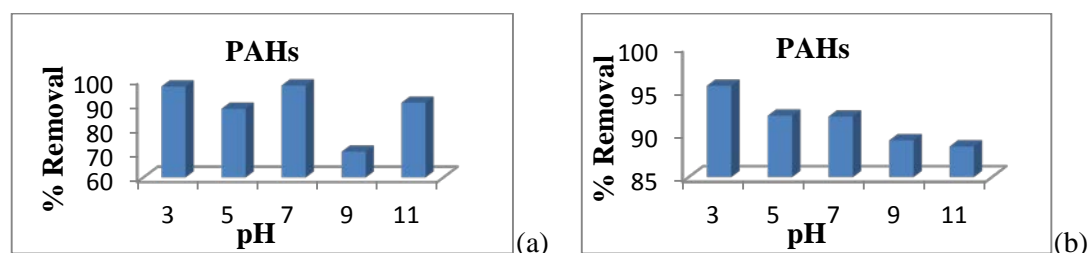
showing removal efficiency of more than 80% at ambient conditions. The good sorptive behavior of PAH may be related to increase in hydrophobicity of the non-polar moiety of the aromatic rings [26]. Adsorption process in polyaromatic hydrocarbons results due to hydrophobic interactions [27].

Sequence depicted more efficient removal of phenanthrene followed by pyrene and anthracene. This order is also observed by Kumar et al., [28] in the batch experiments reporting lower removal percentages of pyrene to its recalcitrant toxicity and higher molecular weight. However,  $Ag_p$  particles stamp its preference by showing 3, 3 and 11 orders of magnitude more removal of selected PAHs in respective order.

#### 3.4.1. Effect of pH.

The pH is one of the important parameters controlling the removal of poly aromatic hydrocarbons. In adsorption processes, the pH of the aqueous solution directly affects the surface binding properties of the proposed adsorbents and the nature of the functional groups of both adsorbate and adsorbent molecules [12].

Batch was conducted at different pH to cover acidic, neutral and alkaline range. pH effect was determined on adsorption keeping other parameters constant.



**Figure 6.** Effect of pH on the removal (in %age) of PAHs (a)  $Ag_p$  and (b)  $Ag_w$  adsorbents.

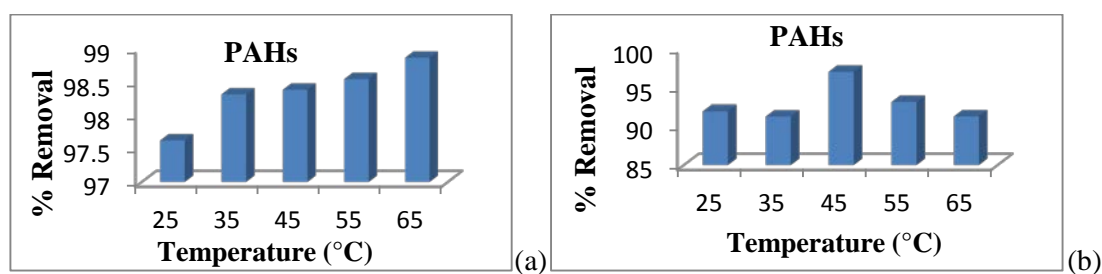
The results for the average removal of PAHs on silver particles are presented in Figure 5 (a) and (b). It is observed that generally acidic pH is more suitable for optimum removal of PAHs. This trend is also depicted in study conducted by Kumar et al., [28] reporting higher PAHs removal in acidic compared to alkaline conditions. Sponza et al., [29] relates higher removal under acidic conditions with the effect of protonation. It is concluded that  $Ag_p$  has greater removal efficiency at wide pH range through acidic to neutral (3-7 pH) in comparison to regular decreasing adsorption trend with increasing pH for  $Ag_w$ .

#### 3.4.2. Effect of temperature

The temperature influence is an important controlling factor in the applications of removal process. In the present investigation, adsorption experiment was conducted at 5 different temperatures (25°C, 35°C, 45°C, 55°C, and 65°C). Results are shown in Figure 5 (a and b).

A general increase in percent removal of PAHs with increasing temperature is observed. The tendency to adsorb PAHs is more pronounced in moving from 25°C to 35°C followed by only incremental rise upto 65°C. However, Christensen et al., [30] observed that biological PAH removal was significantly enhanced by increasing the temperature from 35°C to 55°C

On the other hand,  $Ag_w$  as adsorbent depicts 45°C as optimum temperature for 97% removal of PAH. This suggests relatively wider applicability of  $Ag_p$  in terms of temperature like effect of pH. It is also supported by Belguith et al., [31] suggests that compounds present in *Allium sativum* are stable at high temperature (80°C).



**Figure 7.** Effect of temperature on the removal (in %age) of PAHs (a) Ag<sub>p</sub> and (b) Ag<sub>w</sub> adsorbent

#### 4. Conclusions

- The present study offers a simple and convenient method of synthesis of nano-sized particles by using a low cost and non-hazardous sodium hydroxide rather than toxic sodium borohydride as reducing agent.
- PAHs are removed successfully with optimal efficiency of more than 85% following the order of Phenanthrene>Pyrene>Anthracene. The adsorption of PAHs on silver nanoparticles is attributed to hydrophobic interactions.
- The natural and green source provides an adsorbent that has comparable efficiency to chemically synthesized expensive adsorbent under ambient conditions.
- Ag<sub>p</sub> is relatively a better adsorbent than Ag<sub>w</sub> in removing PAHs. It may be attributed to more functional groups in the plant extract participating in binding of PAH to the surface.
- Ag<sub>p</sub> can be applied over a wide range of temperature, due to stability of compounds present in *Allium sativum* at high temperatures.
- The study recommends the use of alternate economical and green natural adsorbents for control of poly aromatic hydrocarbons (PAHs).

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