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## Synthesis of Silver and Copper Nanoparticles from Plants and Application as Adsorbents for Naphthalene decontamination

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## ABSTRACT

Synthesis of nanoparticles by using plants is biological method of synthesis that is ecofriendly as well as low cost. Naturally available precursor in the form of plants extract is used. In our research we used three different plants such as *Aloe barbedensis*, *Azadirachta indica* and *Coriandrum sativum* that are easy to cultivate and also available everywhere. By using above mentioned plants we synthesize two types of nanoparticles one is (Ag-NPs) and other one is (Cu-NPs). Chemical method of nanoparticles synthesis have hazardous to health as well as have environmental threats but as comparison with biological method of nanoparticles synthesis is very environment friendly also safe in use. FTIR (Fourier Transform Infrared) spectroscopy analysis and UV–Visible Spectrophotometer are used for characterization. Our research work is actually based on wastewater remediation by using silver and copper nanoparticles. Water that is contaminated with naphthalene used, further decontaminated and purify by using nanoparticles. Different batch experiments are conducted to check the efficiency of these synthesized nanoparticles by using naphthalene (PAHs) as removal area. 98.81% removal is higher by using plant *Azadirachta indica* and least adsorption power is in case of *Coriandrum sativum* that is 95.29%. At the end, kinetic and equilibrium study applied.

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## 1. Introduction

Gold nanoparticles have stronger ability because of its electronic, photovoltaic and pharmaceutical applications. Synthesis of gold nanoparticles is done by using AuCl<sub>4</sub> ions reduction in the presence of extracts of fruit such as *Emblica officinalis* that is locally name as Indian Gooseberry and *Tamarindus indica* leaf (Pattanayak and Nayak, 2014). As we know silver has strong antibacterial properties as silver nanoparticles have larger surface area and smaller size thus have greater efficiency power against bacterial diseases. Silver nanoparticles are synthesized by reacting guava and tomato fruit extract with AgNO<sub>3</sub> thus the product obtained after this reaction is silver nanoparticle. These synthesized nanoparticles have

antibacterial properties against Gram +ve such as *S. aureus* and Gram –ve such as *E. coli*. Silver nanoparticles have mainly pharmaceutical applications as used in burn cure and many other health related properties. Silver nanoparticles have many other applications in daily based life as are used in soaps, detergents, shampoos and in other daily used things (Bawskar et al., 2015). Nanotechnology is synthesis of nanoparticles as have greater physiological effect with respect to reactivity, conductivity. NPs have greater role with respect to various fields such as medicine, cosmetics, industries and optical fields. Nanoparticles are synthesized by green method in which different plants extracts are used as cheaper precursor and reacts with AgNO<sub>3</sub> to produce silver NPs. Plants extract are used because these are environment friendly and are not hazardous nor toxic so are climate friendly. Hence purpose of present research is preparation of Ag nanoparticles by using *Aloe barbedensis* as is cheaper precursor and environment friendly (Khan et al., 2017) Without using toxic chemicals, synthesis of nanoparticles through plants extracts is actually biological method. In present decade, nanoparticles are synthesized through various plants such as *Avena sativa*, *Aloe barbedensis* and many more. These plants extracts reacts with AgNO<sub>3</sub> to produce “Ag” nanoparticles (Lal and Nayak, 2012). Nanoparticles are synthesized from various physical, chemical

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and biological methods. By using plants, fungi and yeast nanoparticles are widely synthesized (Sinica et al., 2014). Metal nanoparticles have stronger ability towards biological and chemical sensor system as well as towards cancer treatment. These nanoparticles have a powerful role towards photography, photonics, information technology and surface-enhanced Raman scattering. For nanoparticles preparation there are various methods such as laser evaporation as well as chemically synthesis but these methods have certain drawbacks that's why people mostly used the methods of biologically synthesis (by which plants are used as precursors) as is environment friendly and there is not any toxic chemical used there. The plants extract that are used to synthesize NPs act as efficient reducing agent for Ag or Au containing metals that than synthesize the required nanoparticles such as Ag and Au (Singh and Srivastava, 2015). In the synthesis of copper nanoparticles, low cost chemical and plant extracts as precursor are used as have several chemical and physical properties (Mittal et al., 2013). Copper NPs have greater application in the heat transfer system, as sensor as well as catalysts. Nanotechnology has greater application in research area. In past, chemical way for the synthesis of copper nanoparticles is used but have hazardous to health as well as environment also has expensive chemicals usage. So people mostly tried to use the safe method for NPs synthesis such as biological method through which various plants extracts are used in the synthesis of nanoparticles. Plants extracts such as from plants *Nerium oleander*, *Punica granatum*, *Aegle marmelos* and *Ocimum sanctum*, *Zingiber officinale* provides greater yield of copper nanoparticles. The antimicrobial activity of these copper nanoparticles was studied against Gram +ve bacteria like *Staphylococcus aureus* and shows good results (Padma et al., 2018). In past, it is observed that copper, silver and gold nanoparticles shown greater antimicrobial activities against different diseases. Now days, copper nanoparticle are used in different textile industries as well as in different drugs industries. Other than copper NPs some other nanoparticles like platinum, gold, iron oxide, silicon oxides and nickel have not shown any bactericidal effects with respect to *Escherichia coli*. The antibacterial effect on *E. coli* and *Bacillus subtilis* using Cu NPs and Ag NPs, demonstrate that Copper NPs have greater antibacterial effects over silver nanoparticles so have greater applications in heat transfer system and many more (Murthy et al., 2018). Due to vast area of industries, there is direct passage of harmful chemicals towards freshwater that is in the form of river, ocean etc. several chemicals released into water contain harmful chemicals such as Poly aromatic Hydrocarbons (PAHs) that have very bad impacts on health as well as towards environment. PAHs are very dangerous to health as well as towards environment as it has benzene structure it means fused structure so by lesser concentration of these PAHs cause severe effects towards health and environment. To remove these industrial pollutants adsorption technique is very helpful as cheapest way as well gaining high efficiency. As bio-nanomaterials that are synthesized from plants have greater surface area as well higher level of porosity so adsorb maximum pollutant by very lower dose, for example silver nanoparticles used to remove mercury particles from polluted water (Rafique et al., 2015). As pesticides are used to remove extra weeds as well as pests from crops so are applied directly or indirectly but is harmful with respect to water also for soil fertility. So there is a need to remove these harmful pesticides residues from water to prepare it for healthy purpose. Nanoparticles are used to remove these pesticides chemicals from water. For this purpose adsorption process is done that is very good as smaller dose have larger surface area and thus have higher porosity thus provide greater efficiency (Taghizade Firozjaee et al., 2018). As we know water is main factor of life thus due to increasing urbanization also increase in industries our water is polluted day by day so that water quality decreased side by side. As we know heavy metals are released directly into water through industries and other

working sites. Today nanotechnology shows great effort towards many household industries such as soap, detergent, wastewater purification shampoos etc. So nanoparticles have great worth towards daily based life the main thing by applying these synthesized nanoparticles is that all are synthesized from plants as have no harmful effects towards environment as well as health (Yang et al., 2019). World face serious problems towards water based quality as water is polluted so there is a need to overcome this problem. Water is mainly contaminated by PAHs so that are difficult to remove and also time consuming. If we talk about PAHs in present paper we mainly discussed about naphthalene that is a white crystal having fused aromatic structure. There are several diseases that are caused due to naphthalene intake, a very common disorder is hemolytic anemia caused due to ingestion of larger dose of naphthalene. There are number of process to remove naphthalene from water but most common one is adsorption (Das et al., 2016). Poly aromatic hydrocarbons (PAHs) structure composition make it difficult to degrade as well as carcinogenic and mutagenic so is essential to remove from life as bad for health and environment (Bawskar, 2015).

The major objective of present study is to synthesize silver and copper nanoparticles by using natural plant extracts and then application of the synthesized metal nanoparticles as adsorbents for naphthalene decontamination from aqueous media.

## 2. Materials and Methods

### 2.1. Silver Nanoparticles (Ag-NPs)

#### 2.1.1. Synthesis from *Aloe barbedensis* (Ag-Ab)

Fresh extract of aloe vera was prepared by using fresh leaves which were collected from Multan (Bio park of Bahuddin Zakriya University Multan), washed with distilled water to remove impurities, air dried. Dried aloe vera leaves (10gm) was chopped with a sterile knife, added 200 ml distilled water in it and boiled for 20 min to prepare extract. When color of solution changes from transparent color to light yellow then cooled and store in refrigerator at  $-15^{\circ}\text{C}$ .

For synthesis of silver nanoparticles, accurately weighed 0.17 gm of silver nitrate and added in volumetric flask to prepare 0.001 M/1mM solution of  $\text{AgNO}_3$ . For reaction took 50 ml  $\text{AgNO}_3$  solution and added 20 ml aloe vera extract and shake well until color of solution changes into grey black color that is indication of successful synthesis of silver nanoparticles.

#### 2.1.2. Synthesis from *Azadirachta indica* (Ag-Ai)

Fresh neem extract was prepared by using neem leaves that were taken from Multan area (Bio park of Bahuddin Zakriya University Multan) washed with distilled water to remove impurities. Neem leaves (20gm) were added into distilled water to make extract and boil for 10 min. After that extract is cooled and filtered by whatman filter paper.

For synthesis of silver nanoparticles, silver nitrate (1 Mm) was prepared and 45 ml of  $\text{AgNO}_3$  is added into 5 ml of neem extract. Mixed well and observed its color change from brown to brick red that is clear indication of silver nanoparticles synthesis, centrifuge at 10,000 rpm for 15 min. Purified the collected pellets with distilled water and dried at  $60^{\circ}\text{C}$  to obtain a powder form of synthesized nanoparticles.

### 2.2. Copper Nanoparticles (CuO-NPs)

#### 2.2.1. Synthesis from *Azadirachta indica* (CuO-Ai)

To prepare fresh extract, neem leaves were collected from Multan (Bio park of Bahuddin Zakriya University Multan), washed with

distilled water until all impurities were removed. Took 250 ml distilled water and added 25 g of neem leaves, boil for 1 h at 60 °C, cool the extract at room temperature, filter with the help of whatman filter paper no.1 and stored in refrigerator.

For synthesis of copper nanoparticles, copper acetate was used as precursor along with neem extract. Solution of copper acetate (50 ml) was added in neem extract (150 ml) and shake well until its color changed into dark green color and brown precipitates settled at the bottom. Age the solution for 24hrs, then collect the nanoparticles and washed with distilled water to remove impurities, dried at room temperature to obtain powder form of copper nanoparticles.

### 2.2.2. Synthesis from *Coriandrum sativum* (CuO-Cs)

Coriander leaves were purchased from local market of Multan (Gardezi market) and washed with distilled water to remove impurities. Coriander leaves (20 g) were cut and washed with distilled water and then mixed with 100 ml distilled water to prepare fresh coriander extract, solution was boiled for 20 min at 80 °C. Extract filtered with the help of Whatman filter paper no 1 and store in refrigerator.

For synthesis of copper nanoparticles, aqueous copper sulphate solution (1 mM) was prepared and 100 ml was added in 10 ml of coriander extract, mixed well until color of solution changes into pale yellow. This was the indicator of successful synthesis of copper nanoparticles. Age the solution for 24 hrs, brown color precipitate settled at bottom, filtered and washed with distilled water. Centrifuge the above solution at 5000 rpm for 15 min. Collected the nanoparticles pallets and dried in an oven at 80 °C.

Synthesized metal nanoparticles are assigned codes that are listed below:

- i. Silver nanoparticles from *Aloe barbedensis* (Ag-Ab)
- ii. Silver nanoparticles from *Azadirachta indica* (Ag-Ai)
- iii. Copper nanoparticles from *Azadirachta indica* (Cu-Ai)
- iv. Copper nanoparticles from *Coriandrum sativum* (Cu-Cs)

## 2.3. Characterization of Synthesized Nanoparticles

Characterization of synthesized materials has been done by using standardized analytical techniques, such as:

### 2.3.1. FTIR for Functional group Identification

FTIR spectroscopy is useful for characterizing the surface chemistry. Organic functional groups (e.g. carbonyls, hydroxyls) attached to the surface of nanoparticles and the other surface chemical residues are detected using FTIR. In FTIR analysis the samples were recorded in the range of 1000–4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ .

FTIR spectrum used to analyze the functional group present in fresh tomato pomace extract. The synthesis of silver nanoparticles was confirmed by changes occurred in the FTIR spectrum after synthesis (Many and Radhika, 2014).

## 2.4. Application of Synthesized Nanoparticles as Bio-sorbents

Synthesized nanoparticles are applied to remove pollutants (PAHs) from aqueous media as bio-sorbents. For this purpose, batch experiment will be conducted at variables of contact time, bio-sorbent dose and adsorbate concentration. The general procedure used for batch series is:

### 2.4.1. Batch as a function of Contact Time

A twelve set of batches are conducted for a pollutant PAH (naphthalene) in order to investigate the effects of varying adsor-

bent dose and initial concentration of induced adsorbate on adsorption, also record adsorption capacity with respect to time.

A known mass (mg) of each bio-sorbent (Ag-AI, Ag-AB, CuO-AI, CuO-CS) is added to a known concentration (mg/l) of polyaromatic hydrocarbons (naphthalene) solution. The contact of bio-sorbent (adsorbent) and PAH (adsorbate) is made for a known time (30 min) on the shaker (Heidolph, SK-300) at 150 rpm. An aliquot is drawn after every 2 min, filtered and analyzed on UV-Vis spectrophotometer (Cecil CE-74000 Series) at the wavelength ( $\lambda_{\text{max}}$ ) of 275 nm for naphthalene corresponding to maximum absorbance. The concentration uptake was determined from the calibration curve constructed for standard PAH solution of six known dilutions. Batch experiment will then be repeated similarly with varying bio-sorbent mass as a function of time. Plot graph with  $q_e$  versus time. The adsorbed concentration on the adsorbent or uptake on each bio-sorbent is calculated by Eq. (1):

$$q_e = \left( \frac{C_i - C_e}{W} \right) V \quad (1)$$

Removal of PAHs (%R) by the synthesized bio-sorbents is determined from the relation given in Eq. (2):

$$\%R = \left( \frac{C_i - C_t}{C_i} \right) 100 \quad (2)$$

### 2.4.2. Batch as a function of Bio-sorbent Dose

Known concentration of adsorbate solution (10 ml) with variable adsorbent dose (1 mg, 3 mg & 5 mg) were prepared in a conical flask with different Initial concentrations and kept inside the shaker at 150 rpm. After determining adsorbate concentration, plot of  $q_e$  vs adsorbent dose will be obtained.

### 2.4.3. Batch as a function of Adsorbate Concentration

Known concentration of adsorbate solution (10 ml) with different Initial concentrations (3 mg/l, 5 mg/l & 7 mg/l) will be prepared in a conical flask with variable adsorbent weight and kept inside the shaker at 150 rpm. After determining adsorbate concentration, plot of  $q_e$  vs adsorbate concentration will be obtained.

Synthesized nano bio-materials (Ag-AB, Ag-AI and CuO-CS) are applied as bio-sorbents under optimum conditions (5 mg, 7 mg/l) for adsorption of PAHs from aqueous media through batch adsorption experiment.

## 2.5. Kinetic and equilibrium studies

### 2.5.1. Kinetic Studies

In order to study the mechanism of adsorption on different adsorbents, kinetic equations are used to identify the possible mechanisms of such adsorption process. In this study, first order and pseudo second order kinetics is proposed by Eqs. (3) and (4), respectively.

$$\text{Log}C_t = \left( \frac{K_1}{2.303} \right) t + \text{Log}C_o \quad (3)$$

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

### 2.5.2. Equilibrium Isotherms

The experimental data was taken and analyzed by using linearized isotherm models of Langmuir and Freundlich.

- a. Langmuir Isotherm:

This model is very helpful for monomolecular adsorption phenomenon.

$$\frac{C_e}{Q_e} = \left( \frac{C_e}{Q_m} \right) + 1/Q_m b$$

$Q_m$  = Langmuir constant

Slope =  $1/q_m$ ,  $Q_m = 1/\text{slope}$

Intercept =  $1/q_m b$ ,  $b = K_L$ ,  $b = \text{intercept/slope}$

b. Freundlich Isotherm:

This model is very helpful for multilayer adsorption phenomenon.

$$\log Q_e = \log K_f + \left( \frac{1}{n} \right) \log C_e$$

Slope =  $1/n$ ,  $n = 1/\text{slope}$

Intercept =  $\log K_f$ ,  $K_f = \text{antilog } K_f$

### 3. Results and Discussion

Silver and copper nanoparticles have been synthesized by using plant extracts as reducing agents. These synthesized materials are then applied as bio-sorbents for wastewater treatment under variable parameters.

#### 3.1. Characterization of Metal Nanoparticles

Characterization of these synthesized nanoparticles (silver and copper) is done using FTIR (Fourier Transform Infrared) spectroscopy to study their structure property relationship.

##### 3.1.1. FTIR results of Synthesized Nanoparticles (Ag-NPs) and (Cu-NPs)

Two different types of nanoparticles (silver and copper) are characterized that are actually synthesized by plants *Aloe barbedensis*, *Azadirachta indica* and *Coriandrum sativum* (Fig. 3.1a). Results of FTIR for *Aloe barbedensis* (silver nanoparticles) shows that maximum absorption is done at  $598 \text{ cm}^{-1}$ ,  $505 \text{ cm}^{-1}$ ,  $470 \text{ cm}^{-1}$ ,  $483 \text{ cm}^{-1}$  (N-H) bonding,  $424 \text{ cm}^{-1}$ ,  $391 \text{ cm}^{-1}$ . In case of *Azadirachta indica* (Ag nanoparticles) it shows maximum peak (Fig. 3.1b) on  $505 \text{ cm}^{-1}$  (O—H) and  $470 \text{ cm}^{-1}$  (O—H) bonding here means OH functional group confirms,  $459 \text{ cm}^{-1}$  and  $391 \text{ cm}^{-1}$ . Copper nanoparticles, Cu-Ai (*Azadirachta indica*) has maximum peaks

at  $516 \text{ cm}^{-1}$  (O—H),  $494 \text{ cm}^{-1}$  (O—H),  $470 \text{ cm}^{-1}$ ,  $483 \text{ cm}^{-1}$ ,  $413 \text{ cm}^{-1}$  (C—C) and  $402 \text{ cm}^{-1}$  (C—C) (Fig. 3.1c) and for Cu—Cs (*Coriandrum sativum*) have maximum adsorption capacity (Fig. 3.1d). Through FTIR results the best peaks are shown at  $470 \text{ cm}^{-1}$  (C—O),  $424 \text{ cm}^{-1}$ ,  $413 \text{ cm}^{-1}$  and  $402 \text{ cm}^{-1}$ , respectively. FTIR results indicated that metals have absorption limit  $300\text{--}600 \text{ cm}^{-1}$  so all above mentioned nanoparticles synthesis was confirmed.

#### 3.2. Batch Adsorption Protocol

Synthesized materials are applied as bio-sorbents for the treatment of wastewater contaminated due to naphthalene. In case of naphthalene the results are represented in Fig. 3.2 a, clearly indicated that under optimum conditions at initial concentration  $7 \text{ mg/l}$  and adsorbent dose  $5 \text{ mg}$ , Cu-Ai shows maximum removal capacity of  $98.07\%$  than other biosorbents, Cu-Cs have  $82.43\%$ , Ag-Ai shows  $89.71\%$  and Ag-Ab shows  $86\%$ . Overall (Fig. 3.2b) copper nanoparticles show maximum adsorption capacity for naphthalene than the silver nanoparticles. Copper nanoparticles which are synthesized from *Azadirachta indica* have more removal capacity than the silver nanoparticles which are synthesized from *Aloe barbedensis*. Among copper nanoparticles those nanoparticles which are synthesized from *Azadirachta indica* have more adsorption capacity than the nanoparticles which are synthesized from *Coriandrum sativum*. The reason behind this, copper nanoparticles synthesized from neem (*Azadirachta indica*) have more surface area that is available for surface adsorption and shows a good removal power as compared to all other nanoparticles synthesized from other plants sources (*Aloe barbedensis*, *Coriandrum sativum*). As silver and copper nanoparticles re synthesized by green way, it means plants are used here and provide a better way for adsorption by using plant based nanoparticles as are environmentally good and easy to prepare. Silver nanoparticles synthesized from aloe vera have good adsorption capacity both for maximum and minimum level. Silver nanoparticles prepared from neem also shows good adsorption and the higher rate of removal is observed in case of *Azadirachta indica*, copper nanoparticles as there is multiple sites or interporosity available here that may help in adsorption phenomena. Lesser pollutant removal capacity is seen in the case of copper nanoparticles from coriander plant source. The pollutant (naphthalene) we used, have two fused aromatic rings and

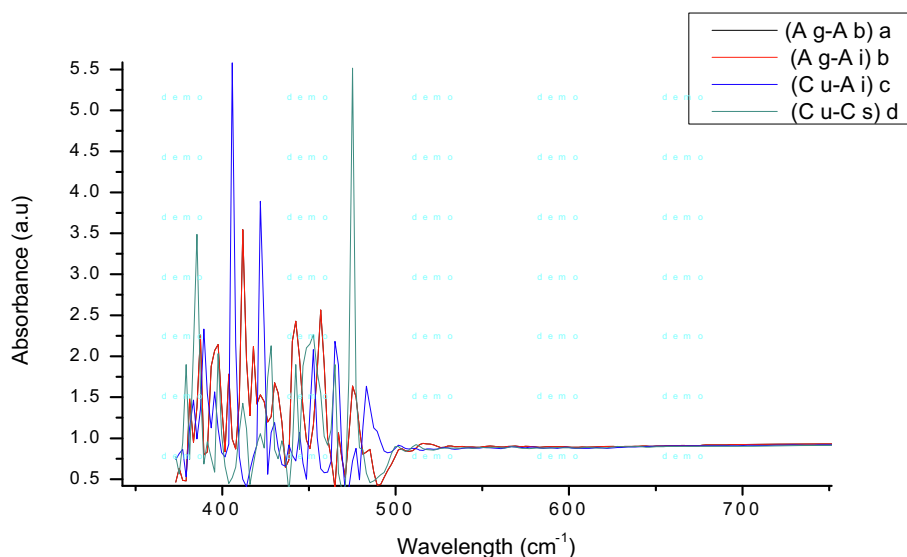
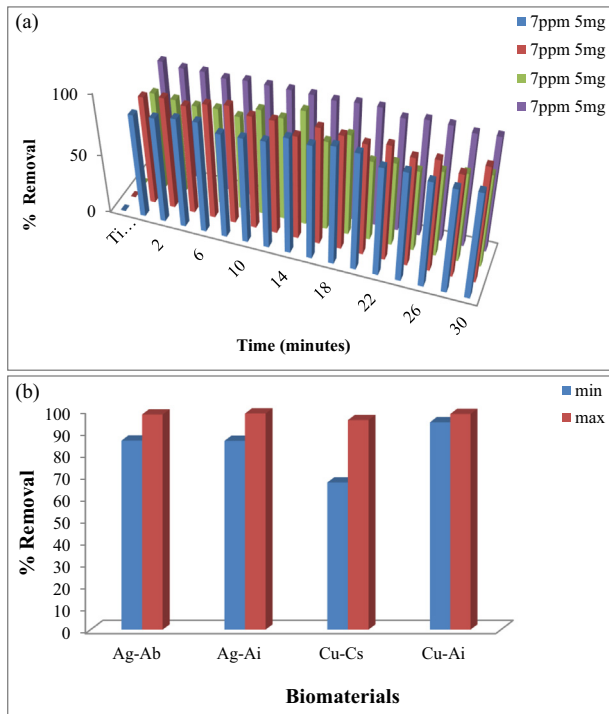


Fig. 3.1. FTIR results of synthesized Nanoparticles.



**Fig. 3.2.** Removal (%) of Naphthalene by Ag-Ab, Ag-Ai, Cu-Ai and Cu-Cs (a) with respect to contact time (b) Minimum and Maximum Adsorption capacity, under optimum conditions (7 ppm, 5 mg).

because of those aromatic rings its removal might be not easy or it may take larger time to remove so its adsorption capacity actually depends on particle size, number of available surface sites, porosity as well nature of pollutant.

### 3.3. Kinetic Study

#### 3.3.1. First Order Kinetics parameters for Naphthalene

First order kinetic result is not suitable for these bio-sorbents. As correlation coefficient of all synthesized nanoparticles was very less (Fig. 3.3a–d, Table 3.1). Also the theoretical values found from

the first-order kinetic parameter did not give reasonable values. Coefficient correlation  $R^2$  of first order is not fit for our synthesized nanoparticles (Ag-AB, Ag-AI, Cu-AI, and Cu-Cs). Reason is that result of  $R^2$  all synthesized nanoparticles is less than 0.700 but we required its coefficient values near to 0.90 or more, shows that the first order absorption system is not fitted in this.

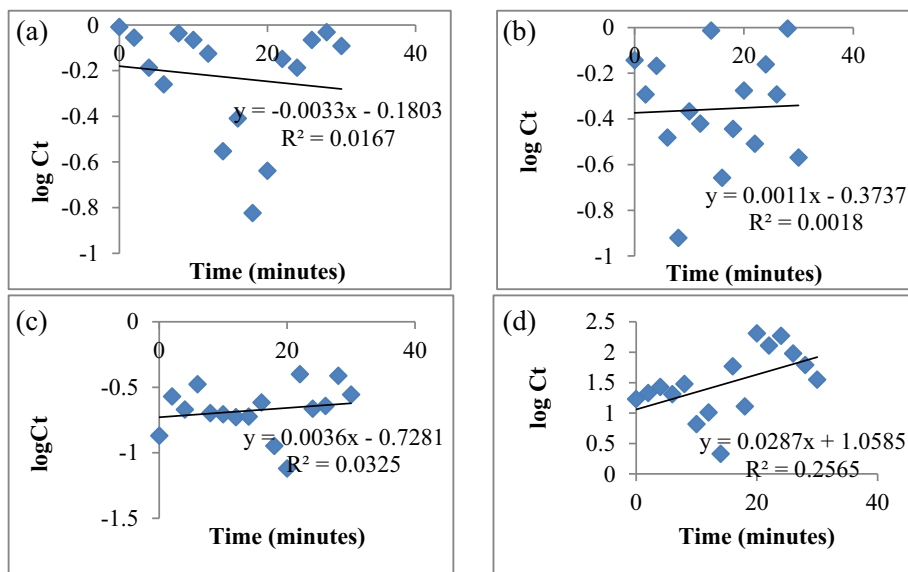
#### 3.3.2. Pseudo Second order Kinetics Parameters for Naphthalene

When  $C_t$  is plotted against time best fit correlation coefficient are seen ( $R^2 > 0.90$ ) for all synthesized nanoparticles (Fig. 3.4a–d). The coefficient correlation of Ag-Ab is 0.9936 which is best fit. Results of Coefficient correlation  $R^2$  are in this order Cu-Ai > Ag-Ab > Ag-Ai > Cu-Cs respectively. Minimum coefficient correlation is of Cu-Cs. Pseudo-second order kinetic ( $R^2 > 0.99$ ) are better fitted according to observed data.

Coefficient correlation  $R^2$  of Cu-Ai 0.999 is best fit which is 0.99 among all other synthesized nanoparticles. Results of Coefficient correlation  $R^2$  are in this order Cu-Ai > Ag-Ab > Cu-Cs > Ag-Ai. Minimum coefficient correlation is of Ag-Ai which is 0.9679. First of all as we know that all four synthesized nanoparticles have greater adsorption power with respect to time also by adsorbent dose and adsorbate we used. We clearly seen here we have greater values for copper nanoparticles obtained from *Azadirachta indica* plant source as its coefficient correlation value is 0.9993 that we may say that equal to 100% so we may conclude that in this case we have greater surface area availability as well as higher porosity level that may lead to greater adsorption power. On the other hand, second highest nanoparticles are obtained from plant source *Aloe barbedensis* (silver nanoparticles) as its coefficient correlation value is 0.9949 that shows silver nanoparticles from this plant source also have greater adsorption power and silver nanoparticles from *Azadirachta indica* plants have  $R^2$  value 0.9936 and for copper nanoparticles obtained from *Coriandrum sativum* have least adsorption as comparison to all other three nanoparticles as its  $R^2$  value is 0.9791 that also have a good adsorption result but with respect to all other nanoparticles have lowest adsorption value.

### 3.4. Equilibrium Isotherms

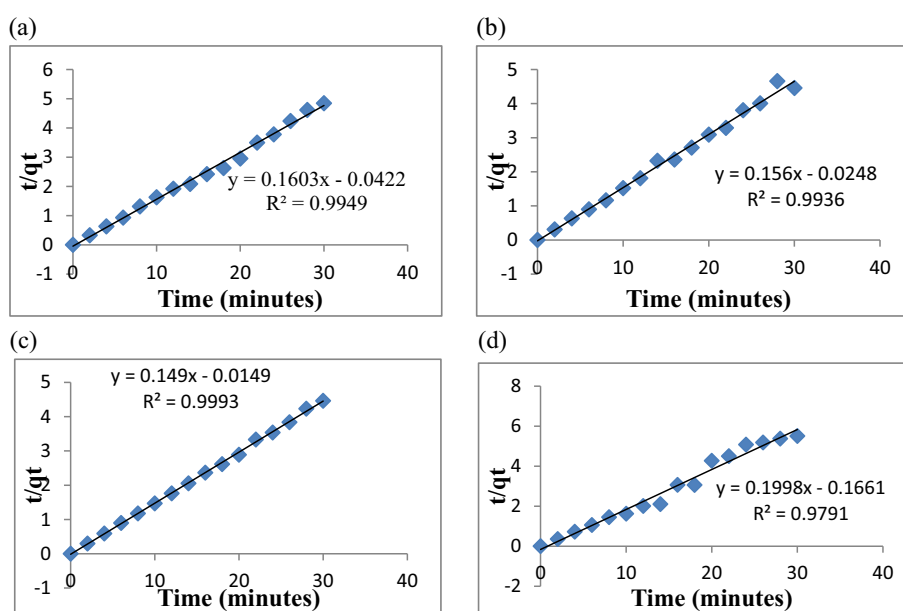
In present study two equilibrium isotherms are applied, first is Langmuir Isotherm and second is Freundlich Isotherm.



**Fig. 3.3.** First Order Kinetics Parameters for Naphthalene by nano bio-sorbents (a) Ag-Ab (b) Ag-Ai (c) Cu-Ai (d)Cu-Cs.

**Table 3.1**  
Kinetic Parameters for Naphthalene adsorption on bio-sorbents.

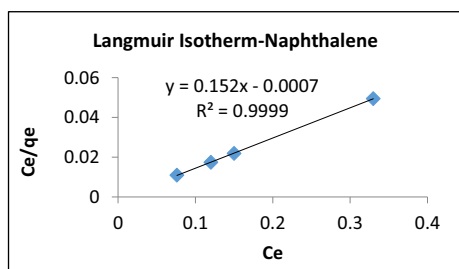
First Order				
	Ag-Ab	Ag-Ai	Cu-Ai	Cu-Cs
Slope	-0.003	0.001	0.004	0.028
Intercept	-0.180	0.373	0.728	1.058
$K_1$	-0.008	0.003	0.008	0.066
$R^2$	0.017	0.002	0.032	0.256
Pseudo Second Order				
	Ag-Ab	Ag-Ai	Cu-Ai	Cu-Cs
Slope	0.156	0.156	0.149	0.1998
$q_e$ (Experimental)	6.41	6.41	6.71	5.01
$q_e$ (Theoretical)	6.35	6.47	6.758	5.02
Intercept	-0.024	-0.024	0.014	-0.166
$K_2$	-258.47	-258.47	450.430	-30.132
$R^2$	0.993	0.993	0.999	0.979



**Fig. 3.4.** Pseudo Second Order Kinetics Parameters for Naphthalene by bio-sorbents (a) Ag-Ab (b) Ag-Ai (c) Cu-Ai (d) Cu-Cs.

### 3.4.1. Langmuir Isotherm

The result of first Langmuir Isotherm is best fitted for our data as all values are on the same line and hence the resultant line is linear that demonstrate that our Langmuir Isotherm result is best applicable here. According to (Fig. 3.5a) with respect to equilibrium time all four nanoparticles (*Aloe barbedensis*, *Azadirachta indica* and *Coriandrum sativum*) show good result. Its coefficient correlation value is best fitted as is 0.9999 that is nearly to 100%, so we may discuss that our synthesized four nanoparticles from three sources



**Fig. 3.5a.** Langmuir Isotherm for naphthalene.

of plants have good result in pollutant (naphthalene) removal with respect to equilibrium isotherms and hence its values relates with our result of these isotherms. As we conclude by our result that all nanoparticles have great power of adsorption with respect to time. And we also conclude that four nanoparticles that are synthesized from plants have greater adsorption power as we all know that plants have naturally power to fight with environmental hazardous. As clearly show by our data, as we obtained a linear line by our graph that represents all synthesized nanoparticles shows greater adsorption power.

### 3.4.2. Freundlich Isotherm

By this isotherm graph it is clearly observed that all the points are on the line that we see here clearly it means multilayer adsorption phenomena best fitted here our coefficient correlation values  $R^2$  is 0.9567 that is best fitted according to rule. All four nanoparticles that are synthesized from plants sources show good adsorption power in the case of pollutant (naphthalene). All nanoparticles (Ag-NPs and Cu-NPs) show good efficiency (Fig. 3.5b) with respect to pollutant removal and equilibrium values give satisfactory result.

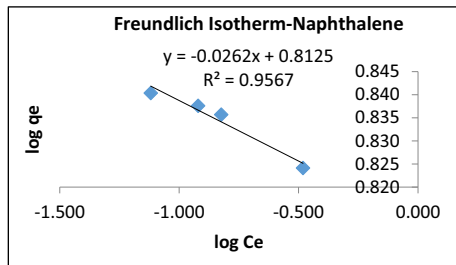


Fig. 3.5b. Freundlich isotherm for naphthalene.

### 3.5. Discussion

Present study is supported by a research reported that synthesized mesoporous silica is prolonged in decontamination of phenolic compounds. Its impact is just explained with respect to variable function of time. In start, results are in undistinguished mode of varying contact time on percentage adsorption. By experiment, calculated that removal percentage for silica is more than 90% that is maximum, from previous literature it is concluded that additionally added surfactant sodium dodecyl sulfate (SDS) decreases the removal efficiency of phenols (Nasreen et al., 2018). The % removal process was established as commonly dependent on the amount, surface practicality, pH of solution that induces nano biomaterials to adsorb metal ions. 100% adsorption rate of Cr(III), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) ions by water collected at pH 8 using nano-biomaterials. Absorbance percentage for As(III) by carboxyl, amine and thiol-functionalized  $\text{Fe}_3\text{O}_4$  pointed as 91, 95 and 97% by the pH 8 (Sadegh et al., 2017). Adsorption capacity of PAHs and metal contaminants by Mag-PCMA-T was fast. By applying this,  $\text{Cd}^{2+}$  are remove from water successfully that change the hardness of water hence proved to have excellent performance for the  $\text{Cd}^{2+}$  removal from wastewater (Huang et al., 2016). For glacial isotherms the Langmuir model, in which a better number of sorption sites are available that can be fully saturated or can be fully filled during isotherm experimentation. Correlation coefficients  $R^2$  of the glacial outwash, Langmuir isotherm is best fitted that were 0.997. The results of the naphthalene contaminated soil, isotherm values of the glacial outwash, the maximum amount of naphthalene are sorbed by the glacial outwash,  $\beta$  that was observed as 0.48 mg naphthalene per gram of soil. The adsorption constant related to binding energy,  $\alpha$ , was 0.24 L/g (Kasaraneni, 2014). Langmuir isotherm is based on the assumption that adsorption phenomena takes place at specific homogeneous sites, within the adsorbent and hence there is no significant interaction among the adsorbed species. The adsorbent is fully saturated or filled after one layer of adsorbed molecules is present on the adsorbent surface. The Freundlich isotherm model takes multi-layer and heterogeneous adsorption occurs here (Yakout and Daifullah, 2013).

### 4. Conclusions

In current research work silver and copper nanoparticles were synthesized from plant extracts such as (*Aloe barbedensis*, *Azadirachta indica* and *Coriandrum sativum*) and their application was done as biosorbents for the decontamination of PAH (naphthalene) from spiked aqueous media. Following results has been concluded from the study:

- Three different plants precursors are used for the synthesis of plant extracts such as *Aloe barbedensis*, *Azadirachta indica* and *Coriandrum sativum* that are further used to synthesize nanoparticles.

- Two different nanoparticles are obtained such as silver nanoparticles (Ag-NPs) and copper nanoparticles (Cu-NPs).
- These synthesized nanoparticles are then characterized through FTIR (Fourier Transform Infrared) spectroscopy. All synthesized nanoparticles are confirmed by identification of different functional groups.
- A batch experiment is conducted that also gives satisfactory result. We conducted all batches by using UV-Visible spectrophotometer (checking adsorption %).
- Maximum adsorption capacity was observed by the synthesized nanoparticles that were checked by conducting batch experiments at different initial concentration, variable adsorbent dose and contact time.
- However, multiple adsorption desorption cycles were noticed in the batch experiment of 30 min.
- Under optimum condition, we actually conclude that copper nanoparticles synthesized from *Azadirachta indica* have more adsorption power as compared to silver nanoparticles.
- The polyaromatic hydrocarbon (naphthalene) removal efficiency by synthesized metal adsorbents was maximum in present study maybe due to the fact that naphthalene has two fused aromatic rings that makes the naphthalene structure less aromatic or lower volatile, that's why are easy to remove.

### 5. Future Recommendation

Present study focused on the economical synthesis of metal nanoparticles by using plant extracts and then synthesized products are applied as bio-sorbents for the decontamination of naphthalene from aqueous media. Reported results indicated that nanoparticles due to large surface area and maximum available adsorption sites act as efficient adsorbents by giving maximum pollutant removal efficiency. It's a gateway for future researchers to develop such type of advanced materials by economical means and then use them as efficient adsorbents for variety of pollutants decontamination.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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