# Biosynthesis of Silver Nanoparticles using Plants and its application on the treatment of textile mill wastewater

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**Abstract** – Textile mill wastewater not only consumes large volume of water but also generate an equally alarming quantity of toxic dye rich waste water. This wastewater if treated efficiently may be further reused for domestic and industrial purposes. Hence it is essential to develop, a cost effective and environmentally friendly technique for adsorption of toxic dyes from textile effluents. Firstly, neem (*Azadirachta indica*), mango (*Mangifera indica*), lemon (*Citrus limon*) and combination of all the three leaves (1 ml) were used for the green synthesis of silver nanoparticles (AgNPs). The AgNPs were characterized using SEM analysis and the particles were within the size of $10^{-9}$ nm. These AgNPs were further utilized for the treatment of textile mill wastewater to remove the colour and COD (chemical oxygen demand). The silver nanoparticles synthesised by neem, mango, lemon and combination of all the leaves could able to remove 97, 92, 91, 93 % of colour and 49, 47, 46, and 43 % of COD from the textile mill wastewater respectively within a time period of 15, 50, 60 and 30 minutes. Various isotherms and kinetics were applied to know the capacity and intensity of adsorbents out of which Freundlich isotherm was found to be the best fit for the silver nanoparticles which were used for the removal of colour and COD from textile mill wastewater. Pseudo – second order kinetics provided a good correlation for the adsorption of dyes and COD from textile mill wastewater using silver nanoparticles as an adsorbent. The plots of Dubinin – Radushkevich isotherm it is indicated that the adsorption is physical adsorption and Liquid diffusion model holds good or rate controlling step for the adsorption of colour from textile mill wastewater. The synthesised silver nanoparticles showed effective antimicrobial activity against bacteria like *Esecherisia – coli* (gram negative) and *Streptococcus* (gram positive).

**Key Words: Biosynthesis, Silver Nanoparticles, Antimicrobial Activity.**

## 1 INTRODUCTION

Industrial revolution for fulfilling the demands of increasing population during production, results in the pollution of water, air and soil (1). The discharge of pollutants from various industries poses threat to the surrounding environment. The industries like textile and paper large quantities of water and produces huge volume of wastewater from different types of dyes and finishing process (1). Different types of dyes are used in paper, leather, textile, cosmetics industry (1). Among all dyes, azo dyes are largest and most versatile class of dyes and are widely used in textile industries (1). More than 2000 structurally different azo dyes are currently in use (1). These dyes account for approximately 60 – 70 % of all dyes used in food and textile manufacture. Several physic – chemical methods such as adsorption, chemical treatment and ion pair extractions have been adopted and proven to be costly while producing large amounts of sludge and thus they also lead to second pollution (1). To overcome such problems research has been moving toward biological methods as these methods are eco – friendly and cost effective (1). The application of nanotechnology will enhance the bioremediation (1).

Nowadays, nanotechnology is regarded as a distinct field of research in modern science and technology with multidirectional applications (2). Useful application of nanotechnology in medicinal purposes is currently one of the most fascinating areas of research, metallic nanoparticles have also been receiving considerable interest in biomedical applications (2). Silver nanoparticles in particular, are finding applications to the researchers as tools for antibacterial and antifungal, anti – inflammatory, wound healing, radio – imaging, retinal neovascularization, antiviral and anti – oxidant agents, and also as novel cancer therapeutics, capitalizing on their unique properties to enhance potential therapeutic efficacy (2). Nanoparticles are known as particles with a size smaller than 100 nm (3). Many methods are adopted for nanoparticles synthesis like physical, chemical, and biological methods (3). Biological method of synthesis of silver nanoparticles was achieved by using bacteria, fungi, algae and plants (3). The use of plants as the production assembly of silver nanoparticles has drawn attention, because of its rapid, eco – friendly, non – pathogenic, economical protocol and providing reduction and stabilization of silver ions by combination of bio molecules such as proteins, amino acids, enzymes, polysaccharides, alkaloids, tannis phenolic, saponins, terpinoids and vitamins which are already established in the plant extract having medicinal values and are environmental benign, yet chemically complex structure (4) and these helps in the reduction of silver ions to silver nanoparticles and act as capping and stabilizing agent (3).

## 2 MATERIALS AND METHODOLOGY

### 2.1 Adsorbent

Silver nanoparticles were used as an adsorbents on the removal of dye from textile mill wastewater. These silver nanoparticles were synthesised by using leaves of mango tree, neem tree and lemon tree and combination of all the three plants. The obtained silver nanoparticles sssswere used as an adsorbent for the removal of colours or dyes from the textile mill wastewater.

### 2.2 Adsorbate

In the present study Batch adsorption studies was conducted for the removal of colour and COD from textile mill wastewater and the samples was collected by the method of composite sampling, from Karnataka silk industries corporation (KSIC) limited, Manandavadi Road, Mysuru, Karnataka.

### 2.3 Synthesis of Silver Nanoparticles by Using Plants

Different leaves of plants (neem, mango and lemon) was used for the synthesis of silver nanoparticles. Fresh leaves were collected from JSS University. The leaves were cleaned with running water followed by distilled water to remove the debris and other contaminants from the leaves. About 100 g of leaves were weighed and grinded well, then the grinded leaves were filtered by using whatmans filter paper which is of grade 1 and the obtained filtrate was boiled for about 10 – 15 minutes to get the plant extract. The plant extract was filtered again to remove the solid part in the extract. About 1 ml of plant extract was taken and it was added to 50 ml of 1mM silver nitrate solution to get or to synthesise the silver nanoparticles. The change in colour from light yellow to dark brown or reddish brown indicates the synthesis of silver nanoparticles (reduction of $Ag^+$ ion to $Ag^0$).

### 2.4 Preparation of Adsorbent by Combination of Leaves

Combination of three leaves were used for the synthesis of silver nanoparticles. Fresh leaves of neem, mango and lemon were collected from the JSS University, mysuru, India. All the three leaves were washed thoroughly with the distilled water to remove the debris and other organic contaminants. About 100 gm of leaves were weighed with the help of weighing balance and the weighed leaves were grinded with the help of domestic grinder and the grinded leaves were filtered by using by using whatsman filter paper of grade one. The filtrate was boiled for about 10 – 15 minutes to get the plant extract. The obtained extract was filtered again so has to remove the solid part from the extract. About 1 ml of combination of leaves extract was taken and it was added to 50 ml of 1 mM silver nitrate solution to get the silver nanoparticles. The change of colour from yellow to red indicates the synthesis of silver nanoparticles.

### 2.5 Preparation of Silver Nitrate Solution ($AgNO_3$)

Silver nitrate which bears the chemical formula of $AgNO_3$ and molecular weight 169.87 g / mol. It was procured from Merck specialities private limited, and it was used for the synthesis of silver nanoparticles by various leaves of plants (neem, mango, lemon, and combination of all the three leaves).

### 2.6 Nutrient Agar

Nutrient agar is a nutrient medium which is used for the cultivation of micro – organisms. Nutrient agar can grow a variety of bacteria and fungi because it contains many nutrients which is needed for the growth of micro – organisms. It was procured from Himedia Laboratories, Mumbi. It is used in the antimicrobial activity of synthesised silver nanoparticle against micro – organisms.

### 2.7 Bacterial Strain

Bacterial strain was procured from ISCTS, Bangalore, India. It is used in the antimicrobial assay of silver nanoparticles.

To study the optimum factors for silver nanoparticles synthesis, the experiment were carried out at different conditions are silver ion concentration (1, 2, 3, 4 and 5 mM), pH (4, 5, 6, and 7), and temperature of (20, 25, 30, 35, and 40 degree celsius). The pH of the reaction mixture was adjusted by using 0.1 N sodium hydroxide and 0.1 N Hydrochloric acid. The effect of these parameters on the synthesis of silver nanoparticles was monitored by UV – Visible spectrophotometer.

### 2.8 Characterization of silver nanoparticles

The reduction of silver ions to silver nanoparticles was spectrometerically identified by UV – Visible spectrophotometer, at different wavelengths (400 – 700 nm). The size and shape of the synthesised silver nanoparticles was analysed by scanning electron micrograph.

### 2.9 Batch experiments

100 mL of textile mill wastewater was to which the dosage of adsorbents (silver nanoparticles) synthesised by neem, mango, lemon and combination of all the three leaves was varied (1 g to 15 g / 100 mL) and the samples were incubated with a constant speed of agitation (180 rpm) (procured from Kodavil Electro Mechanical Industries (KEMI) Company, Kerala, India). The samples were collected for the analysis of residual dye present in the solution. The residual amount of dye present in the solution was investigated by UV – Visible spectrophotometer. The removal percentage of dye was determined by following equation

$$Removal\ (\%) = \frac{(A-B)}{A} X\ 100 \qquad (1)$$

Where A = Initial absorbance of dye, B = Final absorbance of dye.

## 3 RESULTS AND DISCUSSION

### 3.1 Visual Observation

Formation of silver nanoparticles was preliminarily well known by changing of colour from yellow to reddish brown colour while adding leaf extract with silver ion solution due to excitation in the nanoparticles (3). The colour formation was occurred within few minutes after the addition of leaves extract. Metal nanoparticles exhibits different colours in solution due to their optical properties and silver nanoparticles were characterized by forming of brown colour (3) and it is shown in Figure- 1.

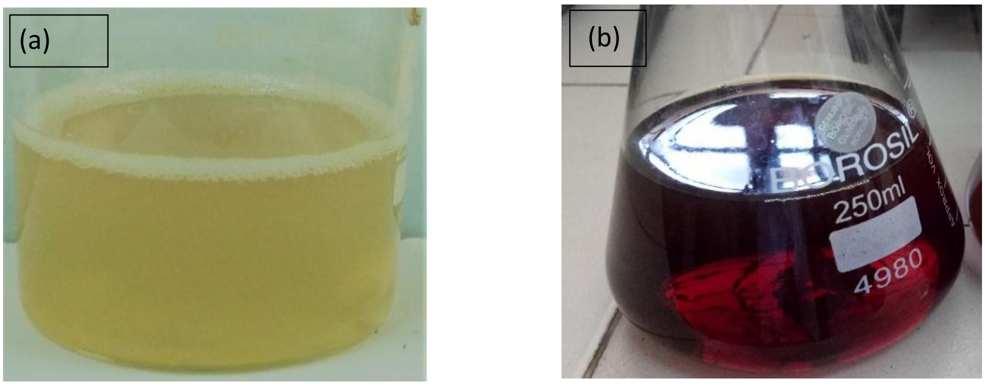



**Figure- 1: Change of colour from yellowish (before the synthesis of AgNPs(a)) to reddish brown (after the synthesis of AgNPs (b))**

### 3.2 Effect of Silver Ion Concentration

The UV – Visible spectrum (Figure - 2) shows the effect of silver nitrate concentration on the synthesis of silver nanoparticles which was synthesised by using neem, mango, lemon and combination of all the three leaves. 1mM concentration shows narrow band with increased absorbance. The adsorption was increased while increasing the concentration of silver nitrate from 1mM to 5 Mm. In 1mM concentration the nanoparticles synthesis and reduction in size was started quickly due to the more availability of functional groups in the leaf extract (3). Thus, the optimization study showed the significant effect of silver nitrate concentration on the synthesis of silver nanoparticles and this research concludes that, 1Mm of silver nitrate concentration is optimum for the synthesis of silver nanoparticles in all the cases (neem, mango, lemon and combination of all the three leaves). Similarly, increasing in the intensity indicated the increasing in the nanoparticles concentration, higher concentration of silver nitrate leads to the formation of larger sized nanoparticles (3).

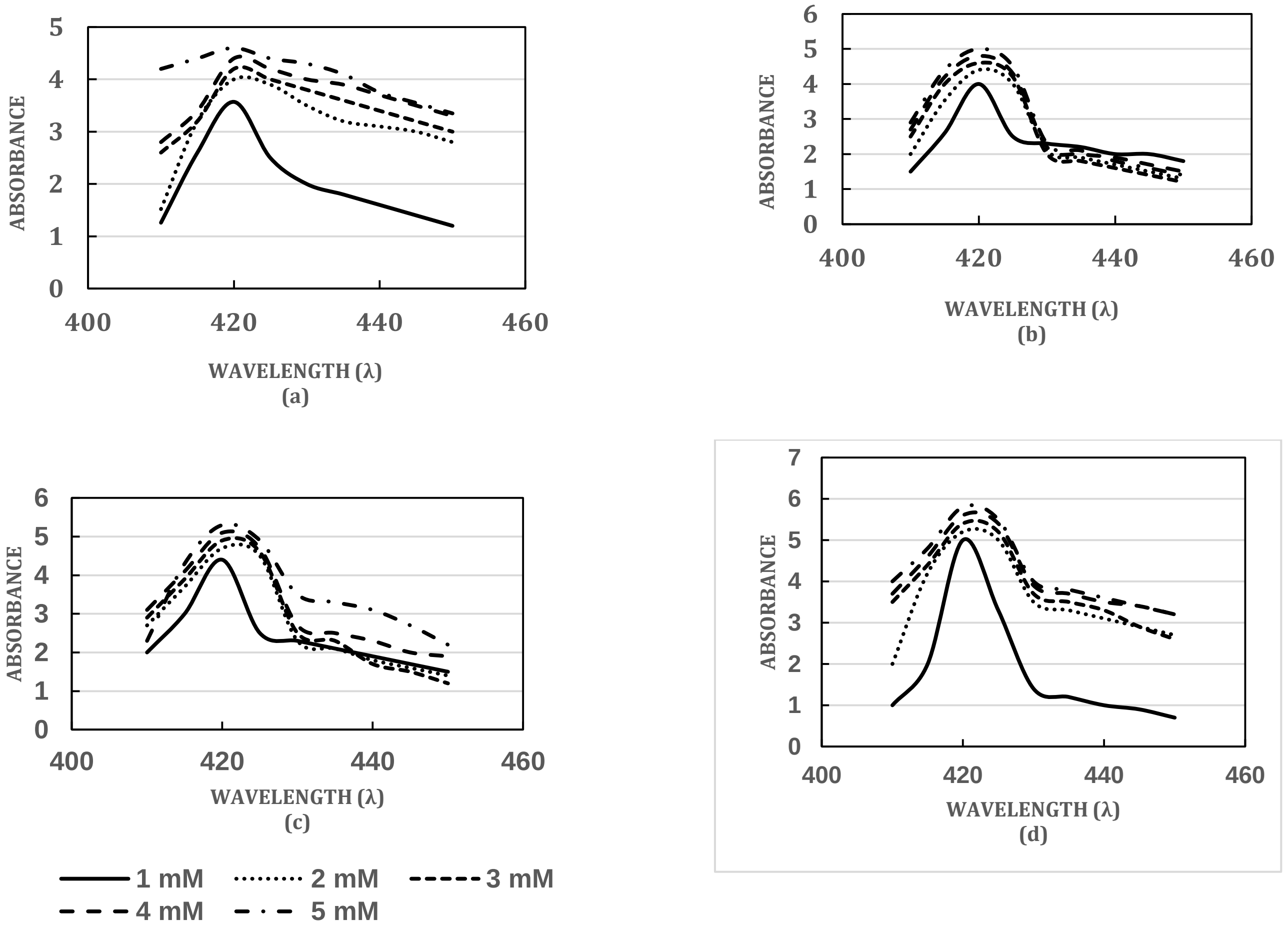



**Figure- 2: UV – Visible spectra showing absorbance with different concentration of AgNO3 for neem (a), mango (b), lemon (c) and combination of all the three leaves (d).**

### 3.3 Effect of Plant Extract

The effect of biomass concentration on the synthesis of silver nanoparticles was studied by exposing 1ml to 5 ml of plant extract in 1mM of silver nitrate solution and it was monitored by using UV – Visible spectrophotometer. 1ml of plant extract in all the cases (neem, mango, lemon and combination of all the three leaves) showed the narrow band with increased in absorbance. The adsorption was increased while increasing the biomass concentration from 1ml to 5 ml. When 1ml of plant extract (neem, mango, lemon and combination of all the three leaves) was added to 1 Mm of silver nitrate solution, the synthesised silver nanoparticles were well dispersed, but when the concentration of biomass increased 2ml and up to 5 ml the so formed silver nanoparticles showed the agglomeration. Higher the concentration of biomass leads to the formation of larger sized nanoparticles (3). The results are shown in Figure - 3.

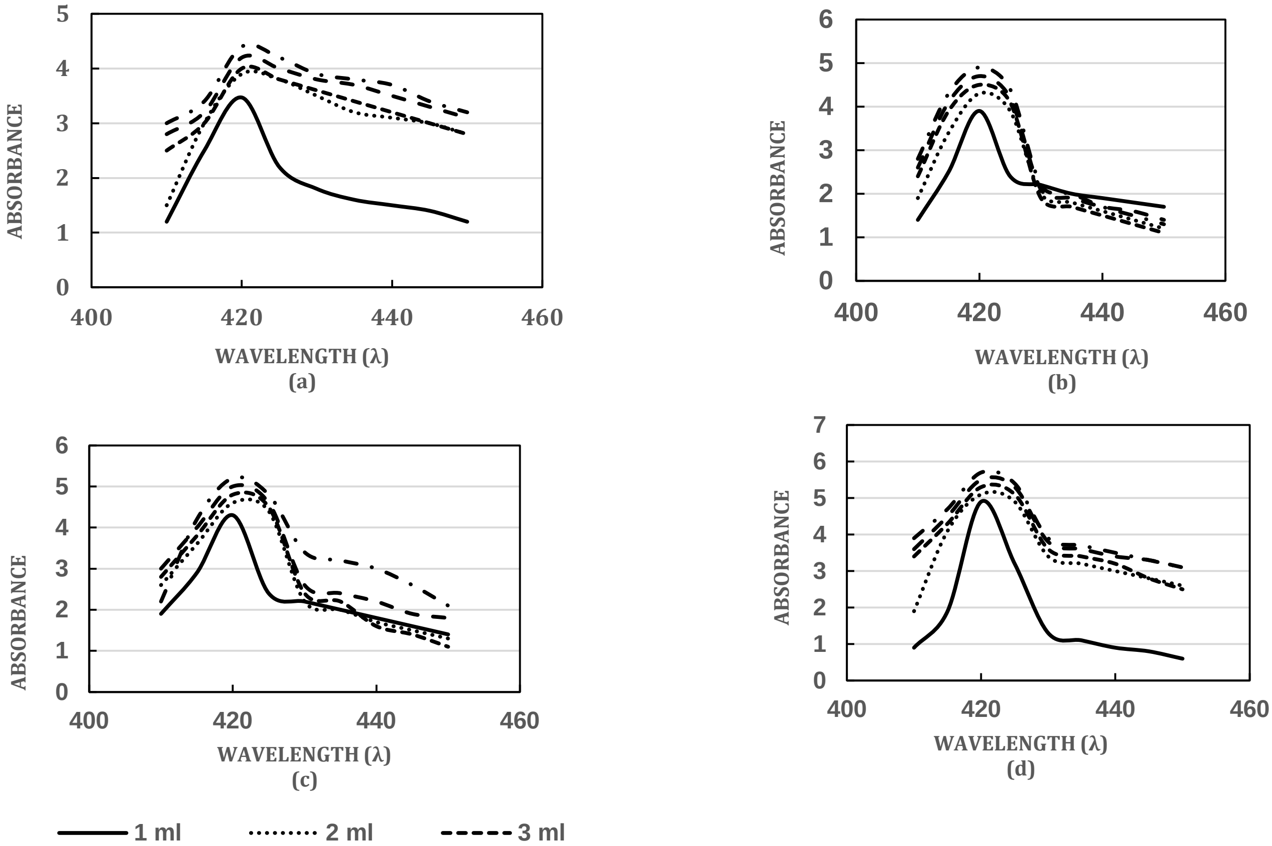



**Figure- 3: UV – Visible spectra showing absorbance with different concentration of biomass for neem (a), mango (b), lemon (c) and combination of all the three leaves (d).**

### 3.4 Effect of Ph

pH play a very important role in the synthesis of silver nanoparticles (3). The effect of pH on the synthesis of silver nanoparticles using leaves extract (neem, mango, lemon and combination of all the three leaves) was investigated by keeping biomass concentration (1 ml) and silver nitrate concentration (1mM) constant, under different pH of the reaction mixture by the leaf extract and it is depicted from Figure - 4. The maximum synthesis of silver nanoparticles were obtained at the pH of 7 (in all the cases of plants) and the highest colour intensity was observed at this ph. At the lower pH the aggregation of nanoparticles is observed this may be due to the reduction in the activity of functional group of the biomass which reduces the stability of the capping agent (5). Thus, the optimization study shows that pH 7 is suitable for the synthesis of silver nanoparticles by using 1 ml of plant extract (neem, mano, lemon and combination of all the three leaves) and 1mM of silver nitrate concentration.

### 3.5 Effect of Temperature

Temperature play an important role in the synthesis of silver nanoparticles. Figure – 5 shows the effect of temperature on the synthesis of silver nanoparticles using plants (neem, mango, lemon and combination of all the three leaves) and it was carried out t different temperatures from 25 degree Celsius to 40 degree Celsius. The maximum production of silver nanoparticles was obtained at 25 degree Celsius. When the temperature was increased to 30 and up to 40 degree Celsius there no much increase in the production of silver nanoparticles this is because at the higher temperature the activity of functional group of plants reduces and which is nothing but the reduction in the activity of capping agent (5). Thus, the optimization study indicates that 25 degree Celsius is optimum for the synthesis of silver nanoparticles using 1 ml of plants (neem, mango, lemon and combination of all the three plants) and 1mM of silver nitrate solution.

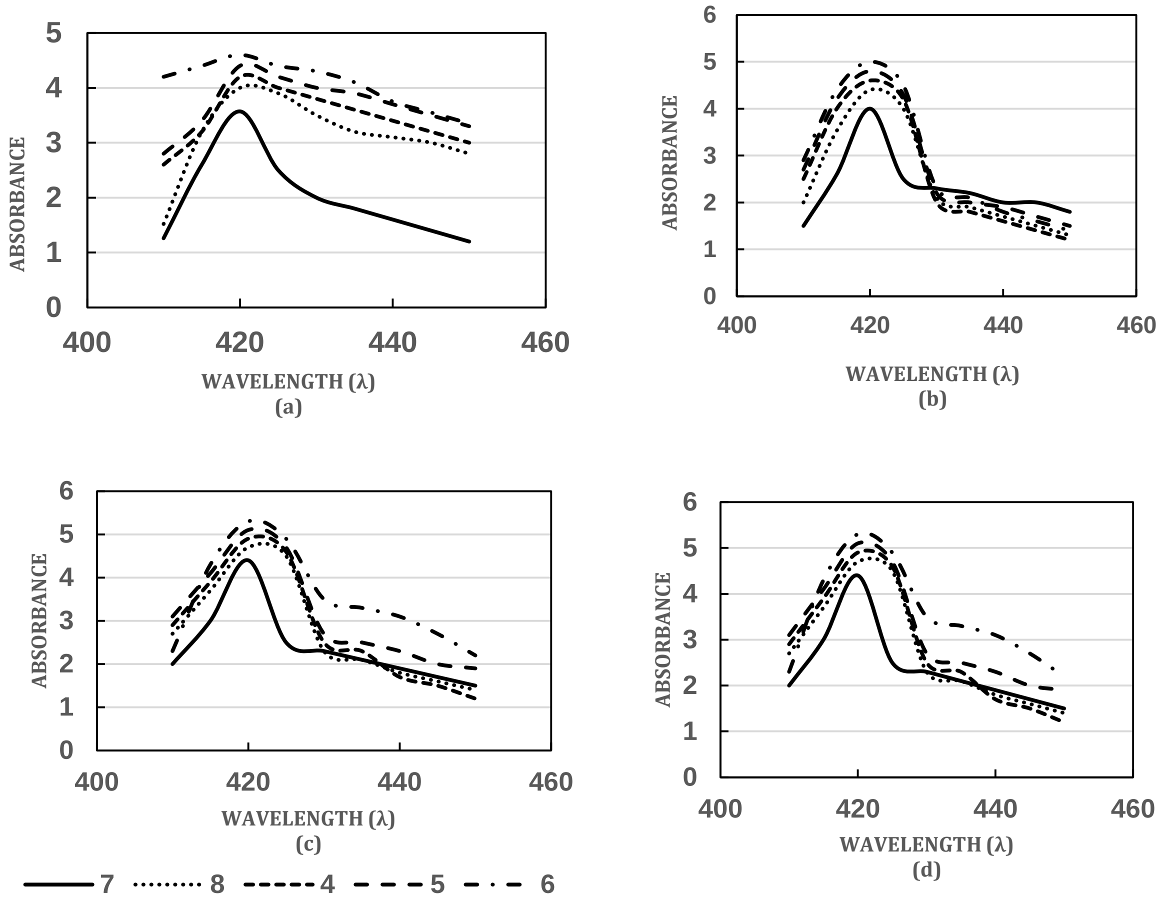
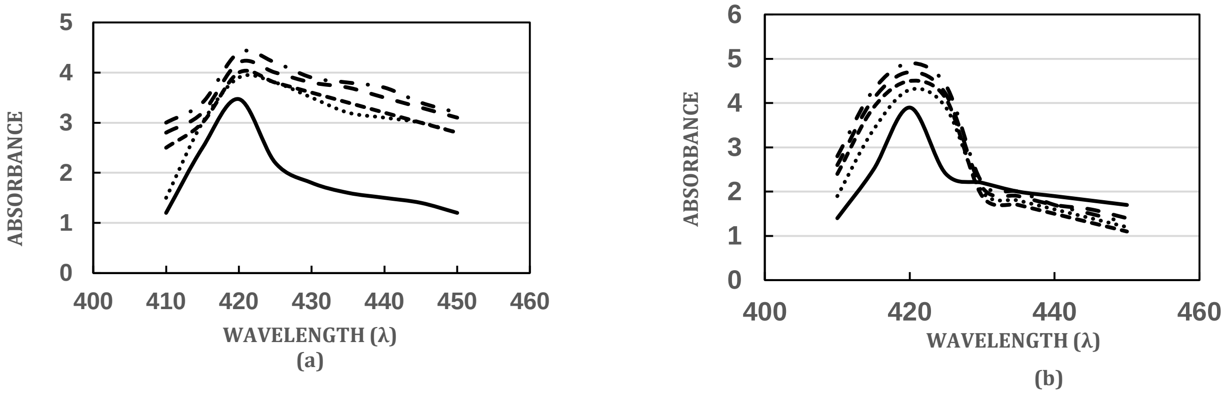



**Figure- 4: UV – Visible spectra showing absorbance at different pH for neem (a), mango (b), lemon (c) and combination of all the three leaves (d).**



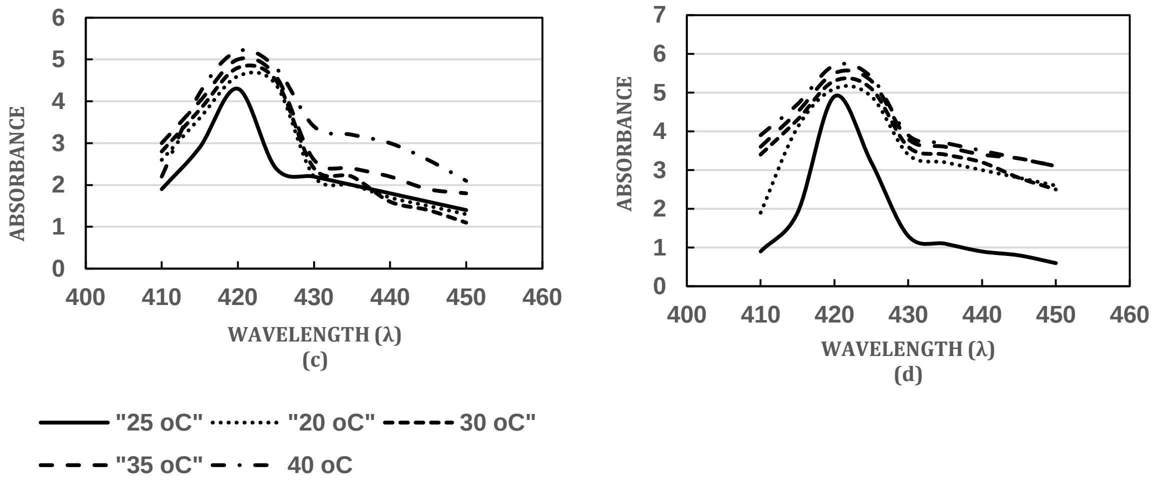



**Figure- 5: UV – Visible spectra showing absorbance at different temperature for neem (a), mango (b), lemon (c) and combination of all the three leaves (d).**

### 3.6 Characterization Studies for Silver Nanoparticles

The synthesis of silver nanoparticles using plants (neem, mango, lemon and combination of all the three leaves were analysed using UV – Visible spectrophotometer. Reaction solution was monitored at the regular interval of time and it showed the maximum absorbance peak at 420 nm and it is shown in Figure- 6, the silver nanoparticles were characterized using scanning electron micrograph (SEM). The results of SEM revels that the size of silver nanoparticles synthesised using neem, mango, lemon and combination of all the three leaves were 20, 100, 200, and 50 nm in size.

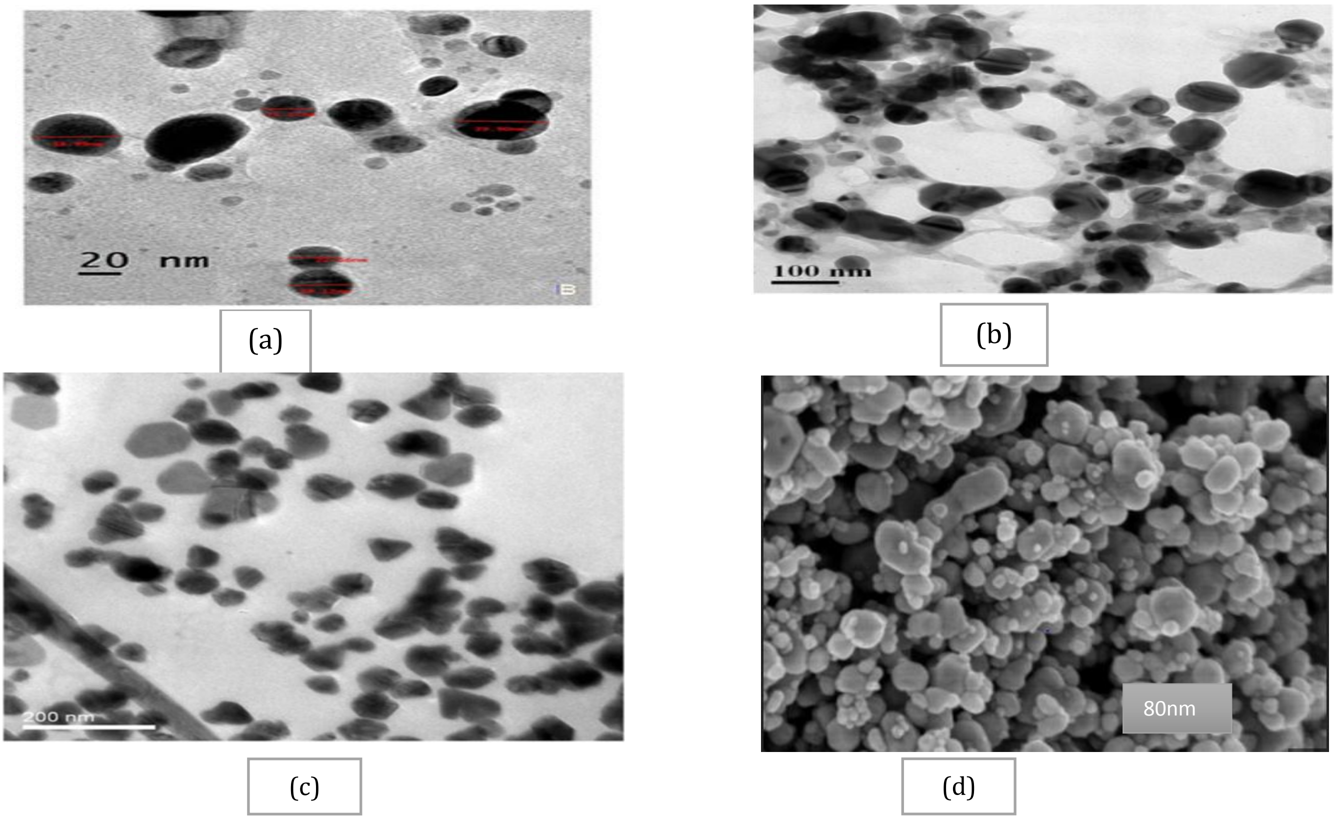



**Figure- 6: SEM images of silver nanoparticles synthesised by neem (a), mango (b), lemon (c) and combination of all the leaves (d)**

### 3.7 Antimicrobial Assay of Silver Nanoparticles Against E – Coli and S. aureus

Antimicrobial assay of biosynthesised silver nanoparticles was studied against E. coli and S. aureus bacteria using agar well diffusion method and zone of inhibition is depicted in figure- 7 and in Table- 1. Plant extract (neem, mango, lemon and combination of all the three leaves) and Silver nanoparticles was loaded into the wells with different concentrations of 20, 40, 60 and 80 micro litres respectively. The silver nanoparticles synthesised by using combination of neem, mango and lemon leaves showed the more antimicrobial activity towards both the bacteria than compare to the silver nanoparticles synthesised by using neem, mango and lemon leaves extract. On the other hand, plant extract alone did not show much antimicrobial activity this may be due to the medium extraction as well as lower concentration during experimentation (4). Thus, from the present research it is indicated that the silver nanoparticles is more effective towards both S. aeurus and E. coli bacteria because the silver nanoparticles not only interact with the surface membrane, but also penetrate inside the bacteria, and it also interact with the DNA of bacteria, preventing cell reproduction (6).

**Table- 1: Antimicrobial activity of synthesised silver nanoparticles.**

| | COMPONENTS | ZONE OF INHIBITION (cm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Gram positive (s. Aeurus) | | | | Gram negative (E. coli) | | | |
| | Dosage (µl/100µl) | 20 | 40 | 60 | 80 | 20 | 40 | 60 | 80 |
| NEEM | Plant extract | NZ | NZ | NZ | 0.9 | NZ | NZ | NZ | NZ |
| | AgNPs | 1 | 1.4 | 1.5 | 1.7 | 0.6 | 0.8 | 2.5 | 2.8 |
| MANGO | Plant extract | NZ | NZ | NZ | NZ | NZ | NZ | NZ | NZ |
| | AgNPs | 1 | 1.1 | 1.2 | 1.4 | 1 | 1.2 | 1.3 | 1.4 |
| LEMON | Plant extract | NZ | NZ | NZ | NZ | NZ | NZ | NZ | 0.9 |
| | AgNPs | 0.6 | 0.6 | 0.8 | 1 | 0.5 | 0.7 | 0.9 | 1 |
| COMBINATION ON ALL THE PLANTS | Plant extract | NZ | NZ | 1.0 | 1.1 | NZ | NZ | 1.0 | 1.1 |
| | AgNPs | 1.2 | 1.4 | 1.8 | 2.0 | 2.4 | 2.7 | 2.8 | 3 |

### 3.8 Effect of adsorbent dosage on the removal of colour

Adsorption efficiency is known to have been influenced by adsorption hence making the adsorbent dose play a vital role in the removal of colour (8). About one litre of wastewater was taken to which the dosage of adsorbent synthesised by neem, mango, lemon and combination of all the three leaves were added individually. The effect of dosage of adsorbent (neem, mango, lemon and combination of all the three leaves extract).on the removal of colour and COD from the textile mill wastewater is as shown in Figure- 7. The effect of adsorbent synthesised by neem leaves extract, the increase in the adsorbent efficiency of colour from 80% to 97 % with the increase in dosage of adsorbent from 0.5 to 1.4 g / 100 mL of wastewater, similarly the increase in adsorption efficiency from 70 % to 92 % was reported for the adsorbent dosage from 8 to 16 g/ 100 ml which was synthesised by using mango leaves extract. The results of effect dosage of adsorbent synthesised by lemon leaves extract shows that, the adsorption efficiency increased from 80 to 95 % with the increase in dosage from 7 to 16 g / 100mL of wastewater and the results of effect of dosage of adsorbent synthesised by using combination of all the three leaves shows that, the adsorption efficiency increased from 70 to 92 % when the dosage of adsorbent was increased from 1.2 to 1.4 g / 100mL of wastewater. In all the cases, as the dosage of adsorbent increased the removal of colour also removed this may be due to the available of surface area of the adsorbent (8).

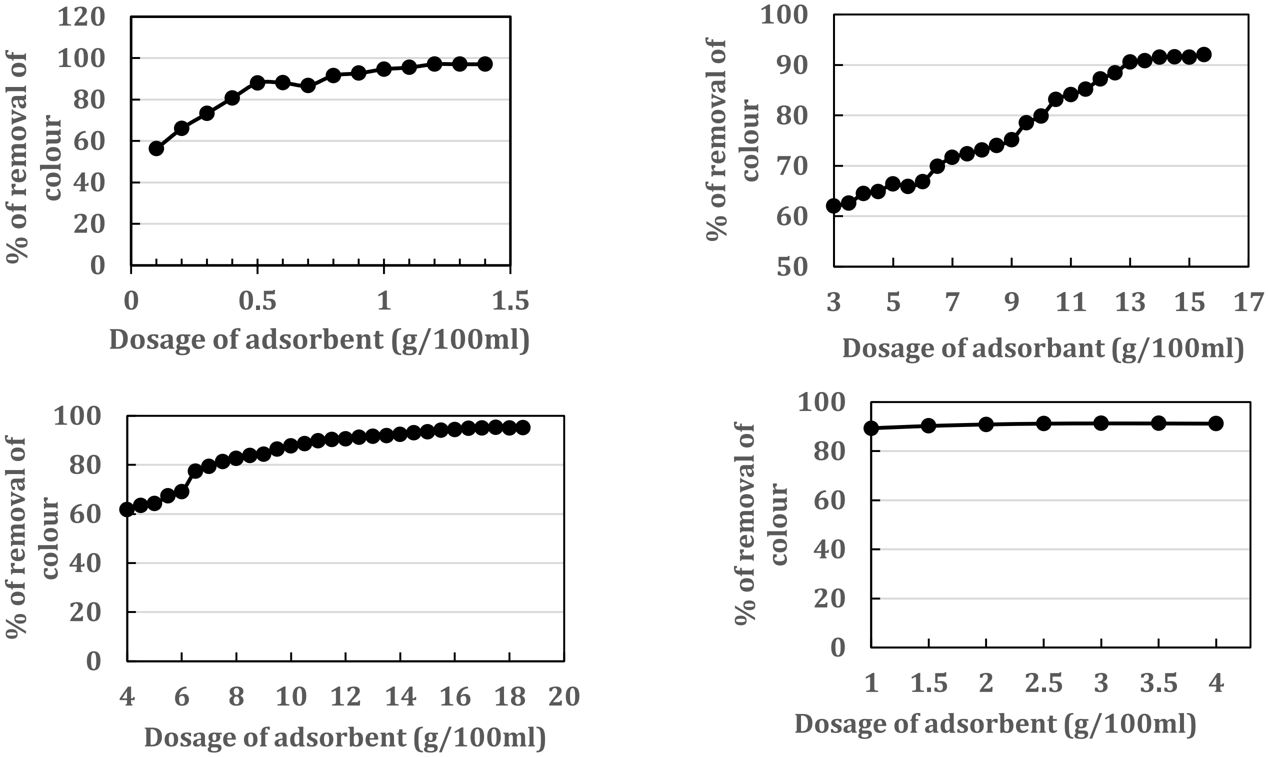



**Figure – 7: Effect of dosage of AgNPs synthesised by neem (a), mango (b), lemon (c) and combination of all the three leaves (d) extract on the removal of colour**

### 3.9 Effect of adsorbent dosage on the removal of COD

Adsorption efficiency is known to have been influenced by adsorption hence making the adsorbent dose play a vital role in the removal of COD (8). About one litre of wastewater was taken to which the dosage of adsorbent synthesised by neem, mango, lemon and combination of all the three leaves were added individually. The effect of dosage of adsorbent (neem, mango, lemon and combination of all the three leaves extract).on the removal of COD from the textile mill wastewater is as shown in Figure- 8. The effect of adsorbent synthesised by neem leaves extract shows that, the increase in the adsorption efficiency in the removal of COD from 30% to 42 % with the increase in dosage of adsorbent from 1.6 to 3.6 g / 100 mL of wastewater, similarly the increase in adsorption efficiency from 31 % to 45 % was reported for the adsorbent dosage from 7.5 to 13.5 g/ 100 ml which was synthesised by using mango leaves extract. The results of effect dosage of adsorbent synthesised by lemon leaves extract shows that, the adsorption efficiency increased from 34 to 50 % with the increase in dosage from 11 to 17 g / 100mL of wastewater and the results of effect of dosage of adsorbent synthesised by using combination of all the three leaves shows that, the adsorption efficiency increased from 35 to 42 % when the dosage of adsorbent was increased from 2.6 to 3.5 g / 100mL of wastewater. In all the cases, as the dosage of adsorbent increased the removal of COD also removed this may be due to the available of surface area of the adsorbent At the initial stages will be more and causes the removal of COD(8).

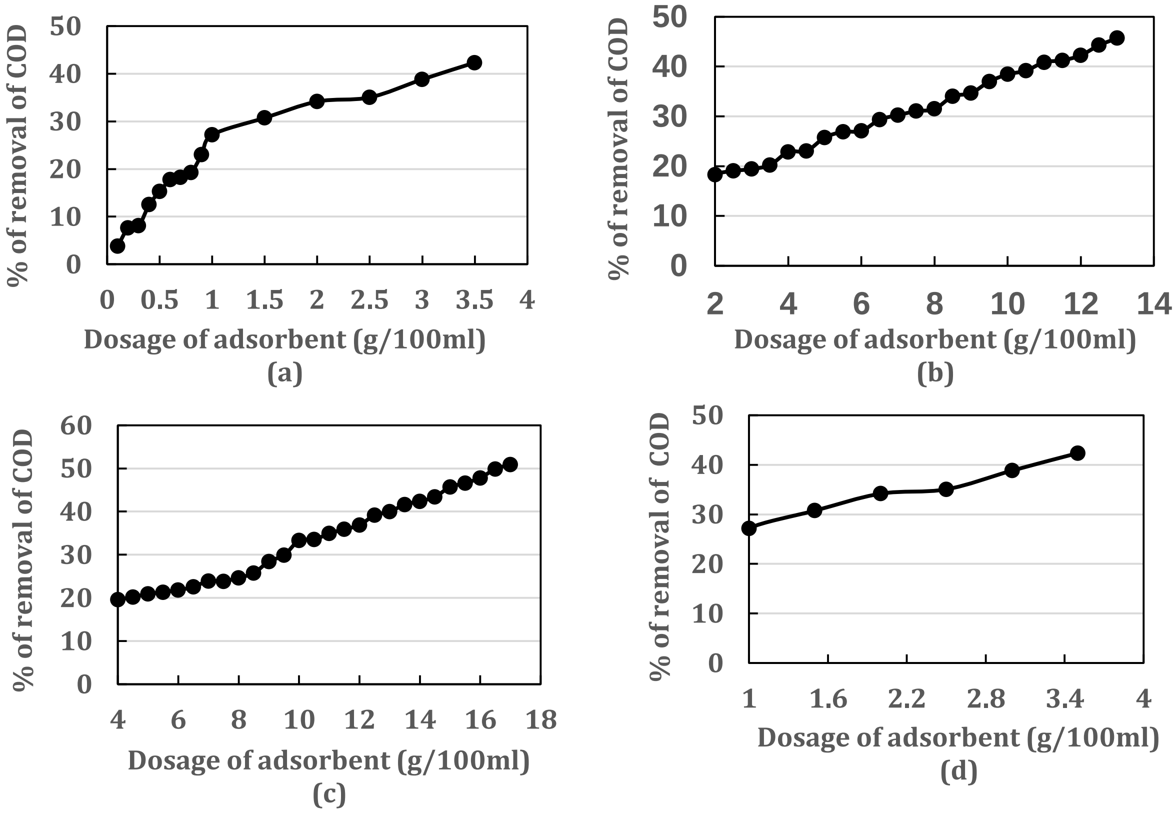



**Figure -8: Effect of dosage of AgNPs synthesised by neem (a), mango (b), lemon (c) and combination of all the three leaves (d) extract on the removal of COD.**

### 3.10 Effect of contact time on the removal of colour and COD

After the optimization of dosage of adsorbent, the experiment was conducted to know the effect of time of contact of adsorbent with the textile mill wastewater (Figure 9). About 1.5 g of AgNPs synthesised by neem plant leaves extract was added to 100ml of textile mill wastewater, results shows that as the time of contact increases the % of removal of colour and COD also increases. About 97 % of colour and 55 % COD was removed within 15 minutes. When 13 g / 100ml of AgNPs synthesised by mango leaves extract was added about 89 % colour and 47 % of COD was removed within 50 minutes. For the dosage of 16 g / 100ml of AgNPs synthesised by using lemon leaves extract there was a removal of 89 % of removal of colour and 47 % of removal of COD within 60 minutes and with the dosage of 4.5 g/ 100ml of AgNPs synthesised by combination of all the three leaves were added there was a removal of about 91 % of colour and 52 % of COD within 30 minutes.

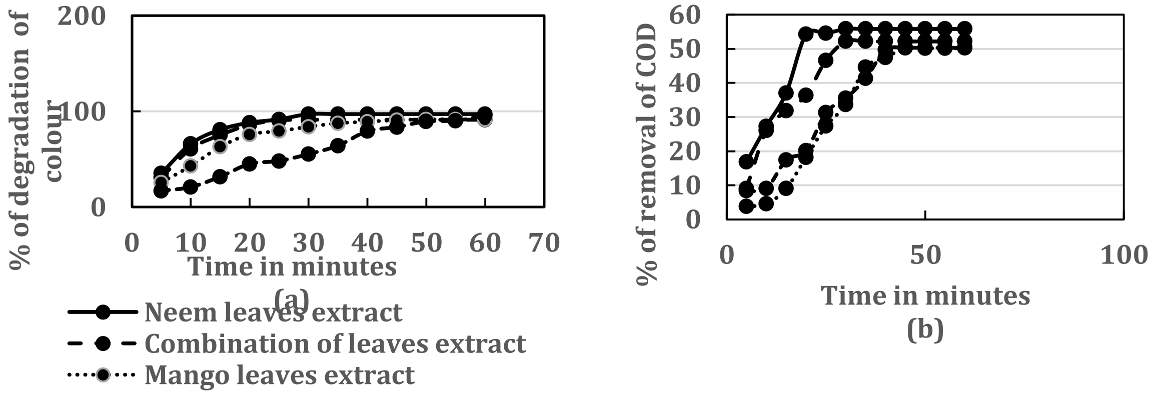



**Figure- 10: Effect of contact time on the removal of colour (a) and COD (b).**

### 3.11 Adsorption isotherms

The adsorption equilibrium isotherm plays a vital role in describing the distribution of adsorbate molecules in the liquid and solid phases when the adsorption process reaches equilibrium. The Langmuir and Freundlich model are commonly being used to describe the adsorption isotherm, and their constants afford significant parameters for predicting adsorption capacities. Recently other isotherms such as Temkin, Dubinin – Radushkevich (D – R), Redlich – Peterson have also been used to determine adsorption isotherm constants.

#### 3.11.1 Langmuir isotherm

The Langmuir isotherm necessitate monolayer adsorption onto a surface having a finite number of sites for adsorption via uniform strategies of adsorption with no transmigration of the adsorbate taking place along the plane of the surface. The well know expression of the Langmuir model is given in equation. (2).

$$qe = \frac{Q0\ b\ Ce}{1+b\ Ce} \qquad 2$$

The linear form of Langmuir's isotherm model is given in equation. (3).

$$\frac{Ce}{qe} = \frac{1}{Qo\ b} + \left(\frac{1}{Q0}\right) Ce \qquad 3$$

Where,

Ce - equilibrium concentration of the adsorbate (mg / L), $q_e$ – amount of adsorbate adsorbed per unit mass of adsorbate (mg / g), Qo and b – Langumir constants related to adsorption capacity and intensity of adsorption. When $C_e$ / $q_e$ was plotted against $C_e$, straight line with slope 1 / $Q_o$ was obtained.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter ($R_L$), which is defined by equation. (4)

$$RL = \frac{1}{1+b\ C0} \qquad 4$$

Where,

B - Langmuir constant, $C_o$ – highest dye concentration (mg / L). The value of $R_L$ indicates the type of the isotherm to be either (Unfavorable – ($R_L > 1$), Linear – ($R_L = 1$), Favorable – ($0 < R_L < 1$) or irreversible ($R_L = 0$)).

In the present study Langmuir isotherm plots of $C_e$ / $q_e$ versus $C_e$ for the removal of chemical oxygen demand present in the textile mill wastewater using silver nanoparticles as an adsorbent which has been synthesised from the various plants leaves extract have been depicted in Figure- 11. The values of Langmuir constant (b = 0.0012, 0.0010, 0.0008, 0.00094 and Qo = 16.477, 3.003, 0.443, 0.693) for AgNPs synthesised by neem, combination, mango, and lemon were calculated from isotherm and values are given in Table- 2. The value of $R_L$ for the adsorption of colour from textile mill Wastewater on silver nanoparticles was found to be 0.00518, 0.0363, 0.00432 and0.00732 indicating that the adsorption is favourable.

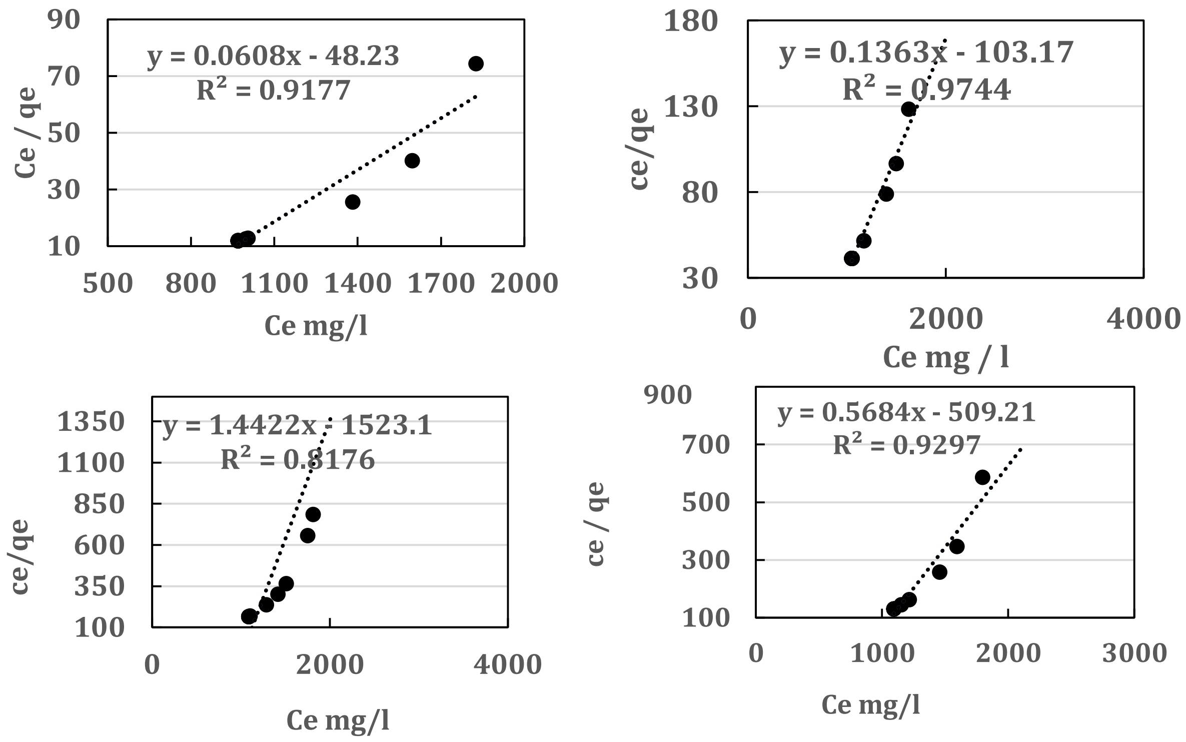



**Figure- 11: Langumir isotherm for the adsorption of dyes from textile mill using AgNps as adsorbent synthesised by neem (a), combination of all the three leaves (b), mango (c), and lemon (d) leaves extract.**

### 3.11.2 Freundlich isotherm

The Freundlich isotherm, on the other hand, assume heterogeneous surface energy for which the energy term in the Langmuir equation varies as a function of surface coverage. Freundlich equation is expressed as equation. (5).

$$qe = KF\ \ Ce^{\frac{1}{n}} \qquad 5$$

The well – know logarithmic form of Freundlich model is given by the equation. (6)

$$\log qe = \log KF + \left(\frac{1}{n}\right)\log Ce \qquad 6$$

Where, $q_e$ – amount adsorbed at equilibrium (mg / L), $C_e$ – equilibrium concentration of the adsorbate, $K_F$ and n Freundlich constants.

The value of n indicate how the adsorption process is favourable and $K_F$ (mg / g) (L / mg) is the capacity of the adsorbent. $K_F$ can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon adsorbent for a unit equilibrium concentration. The slope 1 / n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value 1 / n below one indicates a normal Langmuir isotherm while 1 / n above one is indicative of cooperative adsorption. The plot of log $q_e$ versus log $C_e$ gives straight lines with slope '1/n'.

Plots of ln $q_e$ versus ln $C_e$ were made for the adsorption of dye from textile mill wastewater on to silver nanoparticles are sown in Figure- 12. In the present study the value of $K_F$ and n were calculated and are presented in Table- 2. The results showed that the value of n is greater than unity for AgNPs synthesized by neem, combination, mango and lemon leaves extract (2.66, 3.20, 4.31, and 3.56), indicating adsorption if favourable on to silver nanoparticles. Similar adsorption results was reported by (9) on the adsorption of MB dye on dehydrated wheat bran carbon.

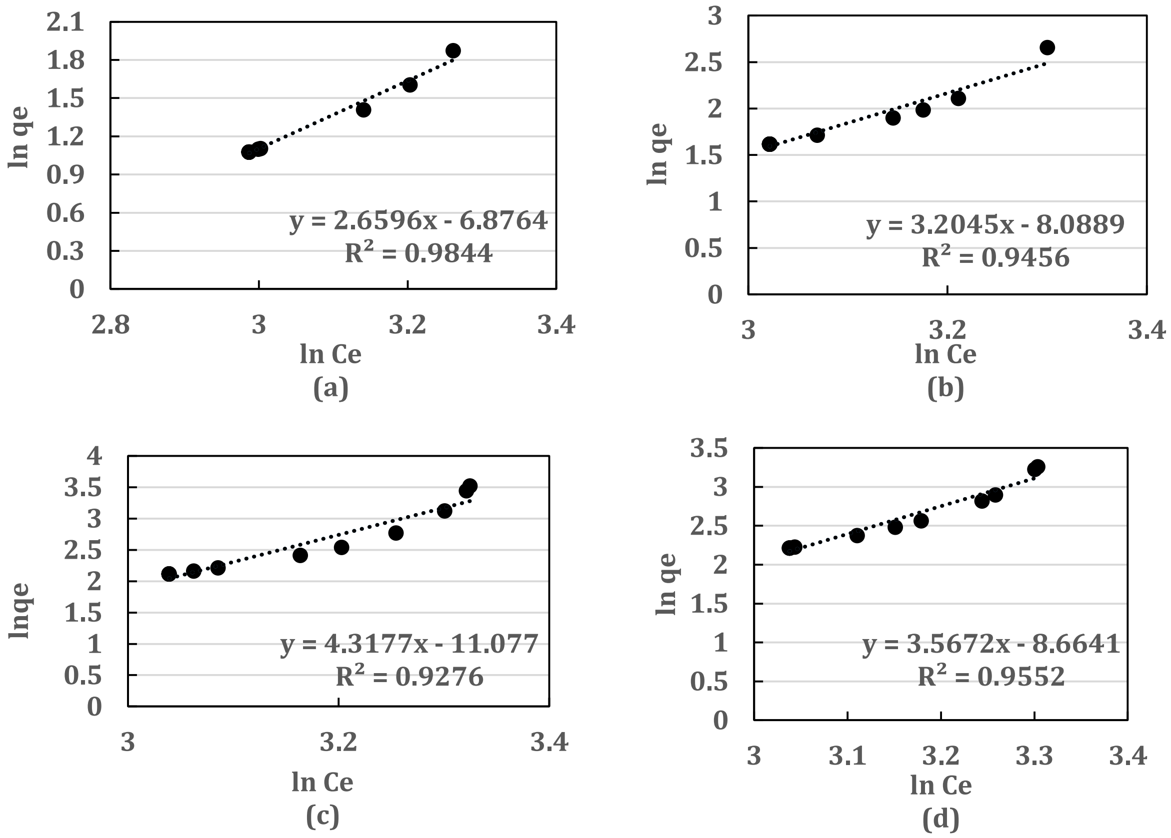



**Figure- 12: Freundlich isotherm for the adsorption of dyes from textile mill using AgNps as adsorbent synthesised by neem (a), combination of all the three leaves (b), mango (c), and lemon (d) leaves extract.**

### 3.11.3 Temkin isotherm

Temkin and Pyzhev considered the effect of the adsorbate interaction on adsorption and proposed the model known as Temkin isotherm, which can be expressed as equation. (7).

$$qe = B \ln(KT\ Ce) \qquad 7$$

Where, KT- equilibrium binding constant corresponding to the maximum binding energy, B – Related to the heat of adsorption, $q_e$ – experimental adsorption capacity (mg / g), $C_e$ – concentration of the adsorbent adsorbed at equilibrium position (mg / L)

$$B = \frac{RT}{b\mathrm{T}}$$

Where, 1/Bt – the adsorption potential of the adsorbent, R – Universal gas constant (8.314 j/mol), T – Temperature in kelvin (k). A plot of $q_e$ against $C_e$ at various temperatures of operation gave good curves. The interaction of adsorbte proposed by Temkin leads to linear decrease in heat of adsorption of molecules layer as adsorbate coverage progresses. It also talks about the uniform distribution of binding energies to certain level, which may be dependent strongly on the density and distribution of functional groups of both the dye and the adsorbent surface. Plots of $q_e$ against $C_e$ were made on the removal of dye from the textile mill wastewater using silver nanoparticles as an adsorbent is depicted in Figure- 13. Tempkin constants ($B_t$ = 28.768, 5.622, 0.757, 1.215 for neem, combination, mango and lemon respectively) were calculated for the removal of dye from textile mill wastewater and is depicted in Table- 2.

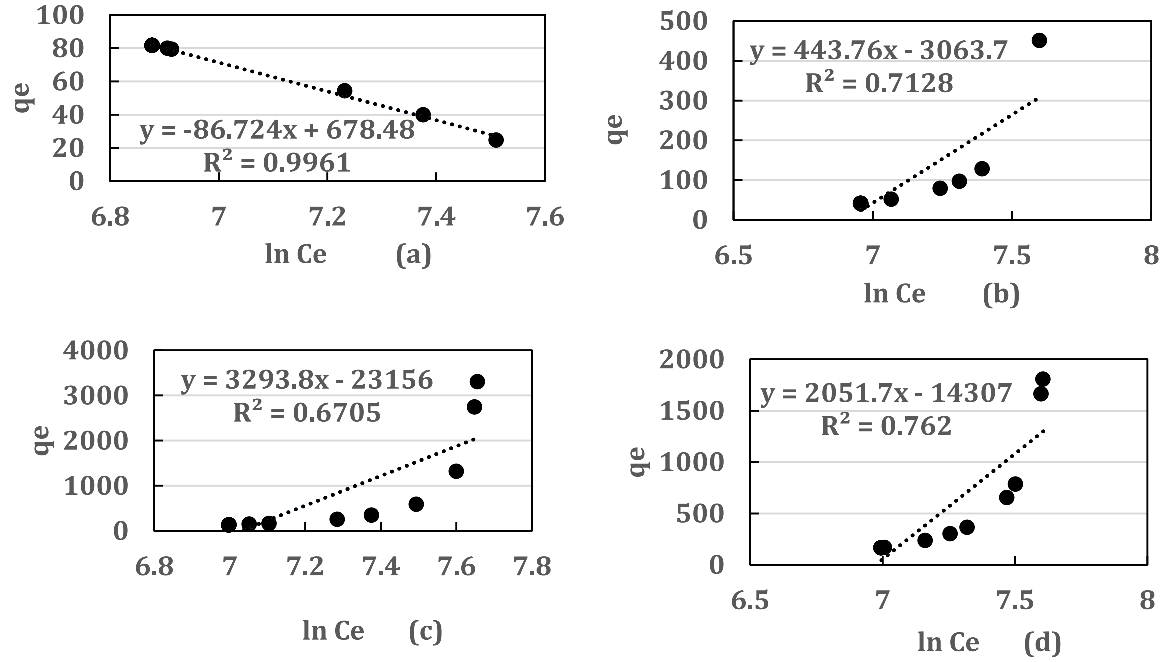



**Figure- 12: Freundlich isotherm for the adsorption of dyes from textile mill using AgNPs as adsorbent synthesised by neem (a), combination (b), mango (c), and lemon (d).**

### 3.11.4 Dubinin – Radushkevich isotherm

The Dubinin – Radushkevich model is used to estimate the characteristic porosity and the free energy of adsorption. It helps to determine the nature of adsorption processes whether physical or chemical. The D – R sorption is more general than Langmuir isotherm, as its derivation is not based on ideal assumptions such as equipotent of the sorption sites, absence of steric hindrances between sorbed and incoming particle and surface homogeneity on microscopic level. The non – linear presentation of the D – R isotherm cab be represented as in equation (8)

$$qe = qm\exp(-\beta\varepsilon^2) \qquad 8$$

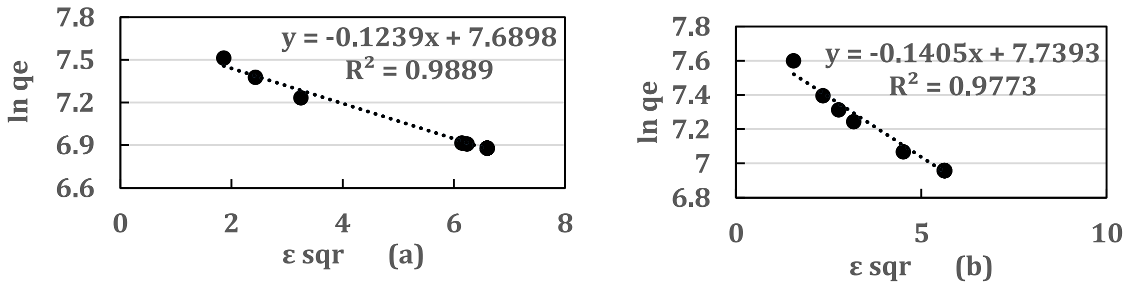
Where, $q_e$ – amount of dye molecules adsorbed on per unit weight of adsorbent (mol / L), $q_m$ – maximum adsorption capacity mol / g, β – Activity coefficient related to adsorption mean free, energy mol2 / J2, ε – Polanyi potential given in equation (9)

$$\varepsilon = RT\ln(1+\frac{1}{Ce}) \qquad 9$$

A plot of $q_e$ against $\varepsilon^2$ gave non – linear graphs. The adsorption mean free energy, E (KJ / mol) is given in equation (10).

$$E = \frac{1}{(2\beta)^{0.5}} \qquad 10$$

The mean free energy (E) of adsorption specifies the adsorption mechanism whether it's physical or chemical. Physical adsorption process occurs if the value of E < 8 KJ / mol while 8 < E < 16 KJ / mol describes chemical adsorption mechanism and results are shown in Figure- 14.



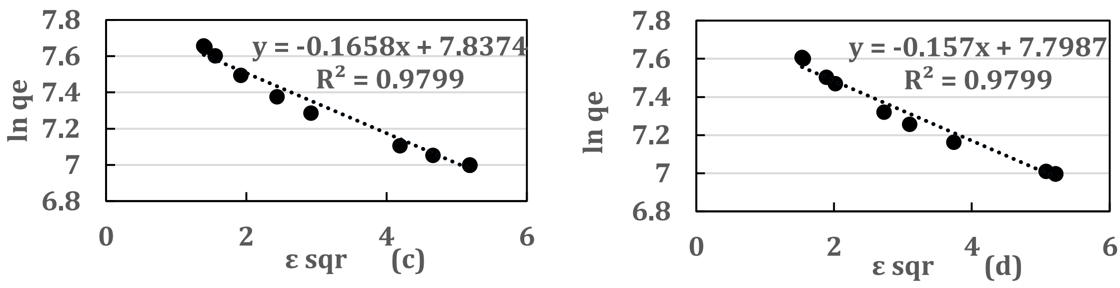



**Figure- 13: Dubinin isotherm for the adsorption of dyes from textile mill using AgNPs as adsorbent synthesised by neem (a), combination (b), mango (c), and lemon (d).**

**Table- 2: Isotherem parameters for adsorption of dyes from textile mill wastewater by using AgNps as adsorbent synthesised by neem, mango, lemon and combination of all leaves.**

| SL.NO | ISOTHERM | PARAMETERS | VALUES | | | |
|---|---|---|---|---|---|---|
| | | | NEEM | COMBINA | MANGO | LEMON |
| 1 | Langumir | Qm | 16.477 | 3.003 | 0.443 | 0.693 |
| | | b. | 0.0012 | 0.0010 | 0.0008 | 0.00094 |
| | | $R^2$ | 0.9176 | 0.7872 | 0.7282 | 0.8176 |
| 2 | Freundlich | $K_F$ | 969.13 | 3258.10 | 64666.59 | 5791.2 |
| | | 1/n | 2.6666 | 3.2045 | 4.31778 | 3.5676 |
| | | $R^2$ | 0.9844 | 0.9456 | 0.9276 | 0.9552 |
| 3 | Temkin | $B_t$ | 28.768 | 5.622 | 0.757 | 1.215 |
| | | $K_T$ | 66.73*10^6 | 80.15*10^6 | 10.17*10^6 | 9.40*10^6 |
| | | $R^2$ | 0.9961 | 0.7228 | 0.6705 | 0.7620 |
| 4 | Dubinin - Radushkevich | $Q_m$ | 48.88*10^6 | 54.86*10^6 | 68.77*10^6 | 62.90*10^6 |
| | | β | 0.1239 | 0.1405 | 0.1658 | 0.157 |
| | | E | 2.00 | 1.886 | 1.736 | 1.785 |
| | | $R^2$ | 0.9889 | 0.9773 | 0.9779 | 0.9799 |

Mean free energy E was found to be less that 8 KJ / mol (2.00, 1.886, 1.736, and 1.785 for neem, combination, mango and lemon leaves respectively) indicating physical adsorption process is taking place. Similar type of adsorption isotherm results by Igwe et al (2010) was reported in adsopton of acid – blue – 25 dye on to waste tea activated carbon and adsorption of BOD, TSS and colour on to boiler fly ash

### 3.11.5 Adsorption kinetics

Predicting the rate at which sorption takes place for a system is the most important factor for sorber design, with sorbate residence time and the reactor dimensions controlled by the systems kinetics. However, sorption kinetics results showed a large dependence on the physical and / or chemical characteristics of the sorbent material which also influences the sorption mechanism. The kinetics of the sorption process was studied using pseudo – second order kinetic models. The pseudo – first order as developed by Lagergren is given in equation (11) (Lagergren 1898)

$$\frac{dqt}{dt} = K_1\,(qe - qt) \qquad 11$$

Where, $q_e$ (mg / L) and $q_t$ (mg / g) are the adsorption capacity at equilibrium and at time t, respectively. $K_1$ – rate constant for pseudo – first order adsorption (per minute). Integrating equation (11) and applying the boundary conditions when t = 0 to t = t and $q_t$ = 0 to $q_t$ = $q_t$, results are given in equation (12)

$$log\,{}^{qe}\!/_{(qe - qt)} = K_1 \frac{t}{2.303} \qquad 12$$

This is the rate law for pseudo – first order reaction. Equation (12) can be rearranged to obtain a linear form given as equation. (13).

$$log(qe - qt) = \log qe - Ki/2.303 \qquad 13$$

Where the values of log ($q_e$ – $q_t$) are linearly correlated with t and a plot of log ($q_e$ – $q_t$) against t, gives a straight line. The best fit with respect to the pseudo – first order kinetic model K1 and $q_e$ can be determines from the slope and intercept of the plot respectively.

The pseudo – second order kinetic model is expressed as (HO and Mc Kay, 1998). (equation.14)

$$\frac{dqt}{dt} = K_2\,(qe - qt)^2 \qquad 14$$

Where, $K_2$ – rate constant for pseudo – second order model (g / mg – min)

Applying the boundary conditions, when t = 0 to t = t and $q_t$ = 0 to $q_t$ = $q_t$ the integrated form of equation. (15) becomes

$$\frac{1}{(qe - qt)} = \frac{1}{(qe + K2\,t)} \qquad 15$$

Equation. (15) Can be rearranged to obtain equation. (16) Which has a linear form as shown in equation. (16)

$$\frac{t}{qt} = \frac{1}{K2\,qe^2 + \frac{t}{qe}} \qquad 16$$

The initial adsorption rate h0 (mg / g / minute) is given in equation. (17).

$$ho = k2\,qe^2 \qquad 17$$

Then, equation. (16) and equation. (17) has been reduced to equation. (18).

$$\frac{t}{qt} = \frac{1}{ho} + \frac{t}{qe} \qquad 18$$

Equation. (18) was used to analyse the experiment data for the pseudo – second order kinetic model. A plot of (t / $q_t$) against (t) using equation. (18) was made which showed straight line, confirms the pseudo – second order kinetics model. $K_2$ and $q_e$ can be determined from the

intercept and slope of the plots, respectively. From Table- 3 and it was found that the correlation coefficients for the pseudo – first order model are low and a wide range of variations of the values of qe were recorded between the experimental and calculated. This indicates that the adsorption of dyes from textile mill wastewater on to adsorbent does not follow pseudo first – order kinetics. The qe, exp and the qe cal values along with correlation coefficients for the pseudo – second order models are also shown in Table- 3. The values of correlation coefficients were very high and the theoretical qe, cal values were closer to the experimental qe, exp values for the dye adsorption. It can be concluded that the pseudo second order adsorption kinetic model provides a good correlation (Figure – 15) for the adsorption of dyes from textile mill wastewater on to the adsorbents, when compared to pseudo – first – order model (Figure – 14). Various researchers have reported pseudo – second order kinetics for adsorption of methylene blue dye on pappya seeds (10), and bamboo based activated carbon (11).

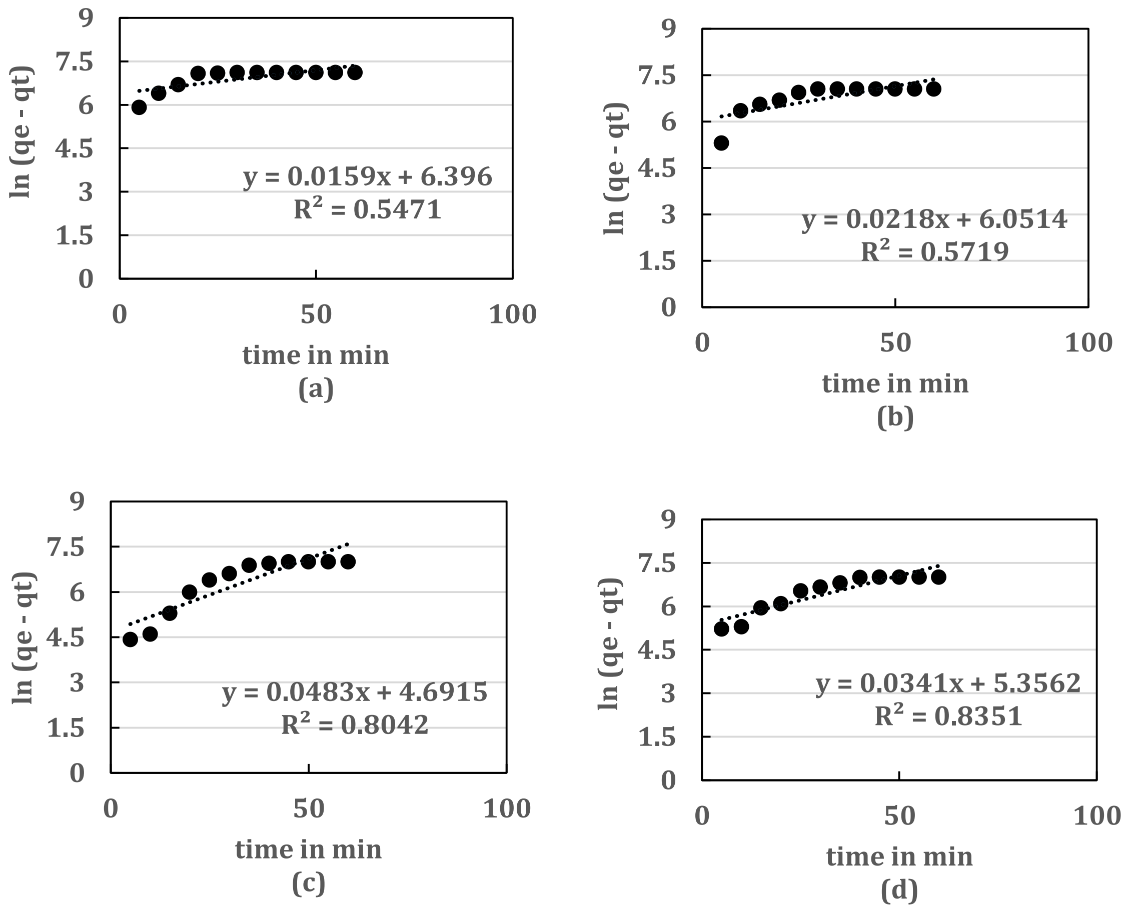
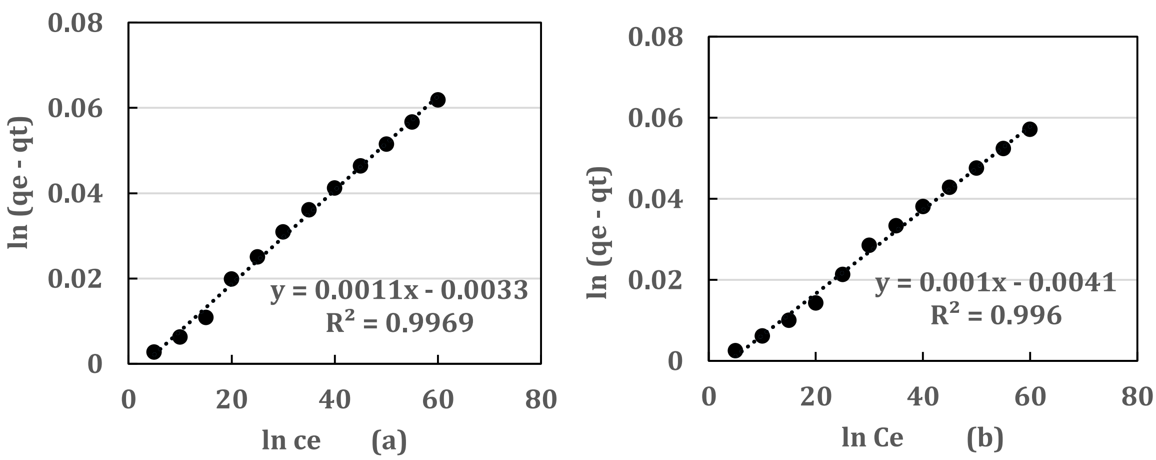



**Figure- 14: Pseudo – first order kinetics for adsorption of dyes on AgNPs as adsorbent synthesised by neem (a), combination (b), mango (c) and lemon (d) leaves extract.**



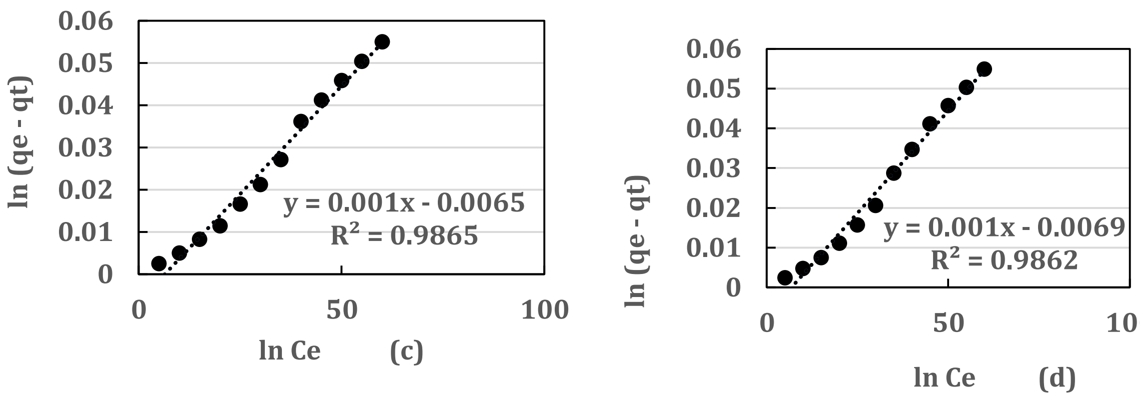



**Figure – 15: Second order kinetics for adsorption of dyes on AgNPs as adsorbent synthesised by neem (a), combination (b), mango (c) and lemon (d) leaves extract.**

**Table – 3: Pseudo first and second order adsorption rate constants values for the adsorption of dyes from textile mill wastewater using silver nanoparticles as adsorbent.**

| SL.NO | PLANT NAME | FIRST ORDER KINETICS | | | SECOND ORDER KINETICS | | |
|---|---|---|---|---|---|---|---|
| | | $K_1$ | $q_e$ | $R^2$ | $q_e$ | $K_2$ | $R^2$ |
| 1 | NEEM | 0.0159 | 24.8*10^5 | 0.5471 | 909.01 | 0.00036 | 0.9969 |
| 2 | COMBINATION | 0.0218 | 11.2*10^5 | 0.5719 | 1000.0 | 0.00024 | 0.9960 |
| 3 | MANGO | 0.0483 | 49.1*10^5 | 0.8042 | 1000.0 | 0.00014 | 0.9862 |
| 4 | LEMON | 0.0341 | 22.7*10^5 | 0.8351 | 1000.0 | 0.00015 | 0.9869 |

### 3.11.6 Intraparticle diffusion models

The sorption rate is known to be controlled by several factors including the following processes (Findon et al. (1993) and Weber and Digni, (1996); (i) diffusion of the solute from the solution to the film surrounding the particle, (ii) diffusion from the film to the particles surface (external diffusion), (iii) diffusion from the surface to the internal sites (surface diffusion or pore diffusion) and (iv) uptake which can involve several mechanisms; physicochemical sorption, ion – exchange, precipitation. Bulk diffusion (i) is non – limiting when agitation is sufficient to avoid concentration gradients in solution; sorption is seen as a quasi – instantaneous mechanism. External mass – transfer resistance (ii) and likely to be rate controlling. Ficks law may be describe mass transfer rates.

In most of the adsorption process the intraparticle mass transfer is the rate controlling, it means that the rate of sorption of the parameters may depend on particle diffusion. The rate of attainment to equilibrium may either due to film diffusion or particles diffusion, even though these two different mechanisms cannot be sharply demarcated. The fraction of solute adsorbed can be expressed in terms of the square root of time. A plot of fraction of solute adsorbed against t 0.5 may be used to estimate the interparticles rate in the linear range. This mathematical dependence of concentration in solid on t 0.5 has been deduced by considering the sorption mechanism to be controlled by diffusion in the sorbent and by convective diffusion in the solution. The solution of the diffusion equation leads to relationship between the concentration in the solid and the parameter $(D_t / a^2)^{0.5}$. D and a are considered as constant during the experiment; the concentration varies as a function of $t^{0.5}$ is represented by equation. (19).

$$q\ (t) = Xi + \ Kt^{0.5} \qquad 19$$

The slope of the linear part of the curve. The initial curve portion of the plot is attributed to boundary layer diffusion effects. The $K_p$ and C values can be determined from the slope and the intercept of linear plots, of q versus t ^ 0.5 is as shown Figure – 16. From the graph the constants $K_{id}$ (145.71, 162.69, 232.14, 205.53) and I (1927.7, 2140.5, 2749.2, 2559.0) were calculated and it is depicted in Table- 4. The intercept value reflects the importance of the boundary layer thickness, that is larger the intercept, the greater the thickness of the boundary layer. As can see from Figure the linear line did not pass through the origin and this deviation from the origin may be due to the difference in the mass transfer rate in the initial and final stages of adsorption. A similar results were reported for MB adsorption on to papaya seeds (11)

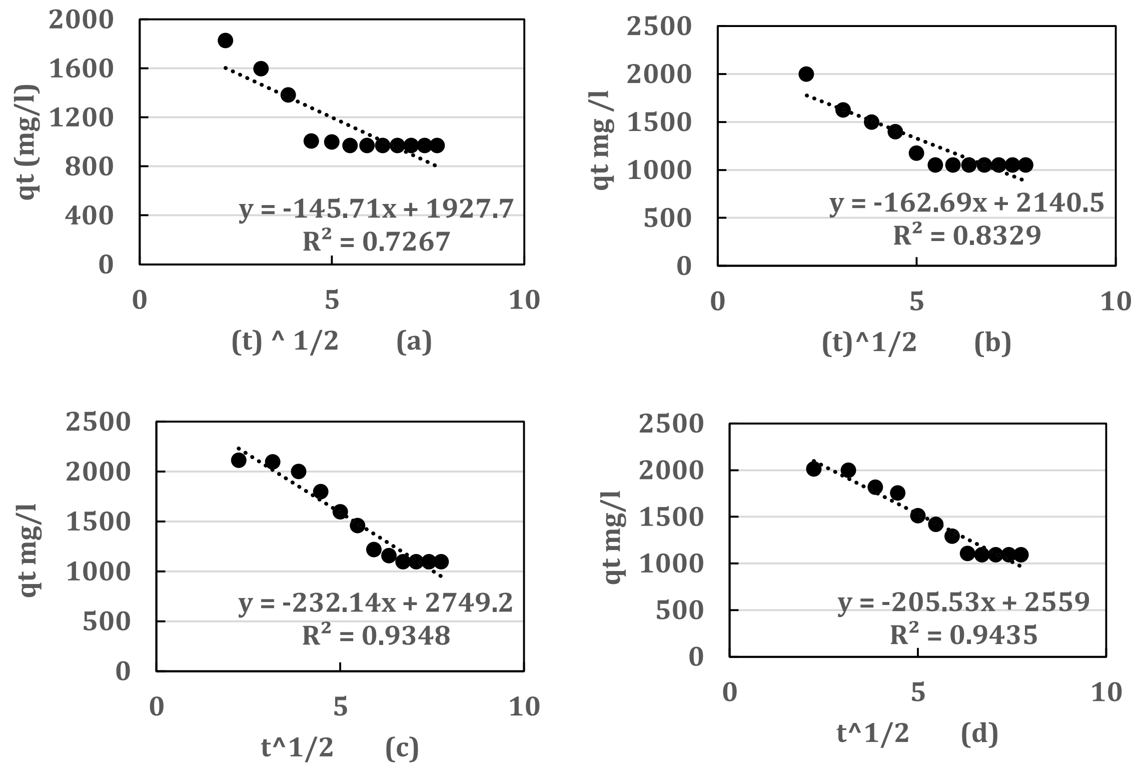


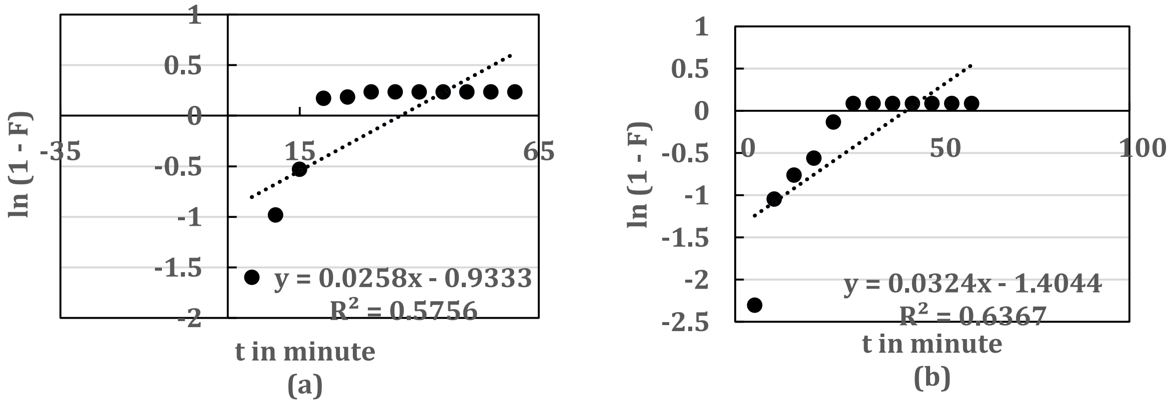

**Figure- 16: Intraparticles diffusion plot for adsorption of dye from textile mill wastewater using AgNPs as adsorbents synthesised by neem (a), combination (b), mango (c) and lemon (d) leaves extract.**

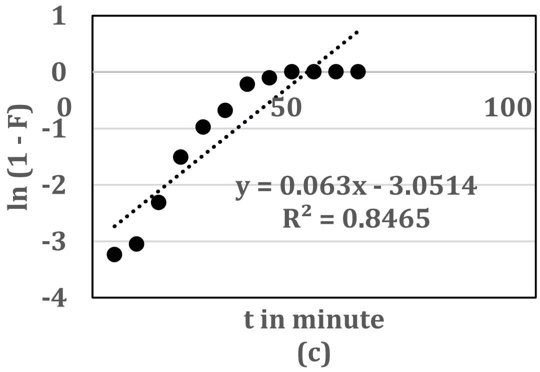
### 3.11.7 Liquid diffusion model

To investigate the transport of dyes to the solid phase boundary from the liquid phase, liquid film diffusion model was used in this study. The liquid film diffusion model was expressed as

$$\ln(1 - F) = k_{fd}\, t \qquad 20$$

For the adsorption system, the plots of ln (1-F) versus t were linear and if the straight line passes through the origin the liquid film is rate controlling step. From the Figure- 17, we can see that the straight line deviates from origin which is due to difference between the rate of mass transfer in the initial and final steps of adsorption. From the graph the constants were calculated and it is depicited in Table- 4.





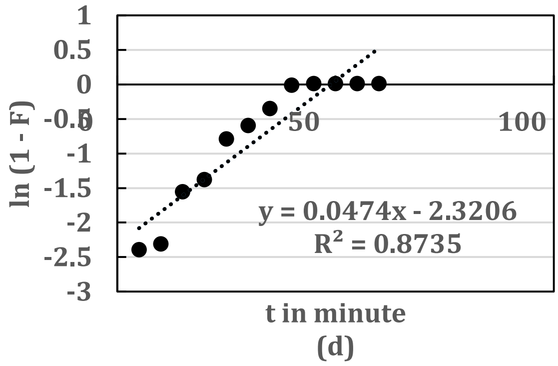




**Figure- 17: Liquid diffusion plot for adsorption of dye from textile mill wastewater using AgNPs as adsorbent synthesised by neem (a), combination (b), mango (c) and lemon (d) leaves extract.**

**Table 4.4: Intraparticle and liquid diffusion model for the removal of dye from textile mill wastewater using silver nanoparticles as adsorbent**

| PLANT NAME | PARTICAL DIFFUSION MODEL | | | LIQUID DIFFUSION MODEL | | |
|---|---|---|---|---|---|---|
| | $K_{id}$ | I | $R^2$ | $K^2$ | C | $R^2$ |
| **NEEM** | 145.71 | 1927.7 | 0.7267 | 0.0258 | 0 | 0.5756 |
| **COMBINATION** | 162.69 | 2140.5 | 0.8329 | 0.0324 | 0 | 0.6367 |
| **MANGO** | 232.14 | 2749.2 | 0.9348 | 0.0630 | 0 | 0.8466 |
| **LEMON** | 205.53 | 2559.0 | 0.9435 | 0.0474 | 0 | 0.87352 |

## Conclusion

The silver nanoparticles synthesised by neem, mango, lemon and combination of all the leaves could able to remove 97, 92, 91, 93 % of colour and 49, 47, 46, and 43 % of COD from the textile mill wastewater respectively within a time period of 15, 50, 60 and 30 minutes. Various isotherms and kinetics were applied to know the capacity and intensity of adsorbents out of which Freundlich isotherm was found to be the best fit for the silver nanoparticles which were used for the removal of colour and COD from textile mill wastewater. Pseudo – second order kinetics provided a good correlation for the adsorption of dyes and COD from textile mill wastewater using silver nanoparticles as an adsorbent. The plots of Dubinin – Radushkevich isotherm it is indicated that the adsorption is physical adsorption and Liquid diffusion model holds good or rate controlling step for the adsorption of colour from textile mill wastewater. The synthesised silver nanoparticles showed effective antimicrobial activity against bacteria like *Esecherisia – coli* (gram negative) and *Streptococcus* (gram positive).

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