

# PURIFICATION OF FLUORIDE-CONTAMINATED WATER USING SILVER NANOPARTICLES SYNTHESIZED BY VITIS VINIFERA FRUIT EXTRACT

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**ABSTRACT:** Providing drinking water with the correct amount of fluoride protects the teeth from decay and decreases the possibility of cavities. Fluoride concentrations exceeding 1.5 mg/l in drinking water can lead to various health effects, such as bone deformation, tooth decay etc. The objective of this research was to synthesize silver nanoparticles in a non-polluting method (Green synthesis) using grape fruit extract as reducing and stabilizing agent and to evaluate its fluoride ion adsorption potential. The evaluation of percentage removal of fluoride was done by optimizing parameters. The synthesized silver nanoparticles showed surface plasma resonance at 452 nm. The presence of silver nanoparticles was confirmed using Scanning electron microscopy and dynamic light scattering analysis. The unknown fluoride concentration in water was measured from standard graph which was obtained by using zirconium SPADNS solution as new spectrophotometric reagent. From experimental results the maximum complexation of the fluoride ions with silver nanoparticles was 67.3% which was observed at optimum conditions of dosage 0.7 g/l, initial concentration 2 ppm or 2 mg/l, pH 6 and temperature 70°C. Adsorption isotherms namely Freundlich, Langmuir and Temkin models are used to establish equilibrium isotherms. From experiments it was discovered that adsorption equilibrium data correlate well with Freundlich isotherm model. Pseudo first order, Pseudo second order, and Elovich kinetic models were also studied and when comparing the experimental data pseudo second order kinetic model provided a stronger correlation. The efficiency of the treatment decreased when the fluoride concentration increased above 2  $\mu\text{g mL}^{-1}$ .

**Key words:** Nano adsorbent, Vitis Vinifera, Green synthesis of nanoparticles, Estimation of fluoride ion concentration

## 1) INTRODUCTION:

The major challenging problem in recent times is dealing with environmental pollution. The chemical composition of water depends primarily on residential, commercial, and agricultural use. 0.6% of the total water resources is covered with the ground water which is suitable for drinking in rural and urban areas in India. But in the current days ground water is getting polluted by the urbanization and industrialisation. The major pollutants

are hydrocarbons, heavy metals like nickel, fluorides, and nitrates etc. which are effecting the human health. As a pollutant found in groundwater, fluoride poses a major drinking water supply problem. This occurs either as inorganic fluorides or compounds of organic fluoride. Fluorinated compounds are widely used in industry for different purposes. Fluorinated compounds were also used in aluminium production and released in the production of tiles, ceramics, and bricks in kilns. Phosphate fertilizers contain around 3.8% of fluorine. Municipal water fluoridation also uses fluorosilicic acid, sodium fluoride, and sodium hexa fluorosilicate [1, 2]. Fluoride could be toxic to plants, animals and may occur with airborne fluoride contamination or high levels of fluoride in ground water. Normal baseline air concentrations are in the range of 0.5 ng/m<sup>3</sup>. If the anthropogenic emissions were also included in it the global background fluorine concentration would be 3 ng/m<sup>3</sup> [4]. Due to the indoor combustion of high fluoride coal which was used for cooking, the concentration of Chinese fluoride in the indoor air ranged from 16 to 46  $\mu\text{g/m}^3$  [5]. A total concentration of 1.3 mg/l of fluoride was recorded in seawater [4]. The highest recorded natural fluoride level is 2800 mg/l in Tanzania. [4]. Due to change in environmental conditions the traces of fluoride present in the minerals gets mixed with lakes and rivers result in increase in fluoride concentration. In ground water fluoride concentration will vary depending on type of rock through which the water flows, normally it will not exceed 10 mg/l [US EPA 1985] [3]. Almost all the food products typically contain small amounts of fluorine, such as fish and fruits, etc., which is extracted from soil and water. Highest levels of field-grown vegetables were found in curly kale (about 40 mg/kg fresh weight) [4]. Approximately 0.2% of the population in USA are exposed to more than 2.0 mgL<sup>-1</sup> of fluoride in drinking water [3]. The fluoride content in the drinking water in some of the African countries could be high due to the presence of fluoride-enriched minerals in soil [3]. An analysis of underground boreholes in Central Australia showed that half of the water samples had fluoride levels above 1.5 mgL<sup>-1</sup>, with a range of 3–9 mgL<sup>-1</sup>[6]. The most important natural fluorine-bearing minerals that are a source of fluoride in drinking water are fluoride, apatite, rock phosphate and topaz igneous and sedimentary stones. Milk is usually responsible for the exposure of fluoride in small quantities. Fluoride is observed in the range of 0.04 mg to 2.7 mg per person per day was recorded as a

consequence of the tea consumption. The presence of alkaline soil near fluoride contaminated water sources is an excellent characteristic for the fluoride. The main sources of fluoride can be broadly divided into two categories of natural and anthropogenic sources. Natural sources mainly comprise of forage grasses, grains, water and volcanic activities. Anthropogenic sources mainly comprises of Mineral Mixture and Other Feed Supplements, Airborne Fluoride, Industrial Effluents, Agrochemicals and Household Products. Fluoride has a severe impact on human health for a long time usage. Several investigators have reviewed the fact that prolonged use of fluoride for a long time results in life-long impact which causes human skeletal and dental damage, as well as changes in DNA structure, volition paralysis, cancer. Prolonged use of fluorine may result in pain in joints, shoulder and knee and it also cause nausea, pain in stomach [7]. The increase in fluoride intake, will have an impact on the bone density, urine and hair of the human being. So the removal of fluorine in drinking water is very important. Maintaining the fluoride content in permissible limit in the water is equally important because the fluorine prevents tooth decay and bone deformation [8]. According to WHO the allowable limit of fluoride concentration is 1.5 mg/L [9]. In India, the maximum allowable for fluoride in potable water is 1 ppm [10]. While there are many organizations which prescribed the permissible limits for fluoride for example US Public health standards advised that the allowable limit of fluoride must be around 0.7 mg/L and the permissible limit prescribed by ICMR is 1.0 mg/L. While BIS imposed a limit of 0.6-1.2 [11]. There are different methods used for removal of fluorine like electro dialysis, reverse osmosis, ion exchange process, precipitation, coagulation and adsorption process. Each process has their own advantages and disadvantages. Out of all process used for removal of fluoride Adsorption process fits best. From various observations like due to poor adsorption capacities, extremely low or high pH and high adsorbent dosage are some of the drawbacks of adsorption process. Now a days several modified adsorbents are using for adsorption process the adsorbent is converted into Nano sized particles to provide more surface area. The adsorbent which was used for this work were silver nanoparticles. There are different conventional methods used for silver nanoparticles synthesis they are polyphenol method, micro emulsions, thermal decomposition, electrochemical synthesis, plasma method, chemical vapor deposition, micro wave irradiation, pulsed laser method, sono chemical reduction, and gamma radiation. These can cause a severe impact to environment. The aim of this research is to synthesize silver nanoparticles in a non-polluting technique in order to use green synthesis for silver nanoparticles synthesis. In general, green synthesis is a bottom-up technique analogous to chemical reduction, in which a costly chemical is substituted with an extract of a natural commodity such as tree leaves,

crops, or fruits for nanoparticle synthesis. The aim of Green Synthesis is to minimize the waste generated and to implement sustainable processes. Green synthesis methods are required to avoid the production of unwanted and harmful products. This desirable green synthesis techniques are free of the shortfalls that come with standard strategies. Green synthesis is a fast, energy-efficient, environmentally safe, and cost-effective way to make silver nanoparticles at room temperature. The physical methods that do not require dangerous solvents, reduce contamination and speed up the synthesis process are green synthesis methods. In the development of nanotechnology to promote environmental conservation, green synthesis methods are using mild reaction conditions and non-toxic precursors have been emphasised in recent years. In conventional method for preparation of silver nanoparticles we use different hazardous solvents as a reducing agents. Where as in green synthesis method we use plant extracts and fruit extracts as a reducing agents. In plant extracts and fruit extracts there are different phytochemicals like ascorbic acid, peroxide catalyse etc. which are responsible for reducing to nanoparticles. In this research Vitis Vinifera (grapes) were used as a bio template. The below table represent the phytochemical composition in vitis vinifera (Thomson seedless) variety

**Table 1.1: Antioxidant radical scavenging activity in vitis vinifera (Thomson seedless) [12]**

S no	Phyto chemical	Presence(+) Absent(-)	Phyto chemical composition
1	FRAP(Ferric Reducing Antioxidant Power)	+	26.6±0.173 µM/g dry wt
2	ABTS(Trolox equivalent oxidant capacity assay)[Inhibition]	+	9.1±0.11 %
3	DPPH(Scavenging activity method)[Inhibition]	+	9.0±0.11 %

**Table 1.2: Ascorbic acid, Antho cyanine and transversal content in vitis vinifera (Thomson seedless) [12]**

S no	Phyto chemical	Presence(+) Absence(-)	Phyto chemical composition
1	Ascorbic acid	+	0.03±0.07 %
2	Anthocyanine	+	1.3±0.004 %
3	Transversal content	-	0 %

**Table 1.3: Antioxidant enzyme activity in vitis vinifera (Thomson seedless) [12]**

S no	Phyto chemical	Presence(+) Absent(-)	Phyto chemical composition
1	Catalyse	+	0.53±0.03 U/g Fr wt
2	Peroxidase	+	0.02±0.01 U/g Fr wt
3	Polyphenoly oxidase	+	0.26±0.01 U/g Fr wt
4	Gluthathionine reductase	+	0.03±0.01 U/g Fr wt

## 2) Methodology:

### 2.1) Estimation of fluoride ion concentration:

The method which was used for the determination of fluoride ion concentration in aqueous solution is the SPADNS- Spectrophotometric Method. The spectrophotometric method of SPADNS is based on the reaction between the fluoride and the zirconium dye. Fluoride reacts with the zirconium dye, breaking it into a colourless anion complex ( $ZrF_6^{2-}$ ) and the dye. The colour produced becomes lighter as the amount of fluoride increases [22]. The acidity of the reaction mixture has a major effect on the rate of reaction between fluoride and zirconium ions. The reaction will be nearly instantaneous if the proportion of acid in the reagent is raised. Maintaining a steady temperature during the colour production process is important to produce better performance. The graph is drawn between absorbance and known fluoride ion concentration and from the graph we can determine the unknown fluoride ion concentration.

### 2.2) Green synthesis of silver nanoparticles (AgNPs):

AgNPs were prepared from standard procedure [13]. Firstly the grapes were brought from the market and they are cleaned with distilled water. Crush the grapes finely and then remove the skin of the grapes and subject the remaining extract to centrifugation process. Centrifuge the fruit extract for 15 min at 4500 rpm [13] then filter the extract using whattman filter paper and separate the filtrate. Meanwhile prepare 30 millimole of silver nitrate solution and add fruit extract drop by drop to the silver nitrate solution in 1:1 ratio. Then keep the solution in the dark place for 72 hours. Then the solution turns to dark brown [13] in colour results in

formation of silver nanoparticles. Now again centrifuge the solution for 12 hours at 4500 rpm. After centrifugation process a small pellet will settle down in the centrifuge tube. Then wash the pellet with distilled water for three times and filter the solution and subject the solid residue to hot air oven for 20 minutes and collect the nanoparticles.

### 2.3) Preparation of samples:

- **Stock fluoride solution.**  
221.0mg anhydrous sodium fluoride was dissolved in distilled water and made up to 1000 ml in a volumetric flask; 1 ml = 100µg F
- **Standard fluoride solution.**  
100 ml stock fluoride solution was diluted to 1000 ml with distilled water and stored in a volumetric flask; 1 ml = 10µgF
- **SPADNS solution:**  
958mg SPADNS reagent was dissolved in distilled water and diluted to 500 ml [22].
- **Zirconyl-acid reagent:**  
133 mg  $ZrOCl_2 \cdot 8H_2O$ , was dissolved in 25 ml distilled water and 350 ml concentration HCl was added and diluted to 500 ml [22].
- **Mixed acid zirconyl-SPADNS reagent:**  
SPADNS solution and zirconyl- acid reagent were mixed in 1:1 ratio of volumes and stored in a volumetric flask with lid which is stable for 2 years [22].
- **Reference solution:**  
10 ml of SPADNS solution has been added to 100 ml of distilled water. 7 ml of HCl concentration has been diluted to 10 ml with distilled water and added to the SPADNS solution, which is stable for 1 year. With this Solution, the UV-Vis spectroscopy is set to zero [22].

### 2.4) OPTIMIZING PARAMETERS:

#### 2.4.1) Effect of contact time:

150 ml of fluoride solution having 6 mg/lit concentration was taken in 250 ml capacity of Erlenmeyer flask. 0.5 gm/lit of adsorbent dosage was added to Erlenmeyer flask and the solution has pH 5. Then keep the Erlenmeyer flask in the orbital shaker and agitated at 100 rpm for 230 min and 5 ml samples were collected for every 10 minutes interval. The residual Fluoride concentrations were observed using UV visible spectrophotometer at 570 nm [14]. The contact time at which maximum Fluoride adsorbed was recorded and it was used for studying further parameters.

#### 2.4.2) Effect of initial concentration:

50 ml of fluoride solution having different level of concentration varying from 2 mg/lit to 10 mg/lit was taken in 5 numbers of 250 ml capacity of Erlenmeyer flask. 0.5 gm/lit of silver nanoparticle pouch was added to each flask and was kept in orbital shaker, agitated at 100 rpm at optimum contact time. After the completion of optimum contact time the orbital shaker was turned off, the flasks were removed and samples were filtered and the residual fluoride concentrations were observed in UV Visible spectrophotometer at 570 nm [14]. The maximum fluoride adsorbed was recorded.

#### 2.4.3) Effect of adsorbent dosage:

50 ml of fluoride solution having 2 mg/lit concentration was taken in 6 numbers of 250 ml capacity Erlenmeyer flask. Silver nanoparticles were added in each flask at various dosage levels ranging from 0.1 gm/lit to 1.0 gm/lit and all flasks were agitated in an orbital shaker at optimized contact time (Obtained from above observations) at 100 rpm. The residual fluoride concentrations were observed in UV Visible spectrophotometer at 570 nm [14]. The maximum fluoride adsorbed was recorded.

#### 2.4.4) Effect of pH:

50 ml of fluoride solution having 2 mg/lit concentration was taken in 5 numbers of 250 ml capacity Erlenmeyer flask. The pH of fluoride solutions were studied at 2, 4, 6, 8, 10 using 0.1 N HCl and 0.1 N NaOH solution. The optimum dosage of silver nanoparticles that was observed were added to all Erlenmeyer flasks and the contents were agitated in orbital shaker with 100 rpm for optimum contact time. After the optimum contact time the orbital shaker was turned off and the residual fluoride concentrations were measured using UV Visible spectrophotometer 570nm [14]. The optimum pH at which maximum fluoride adsorbed was further used to study the effect of temperature.

#### 2.4.5) Effect of temperature:

50 ml of fluoride solution having 2 mg/lit concentration was taken in 6 numbers of 250 ml of capacity Erlenmeyer flask. At optimum values the effect of temperature (30, 40, 50, 60, 70 and 80°C) was studied and the contents were agitated in orbital shaker. At optimum conditions the sample was taken and the residual concentration was measured in UV Visible spectrophotometer at 570 nm [14]. The maximum fluoride adsorbed was recorded.

#### 2.5) Adsorption isotherms:

Adsorption isotherms namely Langmuir isotherm, Freundlich isotherms, Temkin isotherms were studied.

#### 2.6) Adsorption kinetics:

Adsorption kinetics namely Pseudo first order, Pseudo second order and elovich kinetic models are studied in the Experiment.

### 3) Results and discussion:

#### 3.1) Fluoride determination:

The experiment which was used for determination of fluoride ion concentration was SPADNS calorimetry method. In this experiment a water containing fluoride ion (colourless) is made to react red coloured (zr-spadns) complex. The fluoride ion forms a colourless complex with zirconyl  $ZrO_2^+$  ion as  $[ZrF_6]^{2-}$ , leaving behind yellow colour SPADNS. This decrease in red colour and increase in yellow colour due to free SPADNS and the conversion of solution from red to yellow colour is known as bleaching action. By measuring the SPADNS colour (570 nm) using spectrometer the amount of fluoride ion in water can be determined by using beer lamberts law [14].

Beer lamberts law

$$A \propto Cl$$

$$A = \epsilon cl$$

Where A= Absorbance of solution

C= Concentration of the coloured solution

l = Thickness of coloured solution = (m /Ad) [Dmitry Zaitsev weight difference method]

$\epsilon$  = Proportionality constant

Keeping  $\epsilon$  as constant (keeping thickness of the solution as constant) we can determine the Concentration of fluoride by measuring absorbance of the solution. The standard curve for the determination of the fluoride was drawn between absorbance and known fluoride ion concentration. From the graph we can determine the unknown fluoride ion concentration. The linear calibration curve gave the following linearized equation.

$$Y = (-0.0191 x) + 0.5209$$

$$R^2 = 0.9981$$

#### 3.2) Green Synthesis of silver nanoparticles:

Firstly the grapes were brought from the market and they are cleaned with distilled water for 2 times then crush the grapes with hand. Now remove the skin of the grapes and subject the remaining extract to

centrifugation process. Centrifuge the fruit extract for 15 min at 4500 rpm [13] then filter the extract using whatman filter paper and separate the filtrate. Meanwhile prepare 30 milli mole of silver nitrate solution and add fruit extract drop by drop to the silver nitrate solution in 1:1 ratio. Then keep the solution in the dark place for 72 hours. Then the solution turns to dark brown [13] in colour results in formation of silver nanoparticles. Now again centrifuge the solution for 12 hours at 4500 rpm. After centrifugation process a small pellet will settle down in the centrifuge tube. Then wash the pellet with distilled water for 3 times and filter the solution and subject the solid residue to hot air oven for 20 minutes and collect the nanoparticles. In this way silver nanoparticles are prepared through a non-polluting method called green synthesis

### 3.3) Characterization of silver Nano particles:

#### 3.3.1) UV-Visible Spectra for AgNPs Synthesis:

Fig 3.3.1 represent UV spectroscopy result for grape fruit extract. The generation of silver nanoparticles by the reduction of silver ions due to the addition of grape fruit extract (*Vitis vinifera*) was proceeded by UV-Vis spectroscopy. The visible UV spectra for AgNPs ranged from 300 to 600 nm. The high optical density of the silver nanoparticle solution was observed to be close to 452 nm during the experimental duration as the nanoparticles were scattered throughout the solution without the possibility for aggregation throughout the UV-Vis region. The high Optical density of the solution shows a high conversion of  $Ag^+$  to  $Ag^0$  as nanoparticle [13].

#### 3.3.2) FTIR analysis

The FTIR spectrum of pure silver nanoparticles after green synthesis method is shown in the figure 4.1.1(d). The characteristic FTIR peaks of silver nanoparticles alone over the range of 500-4000  $cm^{-1}$ . FTIR study was done to know the different functional groups on the surface of the green synthesized silver nanoparticles.

Wave length	Functional group
3458.67	Dimeric OH stretch [15]
2971.62	C-H Stretching alkanes [16]
1629.4	Amide 1 group [16]
1391.5	C-N stretching aeromatic amine rings [17]
1042.5	C-N Stretching aliphatic amines [18]

#### 3.3.3) Dynamic light scattering analysis:

Figure 3.3.3 demonstrates that the DLS pattern for the green synthesized nanoparticles after separating them from the reaction medium by centrifugation process. From the figure it clearly indicates that the size spectrum of nanoparticles are ranged between 6-50 nm with an average mean diameter of 32 nm.

#### 3.3.4) Scanning electron microscopy analysis:

The figure 3.3.4 (a,b) represent the scanning electron microscopy images for green synthesized silver nanoparticles. From the above figure it is confirmed that the nanoparticles are of different shapes but they are near to the spherical shape and the nanoparticles were unevenly distributed. Scanning electron microscopy images are representing the silver nanoparticles were grouped because agglomeration taking place while preparing nanoparticles.

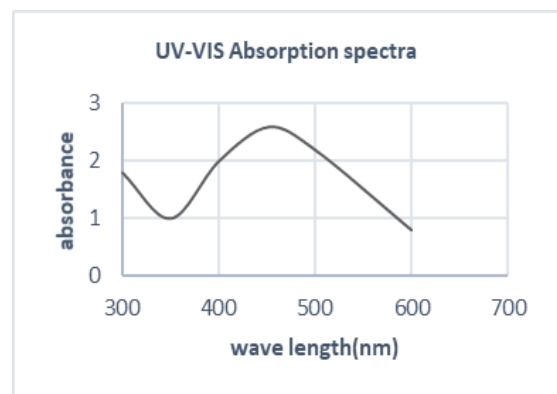


Fig 3.3.1 UV Visible absorption spectra for Agnp's

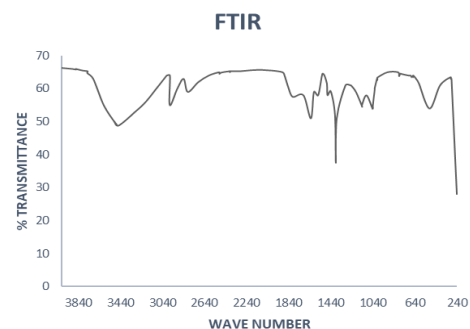


Fig 3.3.2 FTIR spectrum of Agnp's

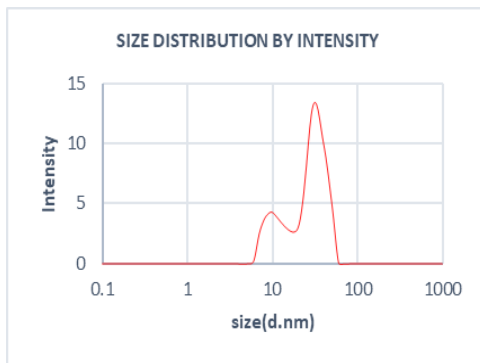


Fig 3.3.3 DLS pattern for green synthesized Agnp's

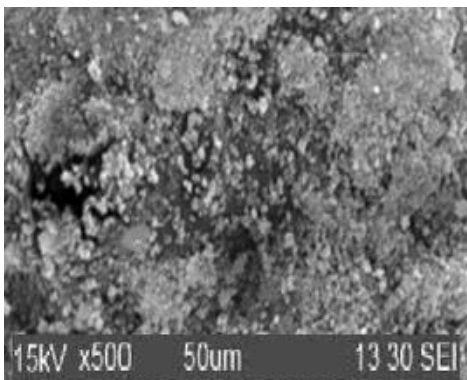


Fig 3.3.4 (a) SEM image for Agnp's

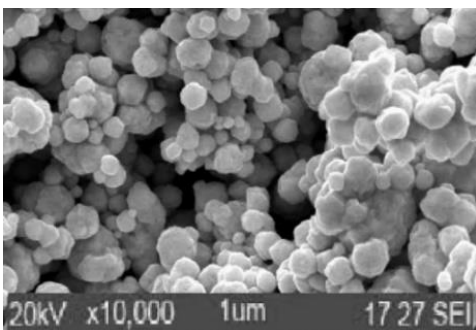


Fig 3.3.4 (b) SEM image for Agnp's

### 3.4) Optimizing parameters:

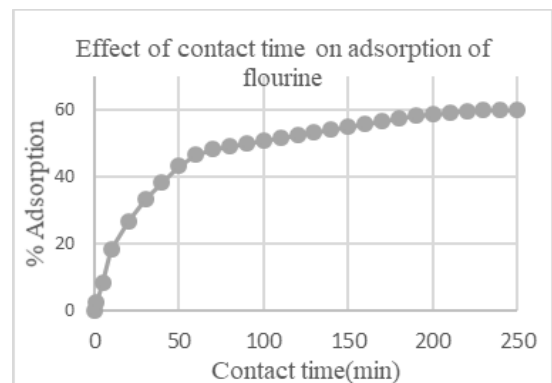
The parameters like Contact time, Initial Concentration, Adsorbent Dosage, pH and the Temperature were optimized and tried to find out the effect of different parameters on adsorption of fluorine on silver nanoparticles.

### Adsorption of Fluoride using silver nanoparticles:

#### 3.4.1) Effect of Contact time:

The effect of contact time was studied for 0-280 minutes at room temperature. The dosage used for optimizing contact time is 0.5 gm/lit and the initial pH is 5. The findings revealed from the graph that, with the

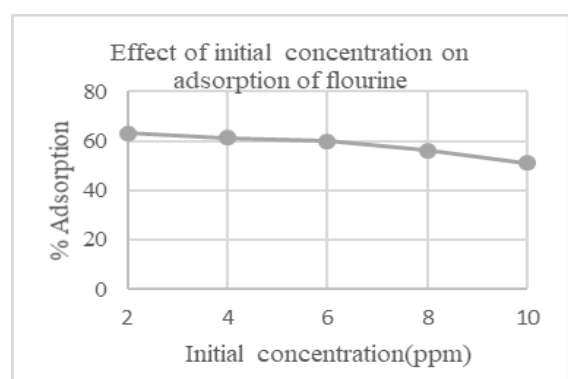
rise in contact time, the percentage of the elimination of fluoride also increased. At the optimum contact time of 230 minutes the maximum Percentage removal (60%) was obtained and after it remained constant. This may be due to the presence of free valencies on the surface of green synthesised silver nanoparticles [19]. The silver nanoparticles are kept in empty tea pouch to make experimentation easy from avoiding filtration process. The maximum adsorption percentage we got from optimum time is 60% were mentioned in the graph.



Graph 3.4.1: Effect of contact time on Adsorption of Fluoride

#### 3.4.2) Effect of initial concentration:

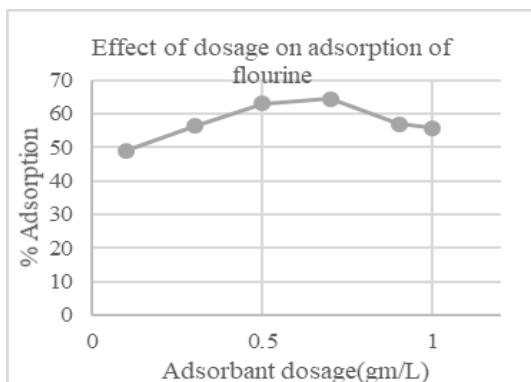
The effect of Initial concentration of fluoride was studied at 2, 4, 6, 8, 10 mg/L. The experiment was carried out for optimum time of 230 min at room temperature with a constant adsorbent amount 0.5 gm/lit and pH 5. As the initial fluoride concentration increases the amount adsorbed per unit mass decrease with increase in initial fluoride concentration which can be seen in the graph. At low initial fluoride concentrations, the ratio of fluoride ions to available adsorption sites is high, and these sites decrease and the fluoride concentration increases [20]. Maximum percentage removal of fluorine was noted at a concentration of 2 ppm of 63 %.



Graph 3.4.2: Fluoride removal percentage at different concentrations

### 3.4.3) Effect of dosage:

The effect of adsorbent dosage was studied by varying the dosage levels as 0.1, 0.3, 0.5, 0.7, 0.9, 1.0 gm/L. The experiment was carried at optimum time 230 min with 2 ppm optimum initial concentration of fluorine at room temperature and the initial pH is 5. It was observed from the graph that the amount of fluoride adsorbed per unit mass of the adsorbent increased with the increase in amount of adsorbent. For affixed initial concentration of fluorine as the amount of adsorbent dosage increases the number of available sites till the saturation. After saturation the adsorption of fluorine gets reduced due to less availability of sites [21]. If the dosage of adsorbent increases, the adsorption potential per unit mass decreases since the active sites in the adsorption phase are not saturated. At 0.7 gm/lit of adsorbent dosage, the maximum fluoride ion removal was 63 %.



Graph 3.4.3: Fluoride removal percentage at different dosages

### 3.4.4) Effect of pH:

The effect of pH on the removal of fluoride was studied for 2,4,6,8 and 10. The experiment is carried out with optimum time of 230 min with optimum conditions of initial concentration 2 ppm of fluorine and the adsorbent dosage of 0.7 gm/L at room temperature. The graph showed that initially the percentage removal was increased in acidic conditions and obtained a maximum percentage removal (65.4%) at pH 6 and decreased in basic medium this may be due to acidic pH conditions. The removal of fluoride is due to the formation of HF in acidic medium. The removal of fluoride was limited in alkaline environments due to competition for active surface sites between fluoride ions and OH<sup>-</sup> ions [21].

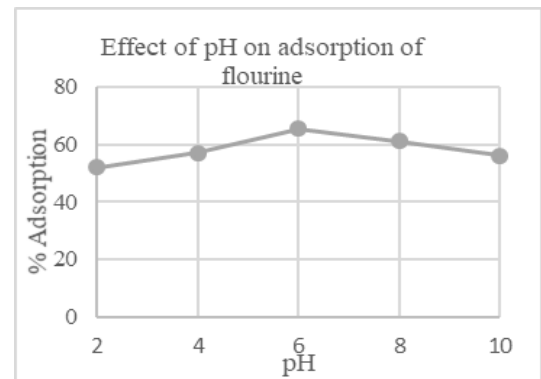
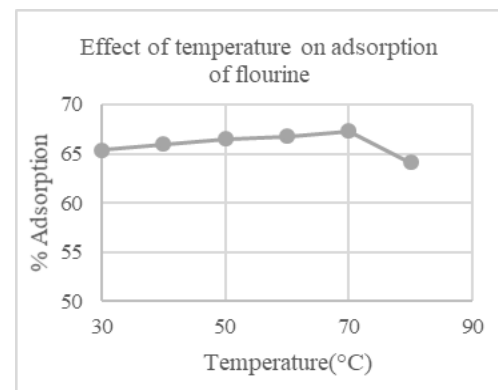


Fig 3.4.4: Fluoride removal percentage at different pH

### 3.4.5) Effect of temperature:

The effect of temperature on the removal of fluoride was studied for the temperatures 30,40,50,60,70 and 80°C. The experiment is carried out at optimum parameters which were obtained from above results .It was observed from the graph 3.4.5 that the fluoride removal increased with the increase in temperature and then slightly decreased. The optimum temperature obtained was 70°C with the removal percentage 67.3 %. The decrease in percentage removal may be due to the decomposition of adsorbent or solution at high temperatures [19].



Graph 3.4.5: Fluoride removal percentage at different temperatures

## 3.6) Adsorption Isotherm Models

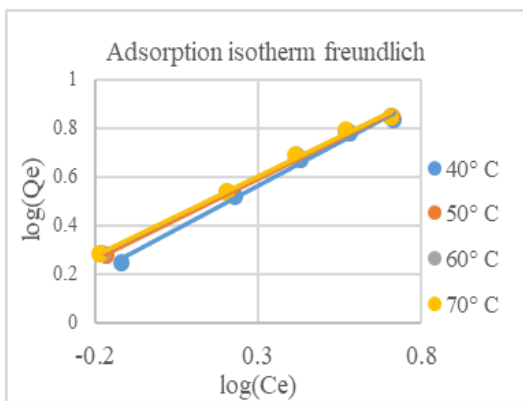
The adsorption isotherm analysis provides data on the efficiency of the adsorbent. It is possible to evaluate equilibrium data using widely known adsorption systems. Experimental data on adsorption isotherms can be represented by several mathematical models.

### 3.6.1) Freundlich isotherms:

The Freundlich sorption isotherm gives an expression for the heterogeneity of the surface as well as the exponential distribution of active sites and their energies. It is written as follows:

$$\log q_e = \log k_f + 1/n (\log(C_e))$$

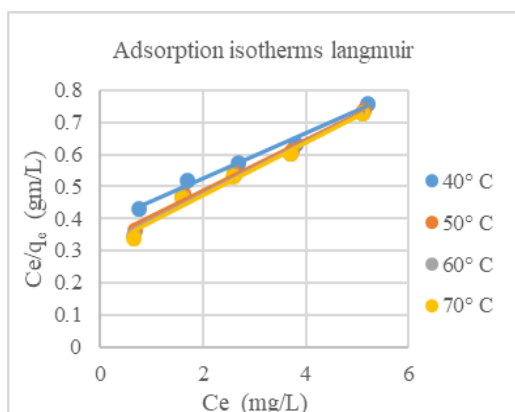
The correlation coefficients ( $R^2$ ) have a higher value than the Langmuir isotherm. Furthermore, a desirable adsorption is implied if the value of  $n$  is between 1 and 10. There are 4  $n$  values for 4 different temperatures they are  $n=1.3848$  for  $40^\circ\text{C}$ ,  $n=1.5028$  for  $50^\circ\text{C}$ ,  $n=1.5316$  for  $60^\circ\text{C}$  and  $n=1.5479$  for  $70^\circ\text{C}$ . From these  $n$  values for different temperature represent favourable conditions for adsorption. . The results are shown in Figure 3.6.1.



Graph 3.6.1: Freundlich adsorption isotherms

### 3.6.2) Langmuir Adsorption Isotherm:

The Langmuir isotherms can be used to evaluate adsorbent efficiency at higher temperatures. The Freundlich isotherms are only useful for obtaining an interpretation of adsorption phenomena at lower temperatures. Langmuir adsorption was laid on the imagination that adsorption follows on monolayer throughout the surface with no interaction between adsorbed molecules. The reduction of fluoride is aided by rising the temperature. The results are shown in Figure 3.6.2.



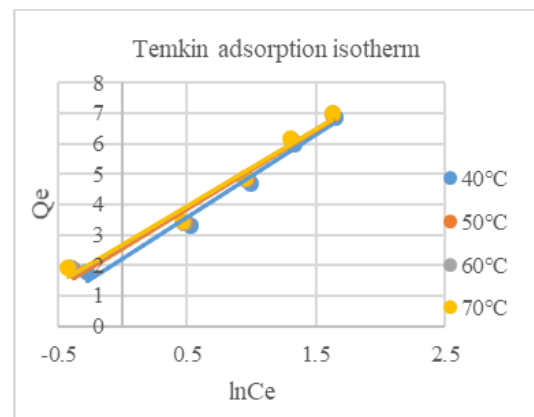
Graph 3.6.2) Langmuir adsorption isotherms plots

### 3.6.3) Temkin isotherm:

As indicated in the Freundlich equation, the Temkin isotherm is derived assuming a linear rather than logarithmic decrease in sorption heat. The Temkin isotherm was used in the following manner in general:

$$q_e = B (\ln A + \ln C_e)$$

The constant  $B$  is related to the adsorption heat ( $\text{L/mg}$ )  $A$  is the equivalent of the maximum binding energy



Graph 3.6.3: Temkin adsorption isotherms

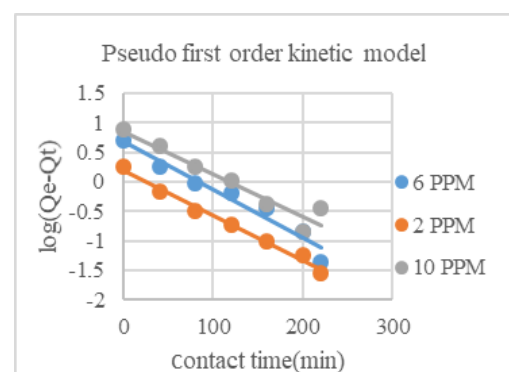
### 3.7) Adsorption Kinetic Models:

#### 3.7.1) Pseudo first order model:

For the result of fluoride adsorption on silver nanoparticles, graph 3.7.1 demonstrates a plot of the Pseudo first order equation. One of the most commonly used rate equations. The equation can be represented as

$$\log (q_e - q_t) = \log(q_e) - (K_1/2.303)t$$

Fig.3.7.1. describes the experimental outcomes of the first order rate constants. The Fluorine removal on Nano adsorbent does not follow this adsorption model due to low regression coefficient in the adsorption results. The results was shown in the graph. These graphs show more driving force for sorption.



Graph 3.7.1: Pseudo First Order kinetic Model

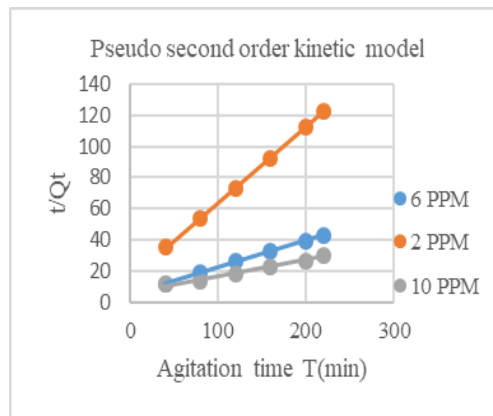


### 3.7.2) Pseudo second order kinetic model:

This kinetic model is based on the imagination that chemical adsorption is the rate determining step.

$$t/q_t = 1/k_2q_e^2 + t/q_e$$

The regression coefficient  $R^2$  for the plot drawn below indicates a strong relationship between the parameters. From the results it is clarified that the adsorption mechanism will fit well with this adsorption model.



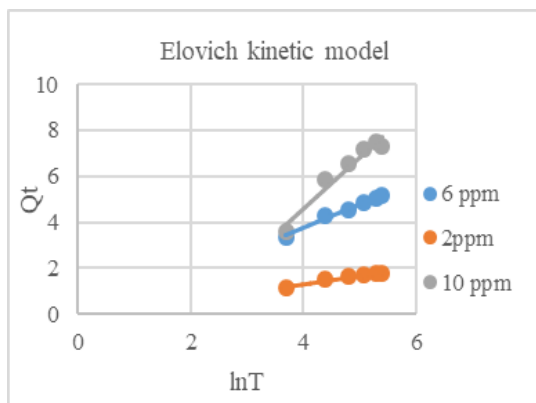
Graph 3.7.2: Pseudo Second Order kinetics Model

### 3.7.3) Elovich kinetic model:

To explain the kinetics of the chemical adsorption of gas on solids, the Elovich equation was first developed. The Elovich model's linear form is represented as:

$$qt = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln(t)$$

The graph is drawn between  $Qt$  vs  $\ln t$ . The constants  $\alpha$  and  $\beta$  were obtained from the slope and intercept



Graph. 3.7.3. Elovich kinetic model

Table 3.7. Kinetic parameters for adsorption of Fluoride by Silver nanoparticles

S no	Parameters	Flouride concentration 2 PPM	Flouride concentration 6 PPM	Flouride concentration 10 PPM

PSEUDO FIRST ORDER				
1	$R^2$	0.9629	0.9551	0.9307
	$K_1$	0.0179	0.0191	0.0165
PSEUDO SECOND ORDER				
2	$R^2$	0.9998	0.9992	0.9877
	$K_2$	0.016	0.0055	0.0018
ELOVICH KINETIC MODEL				
3	$R^2$	0.9738	0.9886	0.9501
	$\alpha$	0.1858	0.7181	0.3216
	$\beta$	2.6392	0.9681	0.4471

Table 3.6. Statistical comparison values of adsorption isotherms for adsorption of fluorine on silver nanoparticles

S no	Parameters	TEMPERATURE			
		40	50	60	70
Langmuir Isotherm					

1	R <sup>2</sup>	0.9894	0.9863	0.9849	0.9841
	Q <sub>m</sub>	14.144	12.547	12.2549	12.1065
	K <sub>L</sub>	0.1851	0.2445	0.2597	0.2684
	R <sub>L</sub>	0.5745	0.5055	0.4904	0.4822
<b>Freundlich Isotherm</b>					
2	R <sup>2</sup>	0.9941	0.9959	0.9962	0.9964
	log(K <sub>f</sub> )	0.3454	0.3918	0.4622	0.4078
	n	1.3848	1.5028	1.5316	1.5479
<b>Temkin isotherm</b>					
3	R <sup>2</sup>	0.981	0.9776	0.9767	0.9761
	A	2.4485	2.7267	2.8451	2.9146
	B	2.6979	2.5679	2.5373	2.5202

### Conclusions:

Synthesis of silver nanoparticles from green route (non-polluting method) was done using grape fruit extract as a reducing agent. SEM and DLS analysis confirmed the presence of silver nanoparticles with size ranging from 6nm to 50nm with mean average size of 32nm. The optimum agitation time for the adsorption of fluorine was 230 minutes. In the range of variables studied, the percentage of adsorption increases from 60 percent to 67.3 %. Percent removal of fluoride (67.3 %) using silver nanoparticles was achieved at an optimum contact time of 230 minutes, a dosage of 0.7 grams/litre, pH 6 and temperature 70°C. Experimental data satisfy the requirements of Freundlich, Langmuir and Temkin isotherms suggesting favourable fluorine adsorption. Freundlich isotherm is perfectly fitted to the adsorption of fluorine using silver nanoparticles. The kinetics study shows that the adsorption of fluorine to silver nanoparticles is better described by a pseudo second-order model. Finally, from experiments conducted so far in my work it is concluded that the initial concentration of fluorine plays crucial role in the adsorption of fluorine using silver nanoparticles.

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