Biogenic Nano Silica Synthesis from Rice Husk and its Potential in Rhodamine 6G Adsorption

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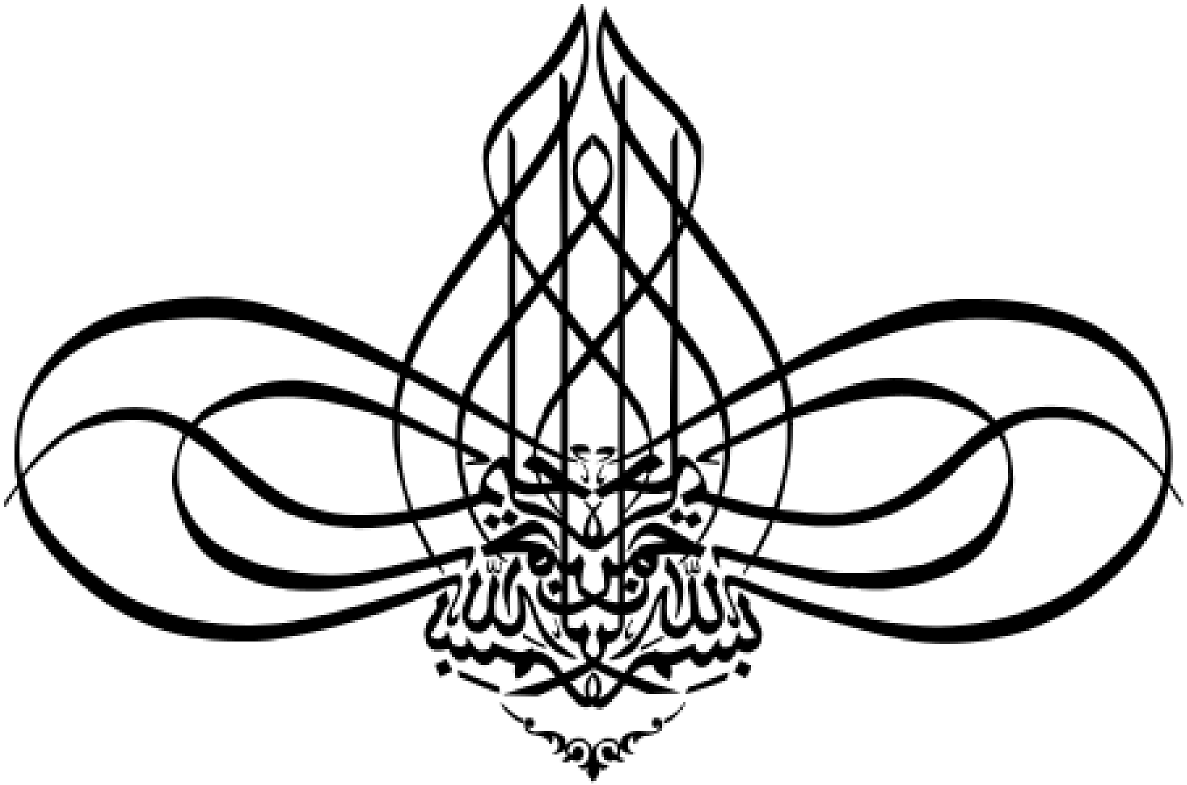

In the Name of Allah, the Most Beneficient, the Most Merciful

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Date: ____

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Date: ____

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Dr. Shah Rukh Abbas (PhD)
Assistant Professor,
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I certify that this research work titled“**Biogenic Nano Silica Synthesis from Rice Husk and its potential in Rhodamine 6G adsorption”** is my own work. The work has not been presented elsewhere for assessment. The material that has been used from other sources it has been properly acknowledged/referred.

Ramsha Sultan

I dedicate this thesis to my beloved parents Jaans:

Sultan & Azra

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In the name of Allah, the most beneficent and the most merciful. To Allah belongs all praise, eminence, magnificence and my gratitude for the execution and timely completion of this research work.

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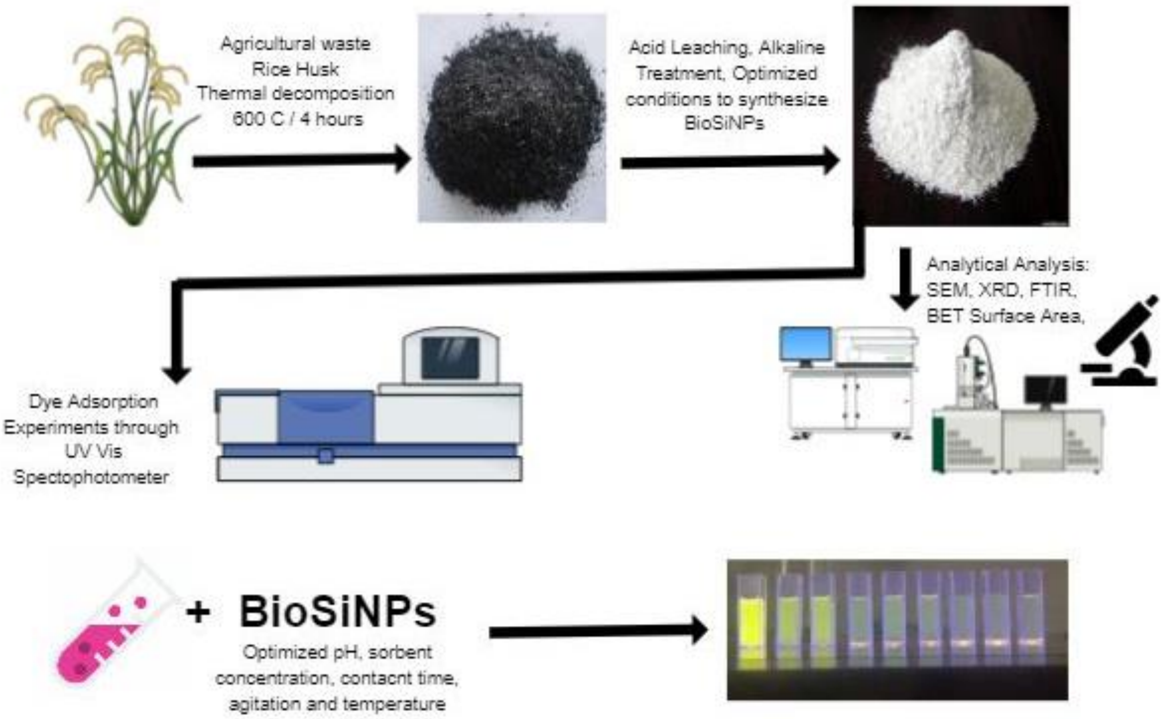
1 Contents

Abstract

Rhodamine dye is frequently employed as dying agent in paper, leather, plastic and textile industries. 15-20% of utilized dye is excreted out as effluent affecting aquatic life. Waste treatment hence becomes a necessary step in reducing its amount to minimum. Utilization of Silica nanoparticles have been exponentially increased since past decade in efficient removal of dye via electrostatic adsorption. In current study, we synthesized amorphous silica nanoparticles via biological route utilizing rice husk owing to its enriched silica content (90% of husk's ash). Biosynthesized Silica Nanoparticles (SiNPs) were characterized with scanning electron microscope with an average size of 95 nm. X-Ray Diffraction was used to assess the crystalline structure and diffused peak at 22^{θ}. Infrared Spectroscopy was performed to assess the composition of nanoparticles which was confirmed by a sharp dip at 1101 cm^{-1} showing Si-O-Si stretching. Stability of aqueous SiNPs was apparent owing to presence of sharp peak at -26.6 mV via Zeta potential. Surface area and surface porosity was confirmed by Brunauer-Emmet-Teller (BET) analysis with a surface area of 99.6886 m^2/g and with total pore volume of 0.426528 cm^3/g. Dye adsorption was increased by optimization of physiochemical parameters including pH (7), temperature (25° C), time (30 min), sorbent concentration (1000 mg/L) and agitation (250 rpm) by taking optical density at 525 nm. The study showed significant dye removal up to 84.5% by using optimized SiNPs thereby proving their excellent potential to be employed in industrial removal of Rhodami

Graphical Abstract



Chapter 1

Introduction

1. Introduction:

Currently, various industries like textile, paper, leather, printing, cosmetics, plastics, rubber, dye producing, and food processing use more than 100,000 commercial dyes (Yagub*et al.*, 2014; Liu *et al.*, 2016) and the annual production is more than 700,000 tonnes (Pearce *et al.*, 2003). During processing 10% to 15% of the dyes are released in the waste water (Pei *et al.*, 2007) and they disrupt the ecological system, effect human health in an adverse way, contaminate both surface and ground water, many of them are carcinogenic, teratogenic, and mutagenic, (Chen *et al.* 2015, Konichi*et al.*, 2017, Farhadi *et al., 2017).* So, focus has been given to the treatment of dyes before their release into wastewater. Multiple methodologies are being used to purify the water including oxidation, treatment by biological methods, various membranes technologies, coagulation, flocculation and adsorption. Out of all these, the most common one is adsorption because of its ease in use and nontoxic byproducts, silica nanoparticles are being studied for their adsorption properties among many other (Chang *et al.*, 2011).

New advancement in the production of silica on a nanoscale using sol gel methodology has brought a development in nano composites of silica and polymers, and by using different experimental conditions, varying sizes and morphological structures of nano silica composites are achieved. But the overall synthesis processes are expensive, consumes a lot of time, and release toxic compounds i.e. silicon alkoxide precursors. New trials are continuously performed in order to save time and money, and multiple researches are focused on rice husk or rice hull as an initial raw source to produce nano silica. Rice husk is made up of 20% of silica, and it is present in a large scale in countries with extensive production of rice, thus proving to be a cheaper and easily available source for cost effective silica. Presently, rice husk is majorly burned to obtain beneficial silica, but in doing so, air pollutants and greenhouse gases are extensively released into the environment, causing silicosis, respiratory problems, loss of hunger and tiredness. So, from clean technology, in order to achieve a better environment, the research community is working to extract silica from cheap sources in an easy and convenient way (Zulkifli et al., 2013).

1.1 Aim:

The aim of this research is to synthesize amorphous nano silica from rice husk with good adsorption properties for cationic dye Rhodamine 6G.

1.2 Objectives:

1. Synthesis and optimization of biologically synthesize silica nanoparticles (SiNps)
    - Acid Leaching treatment
    - Alkali Treatment
    - Ethanol, water dilution
2. Physio morphological analysis of the extracted SiNps
3. Adsorption of R6G:
    - pH, sorbent dosage, temperature, contact time and agitation
    - Kinetic analysis

Chapter 2

Literature Review

2 Literature Review:

2.1 Dyes:

Dyes are used in multiple industries for coloring purposes, from plastic, to paper, to textile, and cosmetics, food, leather etc. almost every second industry is using these organic compounds, whether cationic or anionic in nature. Of all these used dyes up to 15% is released in aquatic streams, rivers or water springs, and ultimately contaminating water with toxic compounds causing brutal impacts on aquatic life and environment. (Geethakarthi and Phanikumar, 2011). Dyes present in the water has the property to absorb sunlight and to reflect it, so they impact the photosynthesis of algae and disrupt the food chain. They have a high thermal stability and a high light stability; they tend to remain for more time in the environment without degrading on their own (Acemioğlu, 2004).

2.2 Rhodamine 6G:

One of the common dyes used in various area like silk, paper, cotton, fiber, wool, plastic, textile etc. is Rhodamine 6G (R6G) (Figure 1) (Farris, 1984). The harmful and cancer-causing properties of R6G are studied and published in depth by U.S. HHS – United States Department of Health and Human Services (French, 1989).

2.3 Dyes removal methodologies:

Among the conventional methods of dye removal, in chemical precipitation the waste material is consumed while releasing the product. This method is sometimes ineffective such as in case of less amount of the metal present. It also requires some additional steps such as oxidation when removing complexed metals. Waste produced in this process is also in very large amount that makes the process costly and difficult to manage.

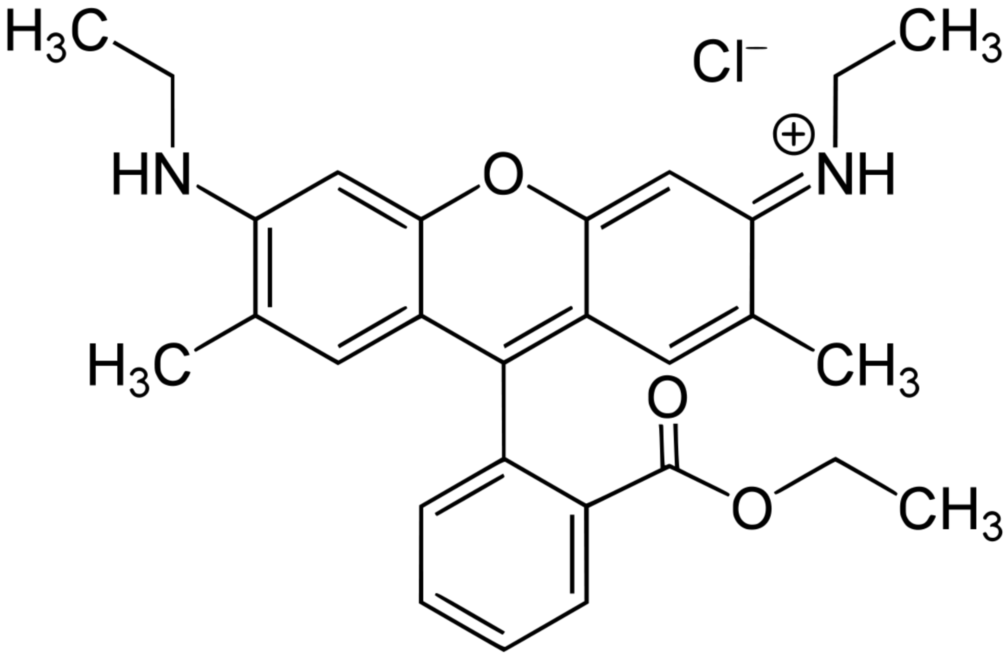


Fig. 1. Structure of Cationic Dye – Rhodamine 6G

Coagulation requires to detect the pH of waste, and managing the sludge created makes is costly too. Flotation is also done for dye removal that is costly. There are methodologies that require any type of oxidant like ozone, hydrogen per oxide etc. These are oxidation treatments, hypochlorite treatment etc. There are so many disadvantages associated to oxidation treatments like sometimes high amount of chemical is required like when dyes are impervious, it needs large amount of ozone to remove them. Aromatic amines and volatile compounds are released during these treatments and many intermediates are also formed.

In filtration cost is very high, this process results in loss of material. Moreover, this is not a feasible technique for paper, pulp and textile industry (Crini and Litchtfouse., 2019).

Water purification is an old method to eliminate the dyes. Equalization and sedimentation were being used to purify wastewater from dyes. But at that time there was no permissible limit of dye defined, which was defined later. Filter beds were devised to remove the dyes, activated sludge process was also introduced.

In conventional methods step of some processes were also used, but it came out to be very costly. Dye waste was equalized and neutralized, then pollutants were eliminated. In next step separation was done using either chemical or physical technique. Rest of the dye particles were removed by biological methods and finally sludge was treated and disposed of (Katheresan *et al.,*2018)

A traditional biological method is also used to eliminate the dyes, in this aerobic and anaerobic techniques are used to treat dye effluent and then waste is released. Although it is a cheap method and its maintenance is also not hard, but it is inadequate to eradicate the dyes from wastewater. Moreover, adsorption by fungus, microbial cultures, enzymes is also a conventional method of dye elimination (Crini and Lichtfoute, 2019).

2.4 Adsorption:

One of the most common methodology used to remove the chemical dyes from wastewater is adsorption. It is a physio chemical treatment process where the dissolved and integrated dye molecules in the water are easily picked up and removed through an adsorbent surface, exploiting its chemical and physical structures. The overall process varies from dye and adsorbent nature, basing upon electrostatic interactions, hydrogen bonds, van der waals forces, thus making an excellent option of treatment.

Adsorbent varies from material to sizes, and recent advancement in nanotechnology has made researched study nano sizes particles for their potential adsorbing properties.

2.5 Nanotechnology:

Nanotechnology, term coined by Norio Taniguchi, is the field of science proposed by Physicist Richard Feynman in the talk "There's Plenty of Room at the Bottom" where he seeded the concept of synthesis through atoms. Basically, it comprises the ability to study and to manipulate the matter ranging from 1 nm to hundreds of nanometres. The matter manipulated is the nanoparticle.

Nanobiotechnology is a juvenile and promptly growing area of research that joins the field of engineering and biology.

2.6 Nanoparticle synthesis and characterization:

The word nano is related to size that is 1 billionth of a meter. Technically, any particle having one or more external dimensions in the size range 1 nm–100 nm is termed as nanoparticle (Holister *et al.*, 2003).

NPs have unique properties because of their particular size and the physical properties (Ghosh Chaudhuri and Paria, 2011) which are of prime interest are: small size (Drexler, 1986), high mobility (Zhou *et al.*, 2012) and large surface area (e.g., 6 ml of silica nanospheres of 10 nm has larger surface area than 12 doubles-sized tennis courts) (Xu *et al.*, 2011). Because of these unique size dependant properties they have a wide area of application in every field of science (Rico *et al.*, 2001).

Broadly, they can be used in agriculture (Sabir *et al.*, 2014), catalysis (Xia and Yang , 2013), consumer goods (Kesseler, 2O11), defence (Cao and Jin 2002), electronics (Liu *et al.*, 2011), ecology and environment (Xhang , 2003), energy (Westenhaus, 2012) , information technology (Teng and Aronson), industry (Schmid and Riediker , 2008), medicine (Zhang *et al.*, 2008) and many others.

Implementation of nanotechnology in catalysis division gives rise to another homogenize field called as nanocatalysis. In catalysis we use substances to fuel up the rate of reaction. These substances are called catalysts. The reaction can be catabolic or anabolic. In synthetic reactions, catalysts are employed to enhance the synthesis of product. This enhancement in rate of reaction can be achieved through various means depending on the type of reaction. For example; if a reaction occurs at high temperature, the use of catalyst can reduce the temperature of reaction (Stucky and Zheng, 2008). When the catalyst is made up of nanoparticles it is called as nanocatalyst. The large surface to volume ratio of NC is the quality that makes them of note.

Nanoparticles can be classified into; inorganic NP and organic NP (Ramya and Subapriya, 2012). Inorganic NPs (metals) exhibits renewed properties and can be easily synthesized by chemical methods. Metallic oxides at nanoscale are noteworthy in nanocatalysis. NPs occur naturally, can be produced incidentally and can be synthesized.

Np synthesis techniques can be physical, chemical, biological and hybrid. There are various techniques for the production of MNPs like precipitation (Oliveira et al., 2003) decomposition (Okuyama *et al.*, 2010) chemical vapor deposition (Chang *et al.*, 2004), template assisited synthesis (Liu *et al.*, 2002), electrochemical (Therese *et al.*, 2000), electro spinning (Li and Xia, 2003), hydrothermal (Li *et al.*, 1999), reverse micelle (Hench *et al.*, 1990) and sol-gel techniques(West *et al.*, 2007). (Table 1.1) The most prominent technique used for manufacturing mnps is SG technique from chemical method. The aspects of SG which makes it incomparable are; high yield, low operation temperatures and low production cost (Sui and Charpentier, 2012).

2.6.1 Sol –Gel method :

The SG method is a standard method for mnps production. It involved soft chemistry. It transforms liquid state (sol) into a gel state which is further transformed into solid oxide material by post treatment. The chemical processes involved in the transformation include; hydrolysis and condensation (Livage and Sanchez, 1992; Hench and West, 1990).

1. $\text{M-O-R} + H_2O \xrightarrow{\text{hydrolysis}} \text{M-OH} + \text{R-OH}$

2. $\text{M-OH} + \text{HO-M} \xrightarrow{\text{water condensation}} \text{M-OM} + H_2O$

3. $\text{M-OR} + \text{HO-M} \xrightarrow{\text{alcohol condensation}} \text{M-OM} + \text{R-O}$

Polymer formation:

1. M-O-M-O-M-O-M-O-M-O-M
2. M-OH-M-OH-M-OH-M-OH-M

Hydrolysis is breaking down of reactant by molecule of water while in condensation reaction two or more molecules combine with the release of a water molecule. The formation of metallic oxide requires the connection of metal with two oxide or hydroxyl groups. The calcination process, heating of a polymer network to high temperatures in air or oxygen, removes the water content from the gel and a porous material is formed (Kruglick, 2011).

Table 1.1 Np synthesis methods

Biological Methods (by using)	**Chemical Methods**	**Physical Methods**	**Hybrid Methods**
Bio membranes	Colloids	Electric Arc Deposition	Electrochemical CVD
DNA	***Sol-Gel***	High Energy Ball Milling	Partial Arresting in glass and zeolites
Enzymes	L-B Films	Hydrothermal	Micro emulsions
Micro Organisms	Inverse Micelles	Ion Implantation	
		Laser Ablation	
		Melt Mixing	
		PVD	
		Sputter deposition	
		Vapor	

2.6.2 Hummers' method:

Hummers' method (Hummers *et al.,* 1958) was developed in 1958. Before the development of this method, the GO production was considered hazardous because of concentrated acids. It is a chemical process used for synthesis of graphene oxide. The procedure involves addition of $KMNO_4$ to a solution of graphite, sodium nitrate, and sulphuric acid (Huang *et al.,* 2011; Paulchamy *et al.,* 2015).

The basic principle of Hummer's method is redox reaction. Graphite oxide is first oxidized and then reduced to form GO. Oxidation increases the inter-planar spacing of graphite (Cecilia *et al.*, 2009). A single layer of closely packed carbon atoms having unique properties is called Graphene (Hu *et al.,* 2010). These unique properties make its application diverse i.e. energy storage, electronics, electrochemistry, biofuel production and waste water treatment (Lim *et al.,* 2011; Zhu *et al.,* 2010).

2.6.3 Green synthesis:

Due to toxicity of chemical, physical and hybrid methods (Hutchison, 2008) for the synthesis of NPs the society has mania for greener synthesis technologies from past several years (Nabikhan *et al.,* 2010). The chemical synthesis involves complex parameters like toxic solvents (Parashar *et al.,* 2009), high temperature and pressure whereas microbial synthesis is not facile because of intricate lab maintenance. The placid optimal conditions like temperature, pH etc gave urgency to the green technology for the synthesis of NPs. This is easy, environment friendly and effective method of synthesis in comparison to chemical methods and others (Mubayi *et al.,* 2012).

The production of MNPs by this method has been reported (Ogi *et al.,* 2010; Vahabi *et al.,* 2011; Agnihotri *et al.*, 2009; Pugazhenthiran *et al.*, 2009). The NPs produced by using greener approach are immensely utilized in automotive industry (Mohseni *et al.,* 2012; GURJAR. & TYAGI), imaging (Reddy *et al.,* 2006), medicine (Nath & Banerjee, 2013) and waste management **(**Krishnaswamy, 2015)**.** Other than these they are also applied in catalysis (Nath & Benerjee, 2013).

There are two strategies for NP synthesis: top-down and bottom-up (Fig. 2).In the former, bulk material is broken down into small pieces and in the later, atoms and molecules are brought together to synthesize nano-sized particles (Wang & Xia 2004).Biosynthesis of nanoparticles utilizes bottom up approach (Nabikhan *et al.,* 2010). Diverse variety of biological sources including algae, bacteria, fungi, plants, plant products and yeast has been reported for biosynthesis of NPs.

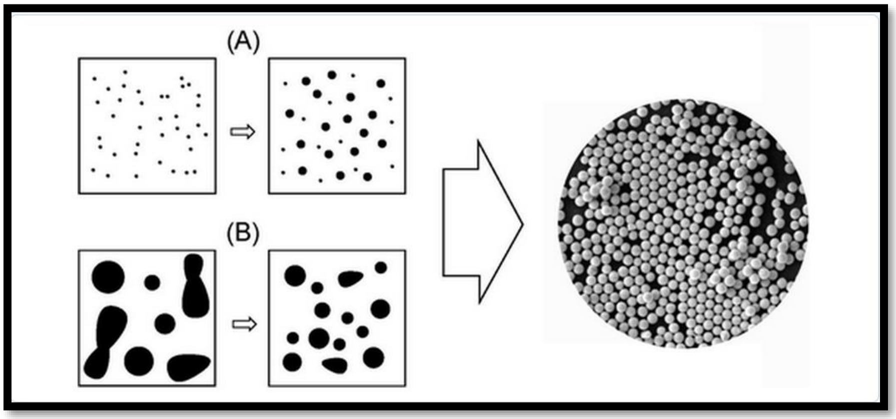


Fig. 2 Two approaches for the synthesis of nanoparticles

a. Bottom up approach **b. Top down approach**

2.7 Characterization of nano particles:

Characterization techniques are: photon, thermodynamic, optical and scanning, ion particle, electron particle probe characterization techniques.

2.7.1 Ion-Particle Probe characterization techniques:

There are many other ion-particle probe characterization techniques that can be used for np's analysis. XRD is a technique for characterization and identification of nps using X-rays to get a diffraction pattern after interaction with the specimen. It makes assessment related to variety of characteristics of nps i.e. structure, crystallinity, particle size, particle shape, homogeneity of the whole sample and size distribution using Bragg's Law (Klug and Alexander, 1954).

Basically, in XRD, X-Ray source is directed on a sample for analysis. The diffracted ray's pattern is detected on a detector and can be displayed on monitor screen in the form of graph. This pattern will tell predict about particle size and crystalline structure of NP (Sun and Li, 2006). Other techniques that are comparable with XRD for np size measurements are BET and TEM but the efficacy of XRD is more pronounced (Dorofeev *et al.,* 2012; Paulchamy *et al.*, 2015).

2.7.2 Electron-Probe characterization techniques

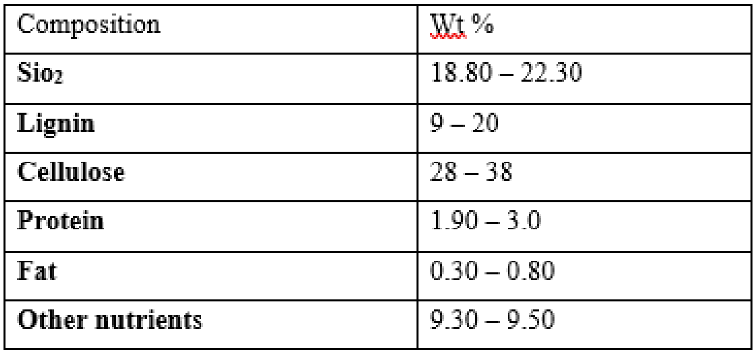
In Electron probe characterization techniques, the interaction between the charged particle and solid material gives information about the structure of the nps. Different types of electron probe characterization techniques can be used for np's analysis. SEM is one of the most commonly used methodology because of best results it generates. (Kempen et al., 2013).

Basically, SEM is all about electron beam diffraction and interaction with the specimen. The electron beam is focused on specimen. The striking of beam with the specimen generates an interaction of electron beams with specimen and produces signals i.e. secondary electrons, back scattered electrons & characteristic X-rays. This signal hides in it the information related to sample's surface topography and composition (Sundar et al., 2010). The SEM and XRD from electron probe characterization techniques and ion-particle probe characterization techniques respectively are the methods of common use (Dorofeev et al., 2012).

2.7.3 **2.13 Rice husk as a source of nano silica**

One of the major crops of edible food in the world is rice. In 2012, 162.3 million hectares of land were dedicated to rice crop and the yield was of 738.1 million tonnes 1 and Pakistan's contribution was 9.4 million tonnes (Countries by commodity, 2014). Since the overall demand in the world is increasing, thus rice production is expected to increase exponentially. The husk or hull also known as chaff of the rice is the outer layer or covering of the rice grain, and it is achieved after the milling. Of the total rice harvested, 20% is made up of rice husk (Giaccio *et al.,* 2007) and yearly the production of rice husk in Asia is more than 770 million. Majorly rice is made up of silica, followed up ligno cellulosic compounds. In the following table weight percentage of the composition of rice husk is mentioned. (Bhatnagar, 1994).

Table 1.2 Main composition of RH



Composition	Wt %
Sio$_2$	18.80 – 22.30
Lignin	9 – 20
Cellulose	28 – 38
Protein	1.90 – 3.0
Fat	0.30 – 0.80
Other nutrients	9.30 – 9.50

2.8 Silica

Silicon dioxide, carrying different names like Quartz, Silica, Silicic Oxide, Silicon Oxide, Crystalline Silica and Pure Silica, is a compound of silicon and oxygen, SiO_2. It is widely present naturally in Earth's crust and as a constituent in many living organisms. Usually, it has a colourless to whitish appearance and is insoluble in water; although there are different forms of silica, termed collectedly as silicic acid, that are water soluble and naturally occur in surface water and well water. Owing to the small size of Silica (SiO2) powders, these are widely used as composite fillers, heat proofing, and thixotropic mediators other than its use in other industrial applications (Sun & Gong, 2001).

Chapter 3

Methodology

3 Materials and Methods:

Rice husk from local source in Islamabad. Distilled water, NaOH, HCl, Whatman Ashless Filter Paper 42, Ethanol, H_3PO_4.

3.1 Synthesis and optimization of SiNps

Simplified green sol gel method was used to prepare amorphous silica nanoparticles.

3.2 Thermal decomposition to obtain rice husk ash

The rice husk was procured by a local vendor from Islamabad district. It was washed multiple times with tap water to remove dirt and dust, sieved and placed in a drying oven for 24 to 36 hours at 80° C. Once the RH was completely dry thermal decomposition at 600° C for 4 hours was performed in a muffle furnace in order to obtain rice husk ash.

3.3 Acid Leaching

Before silica extraction an acid washing step was performed in the following way:

a. RHA was first dispersed in distilled water (1 gram of RHA in 6 ml of water)
b. Using 1 M HCl the pH of the dispersion was adjusted to 5
c. The dispersion was stirred for 2 hours, constant stirring at room temperature
d. Multiple dispersions were prepared; with pH 7, 3 and 1
e. The dispersions were filtered with Whatman Ashless Filter Paper 42 and washed with distilled water
f. The residues were collected, dried in open air over night and used for silica extraction individually. From all of them, silica gel was synthesized

3.4 Alkali treatment, extraction of sodium silicate solution

a. 1 N NaOH was added to the RHA samples and boiled for 1 hour with constant shaking in a covered conical flask. Temperature was maintained in a water bath at 95° C.

b. It was then filtered with Whatman filter paper and the filtrate was left to cool down in a beaker.

3.5 Silica extraction

a. Ethanol was mixed with sodium silicate solution

b. Then, water was added and stirred for 1 hour.

c. The mixture was slowly titrated with 3 M H_3PO_4 until the gel was formed at pH values of 7, 8, 9

d. Then, the gel was centrifuged and washed multiple times with hot distilled water to remove any excess sodium silicate and phosphate

e. The sample was dried in an oven overnight at 95° C

f. Sample was calcined in muffle furnace at 550° C for 30 minutes to obtain the SiNps

3.6 Characterization

Silica powder was characterized through different equipment, XRD, SEM - EDS, BET and BHJ, and FTIR, by preparing fresh samples in DI water &/or Ethanol

3.7 Adsorption Experiments

A stock solution of rhodamine 6G was diluted in deionized water in order to perform all the adsorption experiments. The experiments were carried out in batch operation, and tests performed were of agitation, adsorbent dosage, pH, temperature, equilibrium and kinetic. The agitation rate was 250 rpm and solution volume was 8ml. First of all agitation effect was checked out, whether maximum absorbance is observed at still position or in an agitation position. The adsorbent dosage was evaluated by varying the concentration of SiNps i.e. 125 mg/L, 250 mg/L, 375 mg/L, 500 mg/L, 625 mg/L, 750 mg/L, 875 mg/L, 1000 mg/L, keeping dye concentration constant 4.25 mg/L the lethal concentration of rhodamine 6 G. Thirdly pH effect was evaluated by varying pH from 3 to 10, with dye concentration of 4.25 mg/L, temperature 25°C, in a span of 240 minutes.

Next the kinetic curves were generated with initial dye concentrations of 2 mg/L, 4 mg/L, 6 mg/L, and 8 mg/L with contact time from 0 minutes to 240 minutes at room temperature, using appropriate adsorbent dosage and optimum pH. Equilibrium curves were constructed having initial dye concentrations of 2 mg/L, 4 mg/L, 6 mg/L, and 8 mg/L with contact time from 0 minutes to 240 minutes at 25°C, 35°C, 45°C, 55°C.

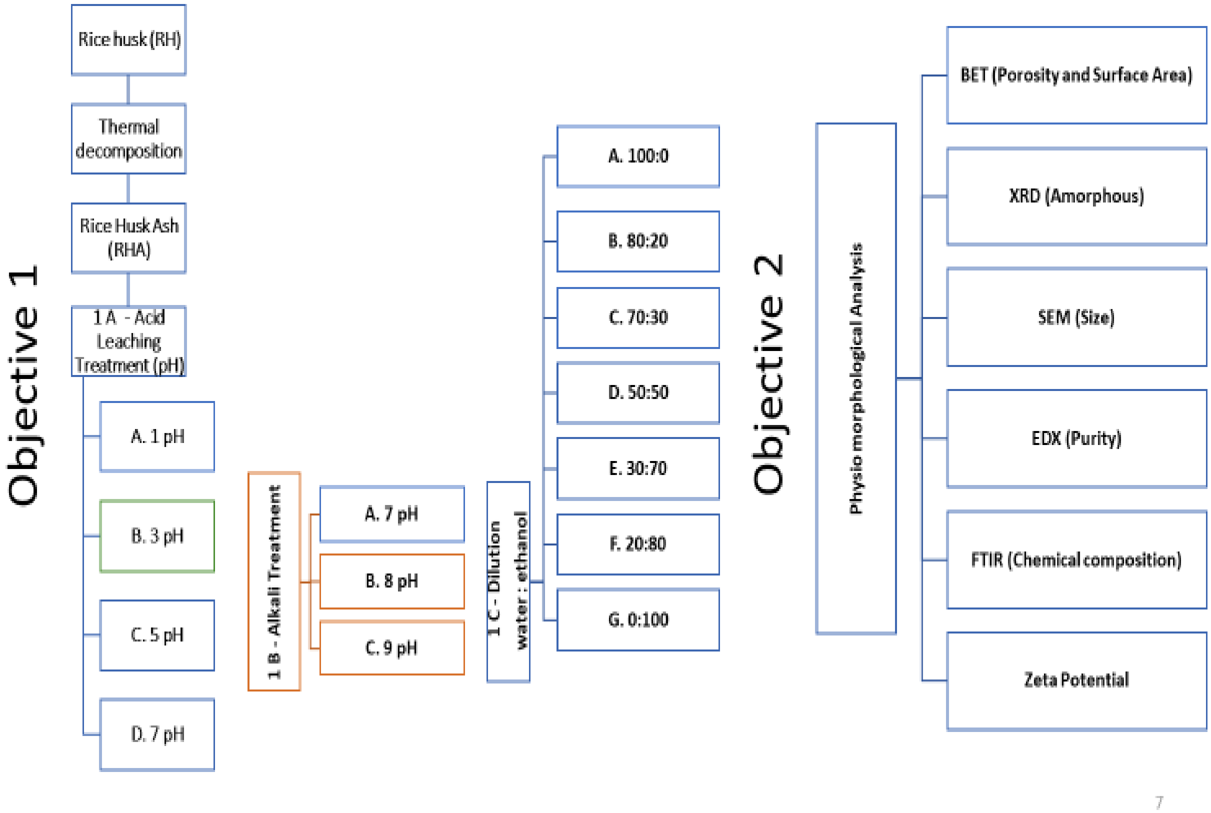
At the end of the experiments the adsorbent was separated out through centrifugation at 6000 rpm for 5 minutes, supernatant was collected and the quantification of the rhodamine 6 G was realized through UV Vis Spectrophotometer at 530nm. All the tests were performed in replicates and mean value were calculated, blanks were performed as well. Following equations were used to calculate the equilibrium adsorption capacity denominated as q_e– Eqs. 1, and the adsorption capacity at time q_t – Eqs. 2:

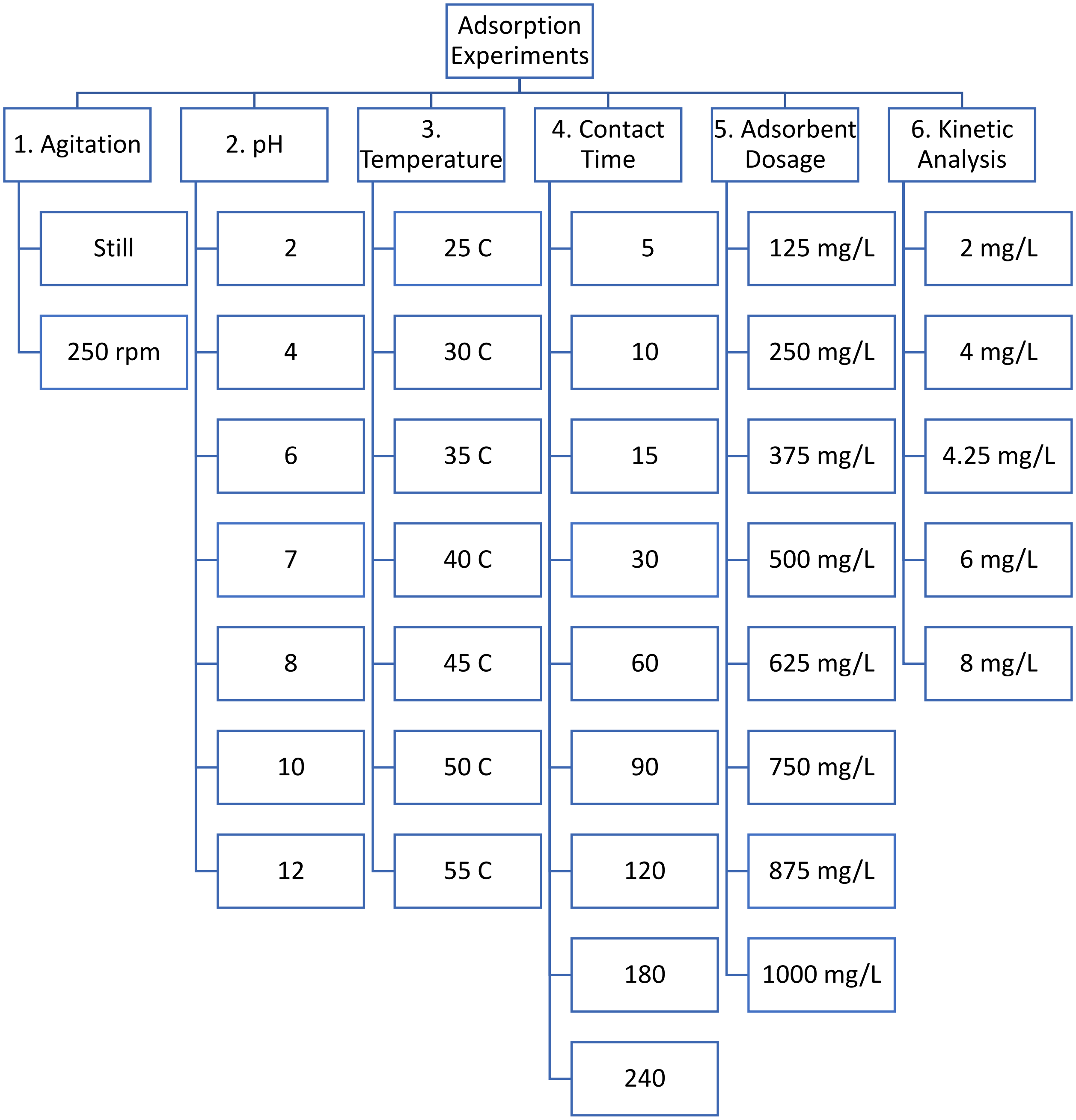
$$q_e = \frac{C_0 - C_e}{m} V \qquad \text{Eqs. 1} \qquad\qquad q_t = \frac{C_0 - C_t}{m} V \qquad \text{Eqs. 2}$$

Where, C_0 is the initial dye rhodamine 6G concentration in liquid (mg/L), C_e is the equilibrium dye rhodamine 6G concentration in liquid (mg/L), C_t is the dye rhodamine 6G concentration at time "t" (mg/L), m is the adsorbent SiNps amount (g), and V is the total volume of the solution (L). Removal efficiency was calculated by the following formula:

3.9 Dye concentration measurement

With the help of UV Vis Spectrophotometer the unknown concentrations of the dye were measured; through a calibration curve acquired using 8 known amount of dye concentrations ranged from 1mg/L to 8mg/L. The test was performed thrice and mean value calculated.


Objective 1
Rice husk (RH)
Thermal decomposition
Rice Husk Ash (RHA)
1 A - Acid Leaching Treatment (pH)
A. 1 pH
B. 3 pH
C. 5 pH
D. 7 pH
1 B - Alkali Treatment
A. 7 pH
B. 8 pH
C. 9 pH
1 C - Dilution water : ethanol
A. 100:0
B. 80:20
C. 70:30
D. 50:50
E. 30:70
F. 20:80
G. 0:100
Objective 2
Physio morphological Analysis
BET (Porosity and Surface Area)
XRD (Amorphous)
SEM (Size)
EDX (Purity)
FTIR (Chemical composition)
Zeta Potential
7


Adsorption Experiments
1. Agitation
Still
250 rpm
2. pH
2
4
6
7
8
10
12
3. Temperature
25 C
30 C
35 C
40 C
45 C
50 C
55 C
4. Contact Time
5
10
15
30
60
90
120
180
240
5. Adsorbent Dosage
125 mg/L
250 mg/L
375 mg/L
500 mg/L
625 mg/L
750 mg/L
875 mg/L
1000 mg/L
6. Kinetic Analysis
2 mg/L
4 mg/L
4.25 mg/L
6 mg/L
8 mg/L

Chapter 4

Results and Discussion

4 Results and Discussion:

4.1 Thermal decomposition, acid leaching and alkaline treatment

Rice husk is composed of ~75% of organic volatile matter and the remaining 25% is ash, denominated as RHA. It is enriched in silica, about 85% to 90%. Carbonization is easily achieved at temperatures below ~700° C, and it is essential to synthesize amorphous silica.

Different pH were sets in order to check the purity of silica produced, whether it is affecting on its characteristics or not. The step of acid leaching was performed to remove the small quantities of minerals from rice husk ash before extracting silica. The solubility of amorphous silica is very low at pH <10 and increases sharply at pH >10. This unique solubility behavior enables silica to be extracted from RHA by solubilizing under alkaline conditions and later precipitating at a lower pH. Basically silica is obtained just like other nps through the process of precipitation with the help of acids like Sulfuric, Nitric, Hydrochloric Acids. Here, with phosphoric acid the following chemical reaction happened:

$$\mathbf{3\ Na_2SiO_3 + 2\ H_3PO_4 \rightarrow 3\ SiO_2 + 2\ Na_3PO_4 + 3\ H_2O}$$

During the addition of phosphoric acid, the ≡Si–OH species formed and condensed together to form siloxane [Si–O–Si] bonds as represented below:

$$\mathbf{(2)\ SiOH + HOSi \rightarrow Si\ O\ Si + H_2O}$$

Initially, the ≡Si–OH make up together to forms dimers and timers and make primary particles, they together aggregate and make stable particles.

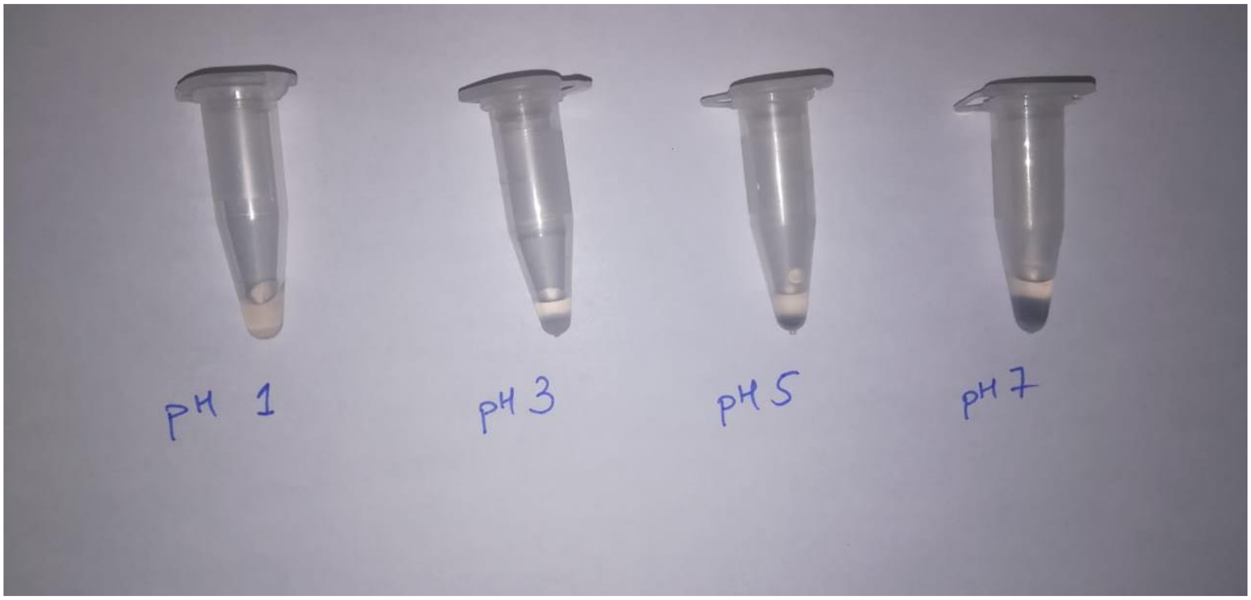
4.2 Effect of Ethanol

As per literature review, ethanol helps in providing higher miscebiliity and combining in the precursor of silica, thus stimulating the bonds ≡Si–OH and ≡Si–O–Si≡ which further produce more defined and large particles while the solution is left for aging.

4.3 Effect of pH and Water Dilution

Optimum gel formation at 7 pH. Gel were not stable at higher pH.Below a table with images -

Acid Washing	**Formation of gel**	**Ethanol/Water Conc**	**Appearance of gel**
1	7 pH	30::70	Clear
3	7 pH	30::70	Slightly grey
5	7 pH	30::70	Grey
7	7 pH	30::70	Grey to Blackish



Physical appearance shows that silica gel formed at pH 1 is clear, so the purest.

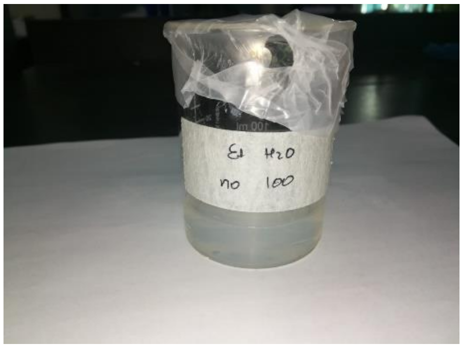
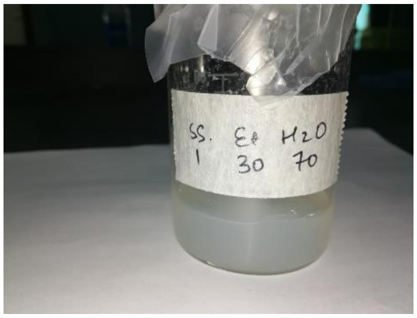
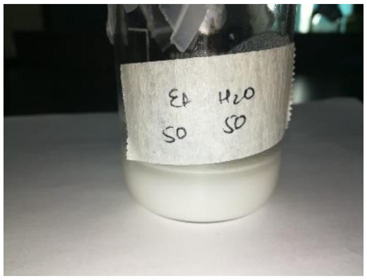
While the remaining three dispersion have increasing concentrations of minerals impurities.

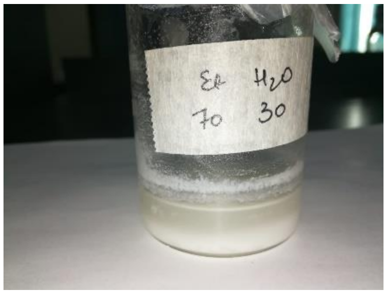
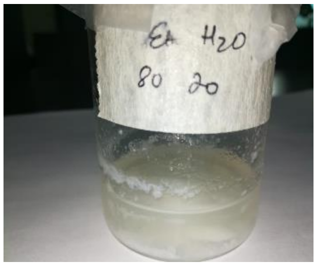
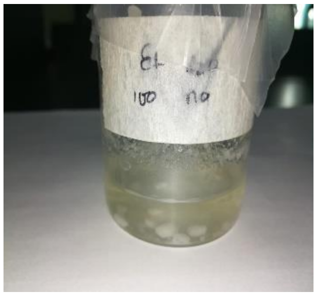
Thus pH 1 for mineral leaching is selected for further studies.

Acid Leaching	**pH at gel formation**	**Ethanol Water Conc**	**Results**
1	7	30::70	Stable gel formation
1	8	30::70	No proper gel formation, gelation time upto 24 hours observation
1	9	30::70	No proper gel formation, gelation time upto 24 hours observation

The optimal gel formation is at pH 7.

Acid Leaching	**pH at gel formation**	**Ethanol**	**Dilution Rate**	**Results**
1	7	No	100%	Gel formed pic A

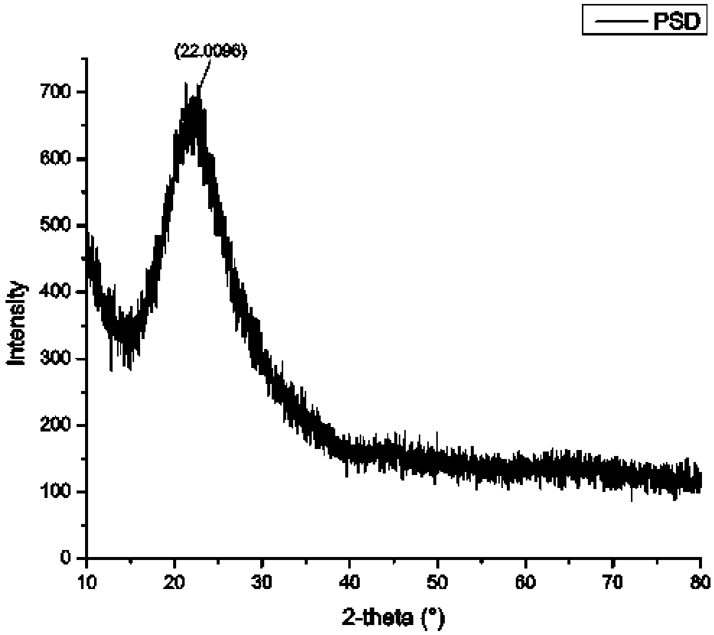
		Ethanol		
1	7	20%	80%	Gel formed pic B 
1	7	30%	70%	Gel formed pic C 
1	7	50%	50%	Gel not formed pic D 
1	7	70%	30%	Gel not formed pic E

				
1	7	80%	20%	Gel not formed pic F 
1	7	100%	No Water	Gel not formed pic G 

4.4 BET and BHJ results

	A (0:100)	B (20:80)	C (30:70)
Surface Area	132.9629 m^2/g	99.6886 m^2/g	83.3823 m^2/g
Total pore Volume	0.051778 cm^3/g	0.426528 cm^3/g	0.361166 cm^3/g

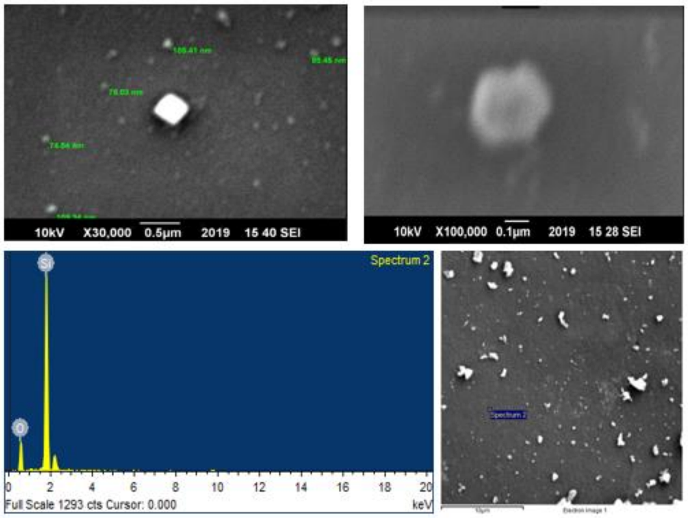
4.5 XRD (X-ray powder diffraction)

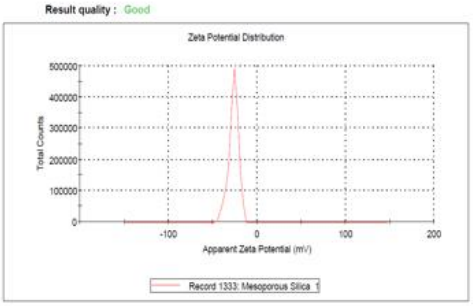


XRD graph of SNP

The pattern shows amorphous nature, a broad peak at angle 22, and no sharps peaks confirmed that no crystalline silica is produced in the sample.

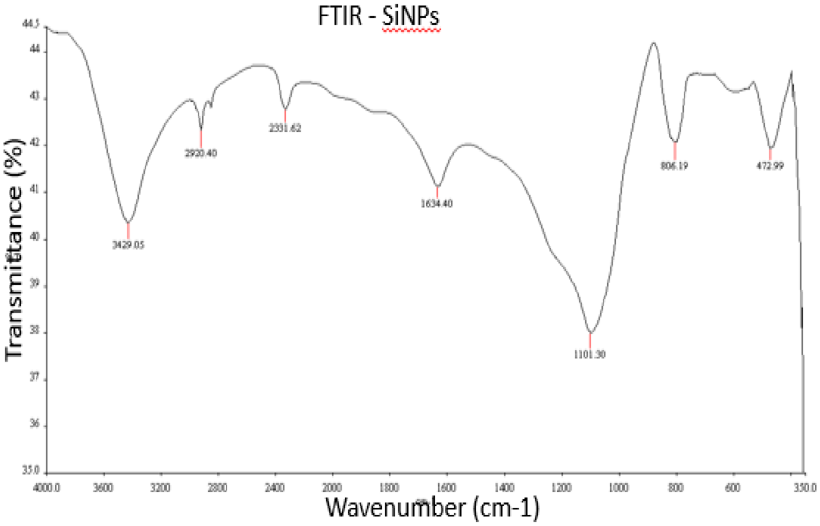
4.6 SEM / EDS and Zeta Potential

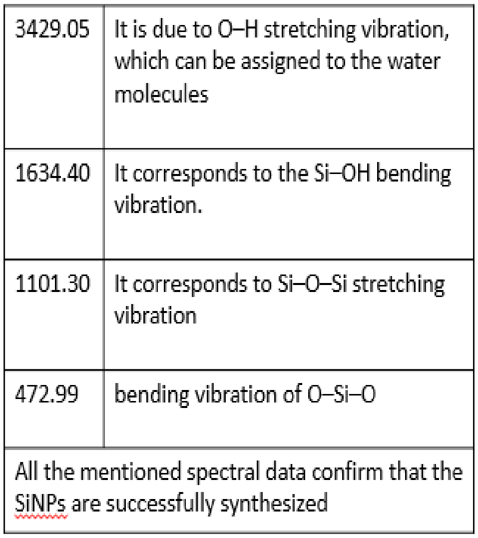




SEM : Average particle size 96nm
EDX: purity
Zeta Potential: Negative Shift -26.6mV

4.7 FTIR





3429.05	It is due to O–H stretching vibration, which can be assigned to the water molecules
1634.40	It corresponds to the Si–OH bending vibration.
1101.30	It corresponds to Si–O–Si stretching vibration
472.99	bending vibration of O–Si–O
All the mentioned spectral data confirm that the SiNPs are successfully synthesized	

4.8 Maximum Absorbance Wavelength of R6G and Calibration Curve

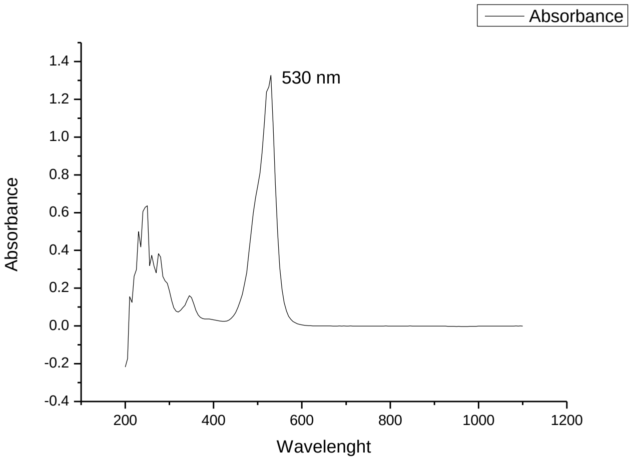


Fig shows the absorbance spectrum of Rhodamine 6G with its maximum absorbance at 530nm.

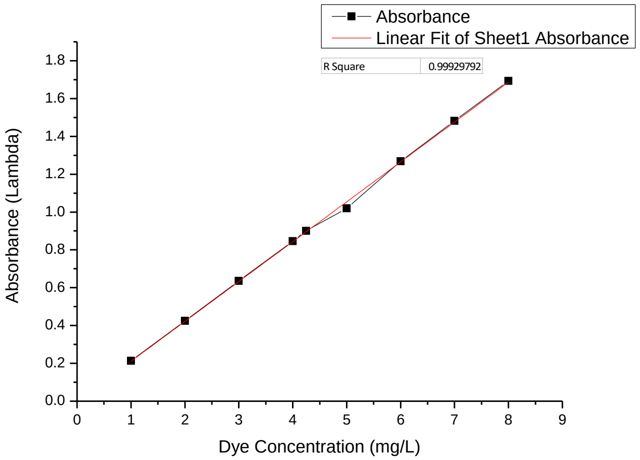
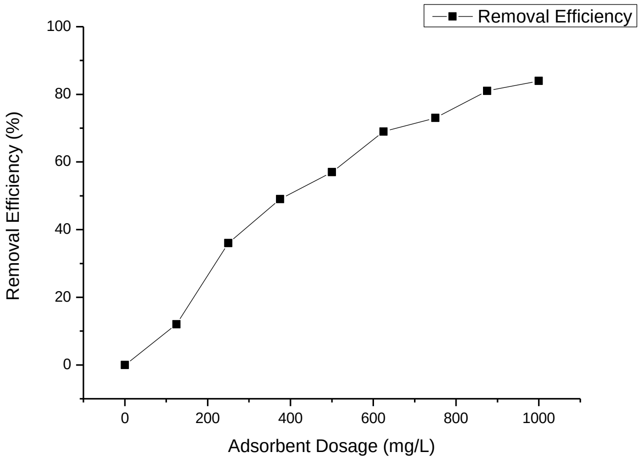


Figure indicates rhodamine 6G's calibration curve, utilized as a reference to calculate the unknown concentration of samples. The value of regression coefficient is 0.99 confirmed a linear dependence of dye concentration and absorbance.

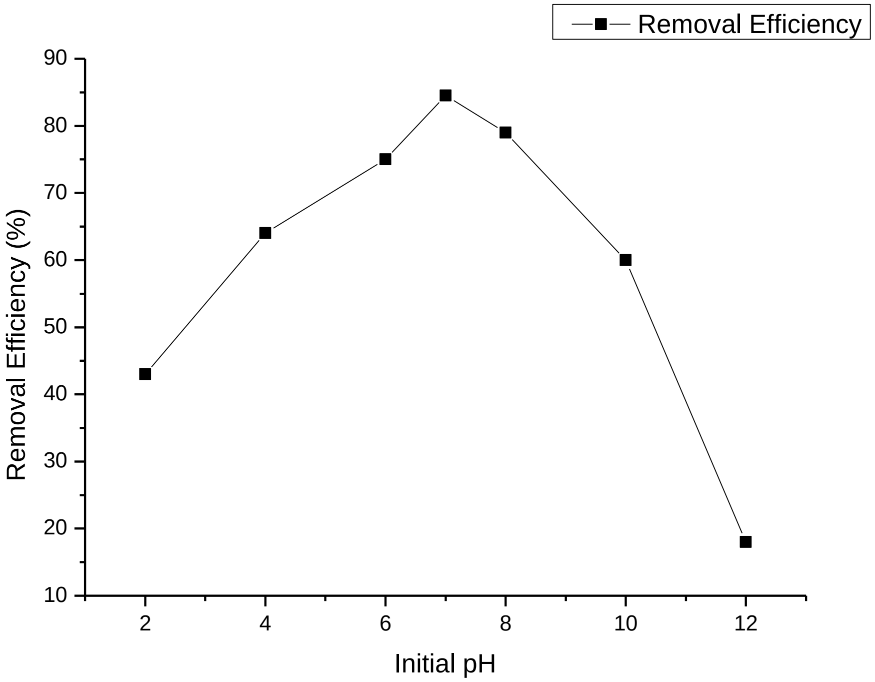
4.9 Optimiziation of Adsorption of rhodamine 6G on SiNps

4.9.1 Adsorbent dosage effect



The determination of sorbent concentration is an important test to know the correct amount of SiNps to use for further experiments. The graph represent dye removal efficiency (%), here we can observe that it is improved steadily with increasing concentration of SiNps because a total number of adsorbent sites increased. The optimum rhodamine 6 G dye removal efficiency was 84% at 1000mg/L sorbent concentration. This was selected for further experiments.

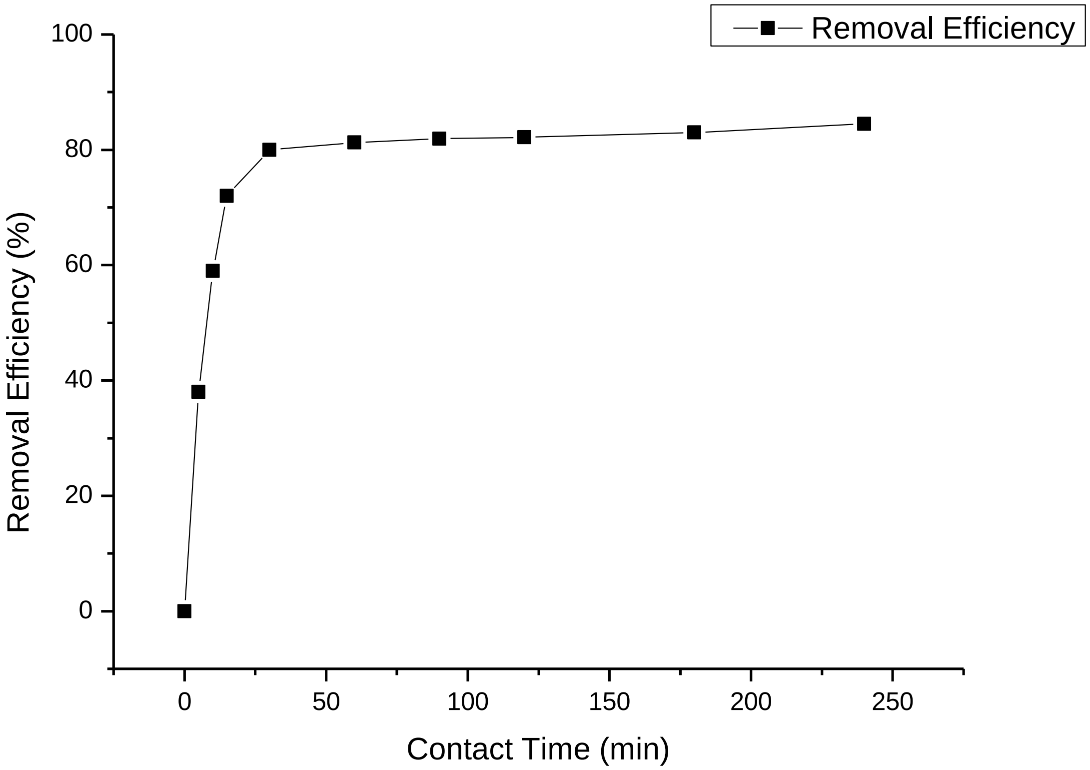
4.9.2 pH effect



In adsorption studies pH is one of the most fundamental factors because it can impact both the dye chemical structure in the liquid phase as well the surface of SiNps. pH variation was studied in the range of 2 – 12 using HCl and NaOH to set the solution at the desired pH. As per the graph a very strong dependence of dye adsorption on pH is shown. With the increase in pH from 2 to 7, the removal efficiency increased, however a further increase in the pH led to a decrease in the removal efficiency. This behavior can be explained as follows:

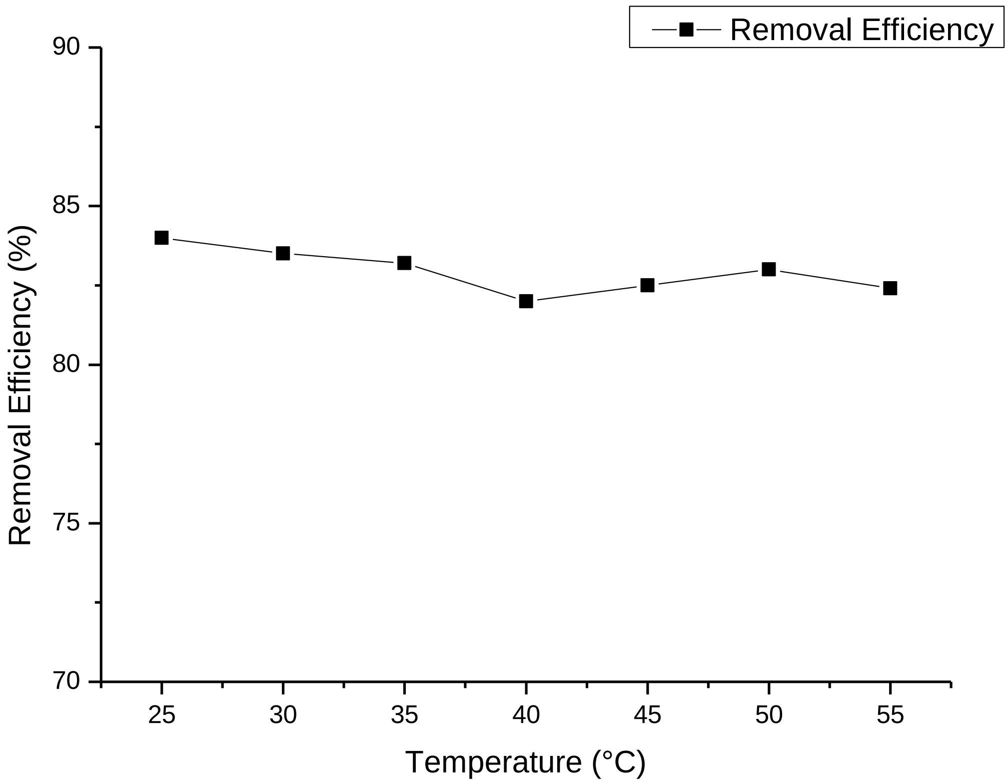
The pKa value of rhodamine 6G is 6.3 means that its molecule is cationic at a higher pH.SiNps have Si-O-Si neutral at ph 5, and Si-OH groups, the latter are deprotonated at pH 5. When the solution is in an acidic condition, these groups are either neutral or with a proton, and the rhodamine 6G molecules are repelled due to opposite charges or if absorbed through weak interactive forces. At pH 7, the adsorbent surface is deprotonated facilitating adsorption of cationic dye onto it. Basically the adsorption of rhodamine 6 G on SiNps is a hydrogen bond control adsorption. While in an alkaline solution, the hydrogen bond would be weaken between rhodamine 6G molecules and SiNps because there is an excess of hydroxyl groups which will enhance the repulsion. The OH groups will combine with the positive charge of the dye rhodamine 6G effecting its interaction with SiNps. Therefore, according to the results obtained, the optimum pH selected for further experiments is 7.

4.9.3 Contact time effect



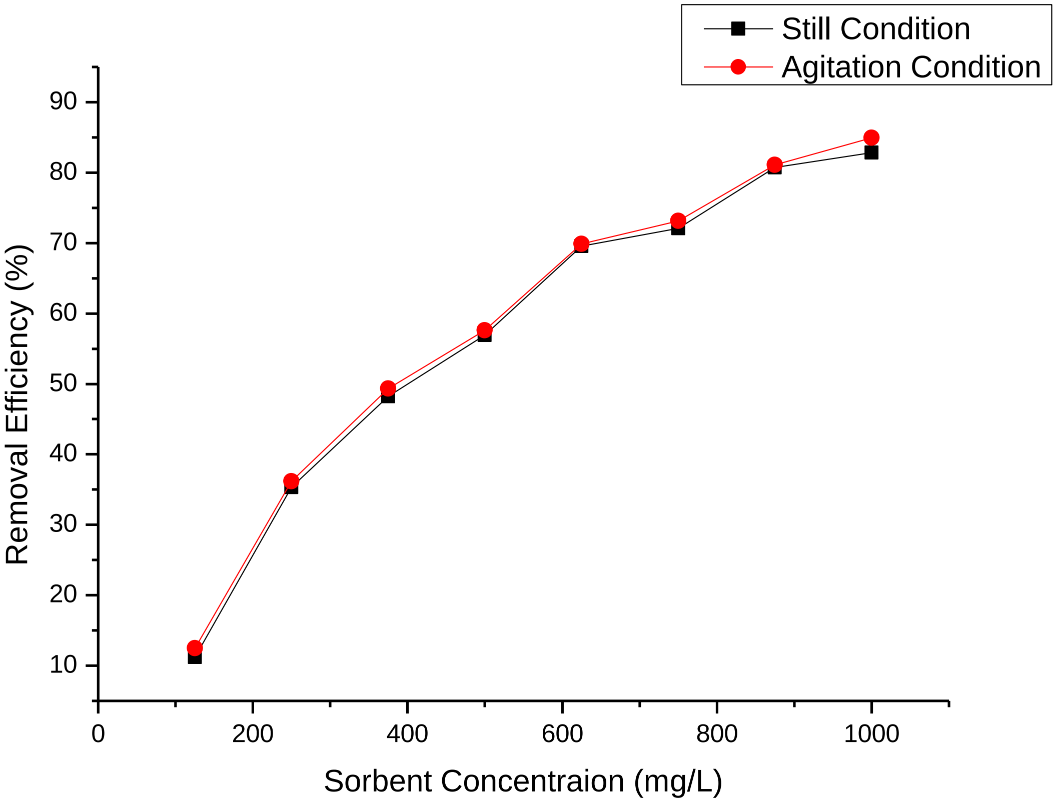
The time range studied in this work was a total of 240 minutes, while keeping the remaining factors fixed, it can be interpreted by the graph that adsorption reach an equilibrium at 30 minutes and slowly changes afterward.

4.9.4 Temperature effect

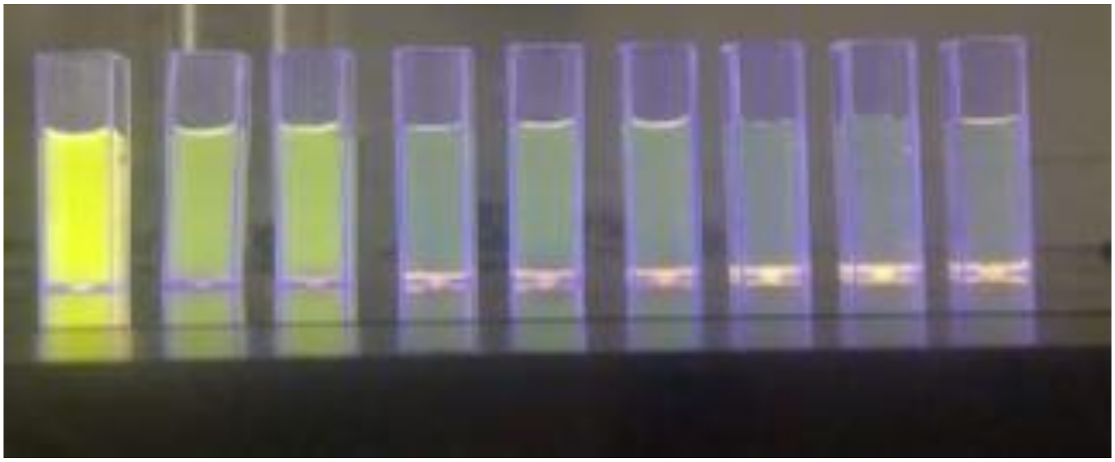


The room temperature 25°C was selected, because with the change in temperature no apparent changes in removal efficiency of dye occurs, therefore we can conclude that temperature has none to little effect on dye removal.

4.9.5 Agitation versus still effect



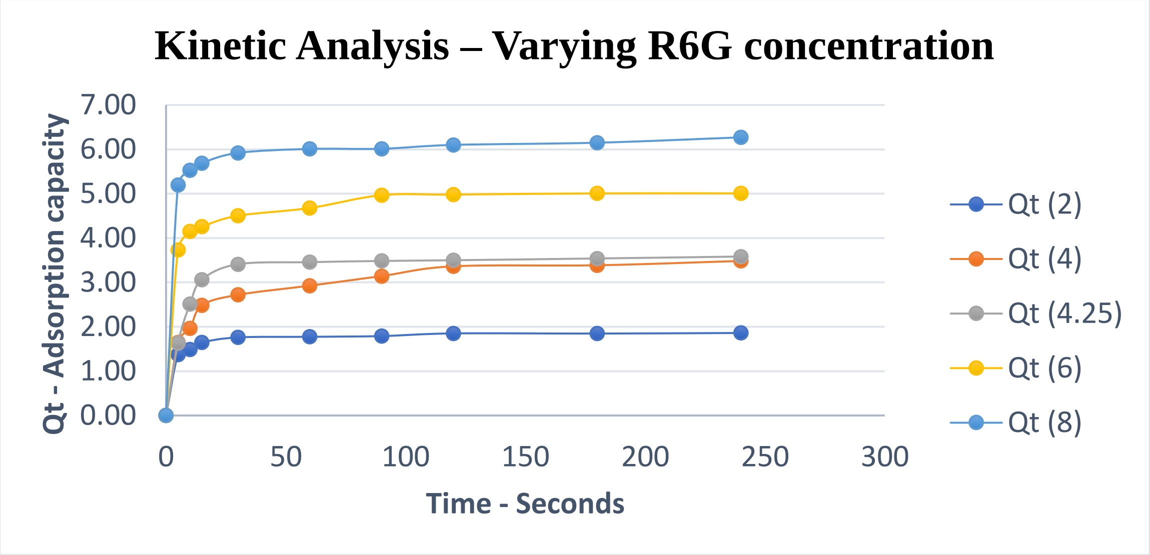
The agitation condition was also checked. As per the graph agitation condition gives better adsorption results, even though a very similar pattern is shown.



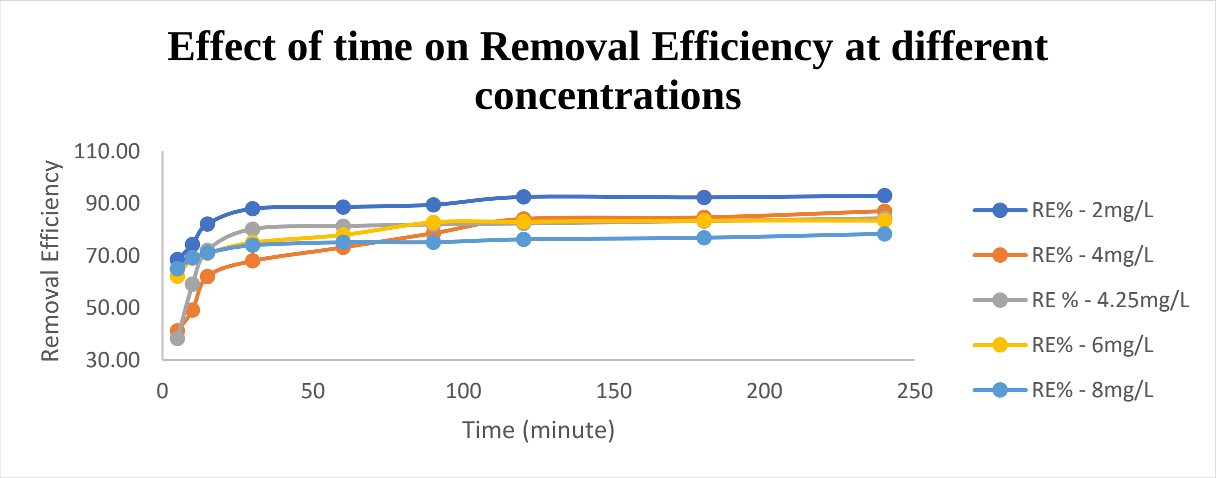
4.10 Kinetic Studies

Following equation were used to calculate the equilibrium adsorption capacity denominated as q_e

$$q_e = \frac{C_0 - C_e}{m} V$$

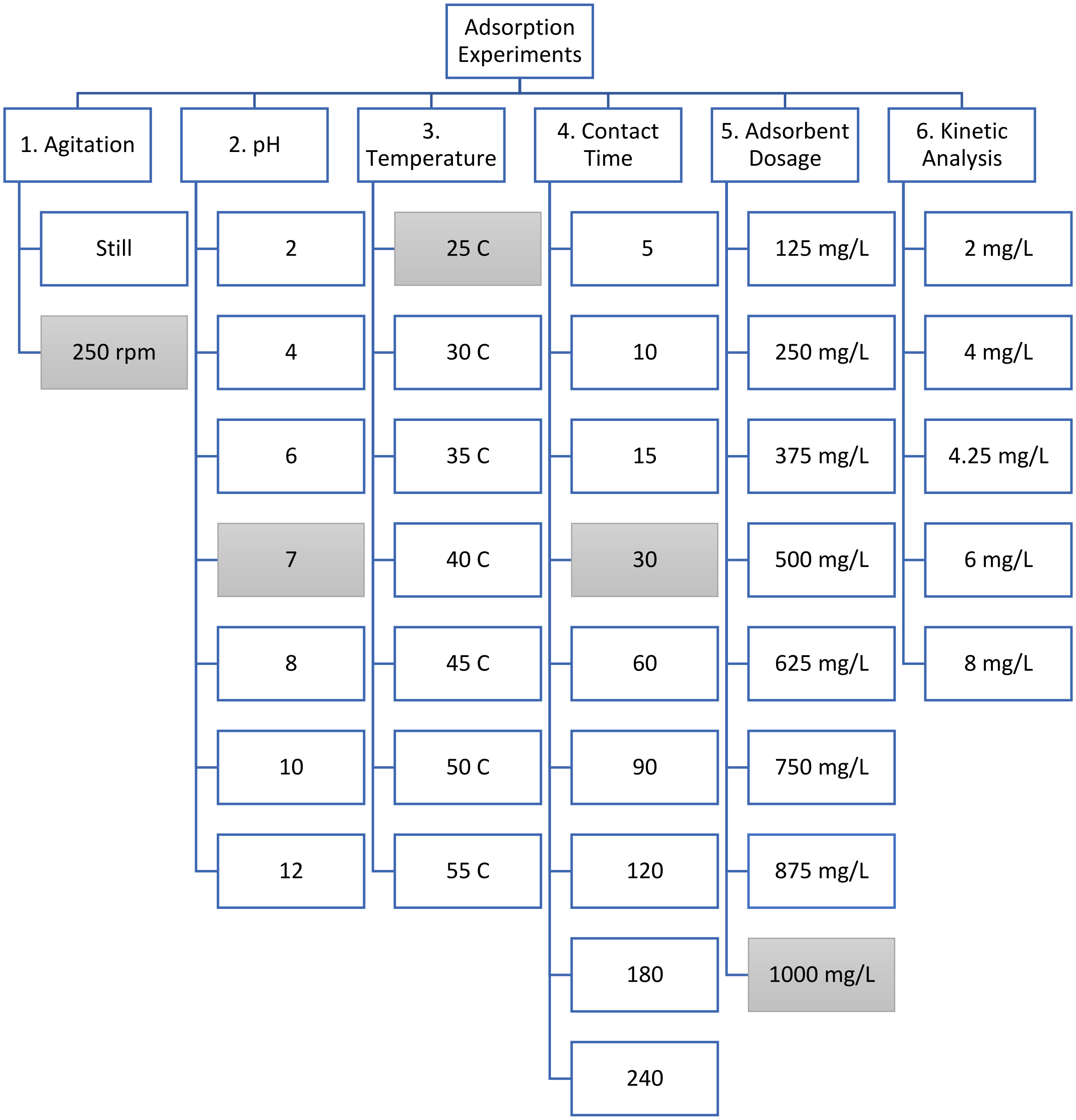


Following equation were used to calculate the equilibrium adsorption capacity denominated as q_e % Removal efficiency = (Co-Ce)/Co)*100



5 Conclusion

- 1. Optimized synthesis of silica nanoparticles were achieved
- 2. 84% removal efficiency was obtained (Rhodamine 6G adsorption on SiNPs)



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