Development of silica and paper based sensor for detection of heavy metal in water and it's applications.

PROJECT TO BE SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF SCIENCE

IN

CHEMISTRY

By

KRUTIKA .K. RATUL

Under the guidance of

Dr. KANCHANMALA DESHPANDE

To the

School Of Chemical Sciences

Goa University

Taleigao Plateau

Goa 403206

2020

CERTIFICATE

This is to certify that the project entitled “Development of silica and paper based sensor for detection of heavy metal in water and it’s applications”. submitted by Miss Krutika Ratul is a bonified work carried out in partial fulfilment of the degree of Master of Science, Goa University in the year 2019-2020. It is further certified that this project has not been the basis for any award of any other degree or diploma of any other university.

Project Guide:

Dr. Kanchanmala Deshpande

School of Chemical Sciences

Prof. V.S Nadkarni

Dean, School of Chemical Sciences

Goa University, Taleigao Plateau

Goa 403206, India

Goa University

DECLARATION

I hereby declare that the matter represented in this project work entitled ‘Development of silica and paper based sensor for detection of heavy metal in water and it’s application’ is based on the results of investigation carried out by me in the school of Chemical Sciences, Goa University under the guidance of Dr. Kanchanmala Deshpande and the same has not been submitted elsewhere for the reward of degree or diploma.

Place: Goa University
Date: /04/2020

Krutika .K. Ratul
Roll Number: CH-18-066
P. R. No.:201507092

ACKNOWLEDGMENT

This Dissertation required huge amount of work, research and dedication. Still, implementation would not have been possible if we did not have a support of many individuals. Therefore, I would like to extend my sincere gratitude to all of them.

First of all, I would like to thank our project guide Dr. Kanchanmala Deshpande for suggesting me the topic of the dissertation and her throughout guidance and encouragement during the dissertation work.

I am very thankful to Goa University for the chemical supply, apparatus and well-equipped laboratory. I would also like to thank the Dean of our Department Dr. V. S. Nadkarni.

I am also thankful to the Laboratory Assistant and Laboratory Attendant for their support.

Nevertheless, I express my gratitude toward my family and friends for their kind co-operation and encouragement which helped in completion of this project. Special thanks to my project partners for their constant support and help.

Table of Content

Chapter1: Introduction to thesis………………………………………6-16

Chapter2: literature review……………………………………………...24-30

Chapter3: experimental work and results…………………………… 31-54

Chapter4: conclusion...55

Bibliography…………………………………………………………..………56

Chapter 1: Introduction

Abstract

The development of selective and sensitive chemo sensors for the detection of metal ions has received considerable attention because of their important roles in medicine, living systems and the environment. Moreover, chromogenic receptors are especially attractive because the recognition process is accomplished with an easy-to-detect perceptible color evolution. Therefore, significant efforts have been carried out in the last years for developing the colorimetric chemo sensors for metal ions. There are numerous other analytical technique to detect presence of heavy metals such as AAS, but Unfortunately, these methods have their own limitations such as tedious sample pre-treatments and expensive instrumentation. Compared to these analytical strategies, colorimetric methods have attracted much attention to overcome these problems, allowing naked-eye detection of analyte.

INTRODUCTION

Iron contamination in environment

Some of the iron compounds may be hazardous to the environment; special attention should be given to plants, air and water. It is strongly advised not to let the chemical enter into the environment because it persists in the environment. Iron is a lustrous, ductile, malleable, silver-gray metal. It is known to exist in four distinct crystalline forms. Iron rusts in damp air, but not in dry air. It dissolves readily in dilute acids. Iron is chemically active and forms two major series of chemical compounds, the bivalent iron (II), or ferrous, compounds and the trivalent iron (III), or ferric, compounds Iron is believed to be the tenth most abundant element in the universe. Iron is also the most abundant (by mass, 34.6%) element making up the Earth; the concentration of iron in the various layers of the Earth ranges from high at the inner core to about 5% in the outer crust. Most of this iron is found in various iron oxides, such as the minerals hematite, magnetite, and taconite. Iron is essential to almost living things, from micro-organisms to humans. World production of new iron is over 500 million tones a year, and recycled iron add other 300 million tones. Economically workable reserves of iron ores exceed 100 billion tones. Seawater contains approximately 1-3 ppb of iron. The amount varies strongly, and is different in the Atlantic and the Pacific Ocean. Rivers contain approximately 0.5-1 ppm of iron, and groundwater contains 100 ppm.

Drinking water may not contain more than 200 ppb of iron.
Most algae contain between 20 and 200 ppm of iron, and some brown algae may accumulate up to 4000 ppm which may be present in extreme environmental conditions. The bio concentration factor of algae in seawater is approximately 10^4 - 10^5. Sea fish contain approximately 10-90 ppm and oyster tissue contains approximately 195 ppm of iron .Dissolved iron is mainly present as $Fe(OH)_2^+$ (aq) under acidic and neutral, oxygen-rich conditions ,Under oxygen-poor conditions it mainly occurs as binary iron. Iron is a part of many chelation complexes.

1.Iron ore mining in goa

Goa which is one of the smallest State of India exports around 50% of the total iron ore exported from the whole country. Iron ore which comprises a share of 95% of total mining and quarrying sector in Goa is 100% oriented to exports with China as the main buyer. After the exploitation the iron ore is carried out by trucks from the open cast mines to the jetties where the ore is discharged on the barges. Tertiary sector dominates the economic structure of Goa, followed by the secondary and primary sector in the third place. Although mining and quarrying contribution to Goa's GDP is around 5%, accounting all direct and indirect activities connected to mining activity, this industry represents the second most important industry next to tourism.Sesa Goa which is the main iron ore producing company exports about 50% of Goan iron ore. Theconsequences of this huge extraction material rate from mining are different environmental impacts such as pollution, water contamination, overburden dumps or health problems.

2.EFFECT OF MINING

2.1 RIVERS

The iron ore mining activity in Goa has left an adverse impact on the sediment of two major rivers in the state, which has ultimately affected the bottom-dwelling organisms in them, The study, conducted by Marine Science Department of the Goa University, has revealed that while the Bicholim river is "strongly polluted" with iron and manganese, the Mandovi river is "moderately polluted" with manganese and lead. Environmental parameters such as contamination factor, geo accumulation, enrichment factor and pollution load index were used to assess the extent of pollution.

FIG :1 EFFECT OF HIGH IRON IN RIVER

2.2 PLANTS:

Iron toxicity is not common, but some plants do secrete acids from the roots, which lowers soil pH. These plants can take up too much iron, leading to toxicity. The symptoms of iron toxicity include bronzing and stippling of leaves. The leaf discoloration is caused by the plant creating enzymes to control free radicals that are present in high iron levels. Some plants that are prone to iron toxicity include tomatoes, basil, phlox and impatiens. Rice place are one of the plant species that are quite effected by increase in amount of iron in the environment. The symptoms are characterized by the development of scattered reddish brown spots on the lower leaves; the spots spread over the leaves, the whole leaf becomes brown, and the lower leaves start to turn dark gray. Toxicity on iron can lead to shedding of leaves and eventually death of the place

FIG:2 IRON TOXICITY IN RICE PLANT

2.3 ANIMALS:

Although iron is the most common trace mineral, it is incredibly toxic to the tissues when there is too much in the blood. Iron poisoning is a common occurrence in dogs, and can be fatal if not treated right away. Iron toxicity is not always caused by medication but is also in heating pads, pesticides, fertilizer, and even oxygen absorbers that are found in dried or dehydrated foods. The iron is corrosive to the stomach and intestinal lining, causing bleeding and possibly abdominal perforation.. The iron attacks the liver, nervous system, heart, gastrointestinal and metabolic system because animals are not able to rid the body of excess iron. symptoms vary according to the amount of iron they ingested and how long it has been since ingestion. Toxicity in animals can be due to drinking of water contaminated with iron, or by eating plants which have high content of iron.

FIG: 3 ANIMALS EFFECTED BY HIGH IRON INTAKE

2.4 HUMAN BEINGS:

heavy metal in drinking water have been seen increasing which can have adverse effects on human health. The median iron concentration in rivers has been reported to be 0.7 mg/litre. In anaerobic groundwater where iron is in the form of iron(II), concentrations will usually be 0.5–10mg/litre, but concentrations up to 50 mg/litre can sometimes be found . Concentrations of iron in drinking-water are normally less than 0.3 mg/litre but may be higher in countries where various iron salts are used as coagulating agents in water-treatment plants and where cast iron, steel, and galvanized iron pipes are used for water distribution..

Chronic iron overload results primarily from a genetic disorder (haemochromatosis) characterized by increased iron absorption and from diseases that require frequent transfusions. Adults have often taken iron supplements for extended periods without deleterious effects ,and an intake of 0.4–1 mg/kg of body weight per day is unlikely to cause adverse effects in healthy persons)unlikely to cause adverse effects in healthy persons. But in many cases prolonged intake of iron can cause depression, rapid and shallow respiration, coma, convulsions, respiratory failure, and cardiac arrest.

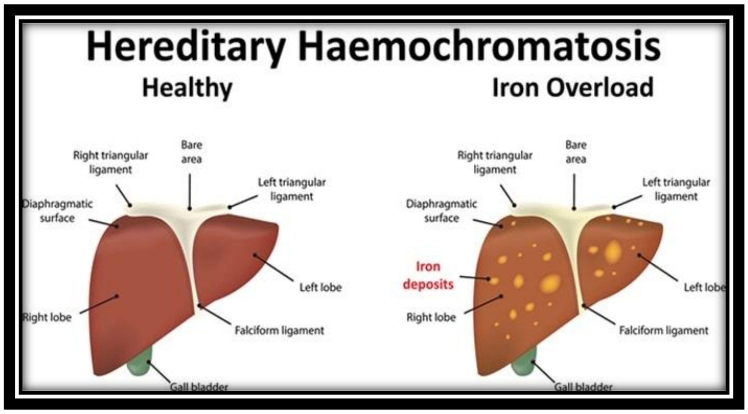


FIG:4 IRON OVERLOAD

Iron toxicity in human beings is mostly due to drinking of iron contaminated water ,eating of plants or animals which have hight toxicity of iron. People living in mining areas undergo a lot of diseases as the water in those areas contain higher level of heavy metals .

3.PERMISSIBLE LIMIT OF IRON IN DIFFERENT MATRIX

The permissible exposure limit (PEL or OSHA PEL) is a legal limit in the United States for exposure of an employee to a chemical substance or physical agent such as high level noise. Permissible exposure limits are established by the Occupational Safety and Health Administration (OSHA). Most of OSHA’s PELs were issued shortly after adoption of the Occupational Safety and Health

Matrix	**Permissible limit**

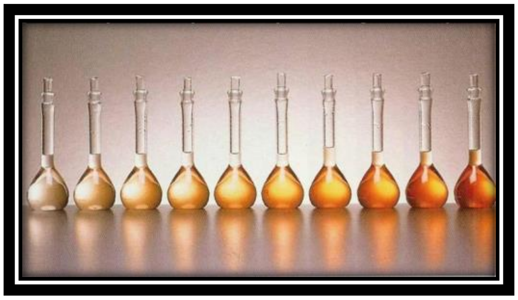
Plants	100mg/kg
Animals	10mg/body weight
Human being/body weight	Man-20mg/day,women-18mg/day, children - 16.3mg/day
Water	1-3mg/L
Soil	100mg/kg

4.COMMON ANALYTICAL TECHNIQUE USED FOR DETERMINATION OF IRON IN WATER

4.1 Colorimetric determination of iron in water

In this method total amount of iron can be determined by titrating iron solution against thiocyanate in acidic medium. Make the presence of these ions in solution visible, thiocyanate ions (SCN^-) are added. These react with the Fe^{3+} ions to form a blood-red coloured complex:

REACTION: $Fe^{+3}{}_{(aq)} + SCN^{-}{}_{(aq)}\ HNO_3 \rightarrow FeSCN^{+2}{}_{(aq)}$



4.2 Spectrometric determination of iron in water

A commonly used method for the determination of trace amounts of iron involves
the complexation of Fe^{2+} with 1,10-phenanthroline (phen) to produce an intensely red orange colored complex: Fe^{2+} + 3 phen gives $Fe(phen)_3{}^{2+}$

Since the iron present in the water predominantly exists as Fe^{3+}, it is necessary to first reduce Fe^{3+} to Fe^{2+}. This is accomplished by the addition of the reducing agent hydroxylamine. An excess of reducing agent is needed to maintain iron in the +2 state (because dissolved oxygen will reoxidize Fe2+ to Fe3+). Fe2+ is quantitatively complexed by 1,10-phenanthroline in the pH range from 3 to 9. Sodium acetate is used as a buffer to maintain a constant pH at 3.5. If the pH is too high, the Fe2+ will be oxidized to Fe3+; if the pH is too low, H+ will compete with Fe2+ for the basic 1,10-phenanthroline (to form phenH+). Either way, you won't get complete complexation. You should discuss these possible problems and their impact in the Introduction section of your report. The determination of the iron-phen complex is performed with a spectrophotometer at a fixed wavelength of 508 nm using external calibration based on iron standard solutions.

4.3 Determination of iron content in water using AAS and FIS

The most common analysis method for the determining the concentration of metal ions in solution uses the atomic absorption spectrometer. In this method, solutions containing the metal ion of interest are aspirated into a nebulizer to divide the sample into a fine aerosol. The aerosol is then swept into a flame where it is desolvated. The metal-containing particles are then vaporized and atomized. The concentration of metal atoms in the flame is then determined by rationing the intensity of light incident on the flame with that exiting the flame at a wavelength specific for the metal of interest. A hollow cathode containing the metal of interest is an essential component for this experiment. The concentration of iron is often determined by atomic absorption spectroscopy.

5.LIMITATIONS OF THESE ANALYTICAL TECHNIQUES

Colorimetry

- The major disadvantage of colorimetry is that colorless compounds cannot be analyzed..
- It needs more amount of sample for analysis.
- You require preparing a standard solution.
- Its sensitivity is low.
- The same colors from interfering material may create errors in results.
- The precise wavelength bandwidth may be required for more accurate analysis.
- The interference with the matrix can lead to poor results in uncontrolled conditions

Spectrometry

The major disadvantage of this technique is that colorless compounds cannot be analyzed ,Sensitive is less for lower concentration and Conditioning of the instrument is required.

Atomic absorption spectrometry

AAS is an expensive technique, it requires skilled operator to handle all the required operation, gives low throughput, solid samples cannot be analyzed. Cathode lamp used in AAS is expensive, low precision. Conditioning of instrumentation is required.

Chemical sensor over existing analytical technique

Chemical sensor is a portable device which allows field work analysis, it is inexpensive then other analytical technique, no professional skills personals are required, they are environment friendly, does not require conditioning, they are highly sensitive, can be seen through naked eyes.

6.CHEMICAL SENSOR

The ideal chemical sensor is an inexpensive, portable, foolproof device that responds with perfect and instantaneous selectively to a particular target. Chemical substance (analyte) present in any desired medium in order to produce a measurable signal output at any required analyte concentration. The sensitivity and selectively aspects of the chemical sensing are affected by the phase. Dimensional and Temporal aspect of the desired determination. The analyte can be present in a gas, liquid or solid phase on various dimensional scale ranging from bulk volumes of liters to picoliters, or surface layers from nanoscopic to monomolecular scale. It may also be persistent or transitory. A further set of requirements can originate from a need for repetitive measurements of the analyte over long times (example days, months) or at multiple and perhaps remote location, such as in environmental analysis and personal monitoring. The design of chemical sensors also requires appreciation of the needed degree of quantitative reliability (precision or accuracy).

6.1 OPTICAL CHEMICAL SENSOR

Optical sensor is a device which consists of following components.

i. The recognition analyte: where specific interaction between sensor and analyte takes place.

ii. Transducer element/ reagent: it converts the recognized signal in some measurable optical signal.

iii. An optical device: it consists of a light source, it detects the change of signal and converts it. The optical device can measure properties such as absorbance, reflectance, luminescence, light polarization and others

7. DEVELOPMENT OF SENSOR

Compared to these analytical strategies, colorimetric methods have attracted much attention to overcome these problems, allowing naked-eye detection of analyte. In spite of these advantages, the colorimetric chemosensors for iron ions are very rare. Iron is the most abundant essential trace element in the human body. Both Fe2+ and Fe3+ play vital roles in many biological processes. Many biochemical processes at the cellular level, such as oxygen transportation and DNA synthesis, involve electron transfer between the two oxidation states of iron . However, iron deficiency leads to anaemia, liver and kidney damages, diabetes, and heart diseases. Therefore, great efforts have been made to develop suitable detection methods for iron. However, sensors capable of detecting Fe2+ by the naked eye in aqueous media are rare.

7.1 NEED FOR SENSOR

Development of sensor for heavy metals such as iron and manganese can be very challenging since its detection limit is very low(0.5mg/l). It is necessary to develop a sensor for detection of such heavy metal to the lowest permissible limit to avoid toxicity in case of prolonged exposure.

7.2 SENSOR

Chemical sensor: is a device that can immediately transform chemical signal into some analytically detectable signal when comes in contact with specific compounds or ions in complex samples. Chemical sensors can be used in many fields such as medicine, environmental pollutions, and many more.

Environmental pollution sensor: Chemical sensors are expected to play a very important role in environmental monitoring (both indoor and outdoor) and environmental control (air, water), facilitating a better quality of life. Chemical sensor consists of a sensing layer which chemically responds to the presence of particular chemical species

Criteria for the sensor

- Sensor should be economical. That is of low cost.
- It should be easily recycled and reuse.
- It should not give toxic effect to the water in which it is used.
- One should be able to use it even in field work

- Color change should be visible and differentiate well.

8. COLORIMETRIC SENSOR

Colorimetric analysis is a method of determining the concentration of a chemical element or chemical compound in a solution with the aid of a color reagent. It is applicable to both organic compounds and inorganic compounds and may be used with or without an enzymatic stage.Colorimetric sensors became more popular and widespread due to high accessibility, ease of use, and low cost together with sensitive and selective response toward various analytes. Colorimetric sensors are a class of optical sensors that change their color when influenced by external stimuli. Any change in a physical or chemical environment can be considered as such stimulus. Therefore a change in a property of the environment that is needed to be detected defines the design of the particular colorimetric sensor. Compared with other methods, the colorimetric method has some obvious advantages, such as low cost, simple instruments (or, in the case of naked eye detection, no instruments), and can be qualitatively or semi qualitatively identified by the naked eye. However, colorimetry is generally less sensitive. Despite the challenges, colorimetric sensor shave been widely accepted for its high sensitive and selective response towards various analytes. ... Multilayer of biomaterials were used as a platform where reflection and interference of scattering light occur due to which color change happens leading to rapid.

Advantages

- Fast, inexpensive, light weight and potable.
- Small sample size
- Minimal instrumentation and power needed.
- Ability to customize array of specific analytes.
- Respond to wide range of analyte.
- Potential to analyze vapor or liquid sample.
- Flexible array size.

Application

Colorimetric chemosensor have wide range of applications ,the most important once are

- Used in detection of different heavy metal which may lead to toxicity in the environment
- To detect presence of trace metal in food and water.
- To detect cyanide and Cobalt ion in water.

OBJECTIVE

Simple methods for the determination of Fe in natural and mineral waters is has gained wide attention due to many drawback of the existing analytical technique. There are numerous Analytical method which can determine Fe but are very expensive, require excessive sample pre treatment, there are various expensive instruments which require professional skilled person to operate them, large amount of chemical are used for these method which leads to pollution. Power consumption required is very high. To over come all these limitations there is a need if an cost effective, reusable, easy to use ,which works with less power and eco-friendly.

Chapter 2: Literature Review

SUPPORTING MATERIALS USED

MESOPORUS SILICA

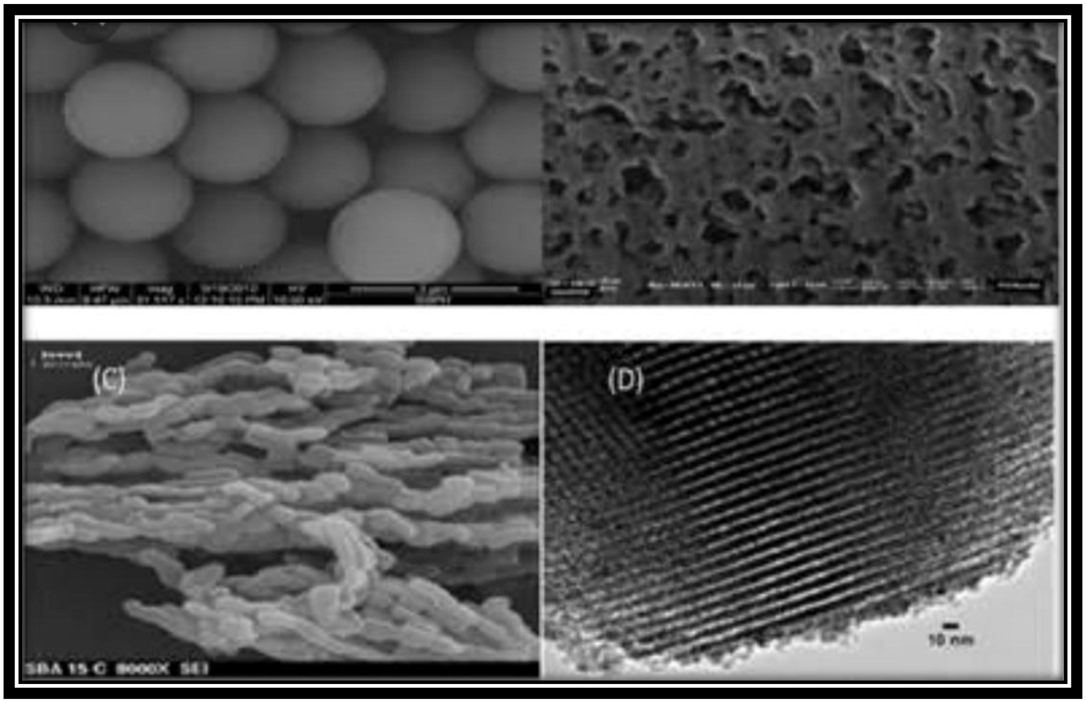


FIG:5 Surface of MCM-41

Mesoporous silica is a mesoporous form of silica and a recent development in nanotechnology. The most common types of mesoporous nanoparticles are MCM-41 and SBA-15. Research continues on the particles, which have applications in catalysis, drug delivery and imaging. Since optical sensors in these studies consist of an indicator, it should be fixed to a surface so that it can be reused for further detection. Thus silica and mesoporous silica is used as a supporting medium. The indicator can be immobilized, dopped or grafted on the silica surface and in the pores of mesoporous silica, which can be then used for an optical sensor or as an optical chemical sensor. Since silica has silanol groups or –OH groups on it, it either chemically binds or simply provides a surface to adsorb the indicator on it. (Ref: IR spectra No Sample_S3 of mesoporous silica: it shows a broad peak at 3404.36cm-1for -OH)

According to literatures the mesoporous material has pore size in between 2 – 50nm. Microporous materials have lower pore size compared to mesoporous material i.e. <2nm. Whereas macroporous materials i.e. >50nm. Mobil Crystalline Material/ Mobil Composition of Matter.

It was discovered in 1992 by Mobil company. It has a honeycomb like structure. Due to the large open pore and large surface area they are widely used as support material for optical sensing.

Advantage of silica

mostly used nanomaterials to build pH nanosensor. Silica nanoparticles are optically transparent, of low toxicity, inert to pH, and (some are) degradable. the rapid development of silica technology makes silica nanoparticles with different sizes and surface functionalities readily available with affordable price. More attractively, their surface can be easily functionalized via the well-established silane technology. Silica can be easily modified and it is reusable so it decrease the cost of this technique making it cost effective.

Application

Silica-nanobead-based sensing systems have been developed and employed in various analytical and bioanalytical applications due to their attractive features, such as ideal modifiable surface, effective combining capacity with other nanomaterials, and good biocompatibility. The typical construction of silica-nanobead-based sensors includes the preparation of silica nanobead and is followed by surface-chemistry modifications **.**The low conductivity of silica provides a method for monitoring humidity by measuring the change in conductivity. Water molecules interact with hydroxyl sites providing a base for physisorption of water layers as relative humidity increases. For a dry surface at relatively low humidity, conductance occurs through proton “hopping” between the adsorption sites. At higher humidity, water concentrates to form multilayers or condenses to fill a pore. Proton mobility, therefore, becomes more facile and conductivity increases with protons moving from molecule to molecule (Grotthus chain reaction model). A mesopore structure increases the surface area and number of hydroxyl groups available for water adsorption. This is the basis for the investigation of mesoporous silicate thin films as relative humidity sensors.

A few reports have demonstrated the versatility of mesoporous silicates as active components in pH sensing. These applications typically involve immobilizing an indicating dye on a mesoporous surface or encapsulating it in silicate walls. Incorporation of the dyes on the surface can be accomplished during synthesis or in a post-synthesis grafting process. Fluorescein isothiocyanate (FITC) has been modified with an amino-bearing siloxane to provide a precursor for direct mesoporous material synthesis. The result is a material with FITC on the pore walls which is responsive to pH changes in the range from 3.1 to 11.2 that can be interrogated through laser excited photoluminescence

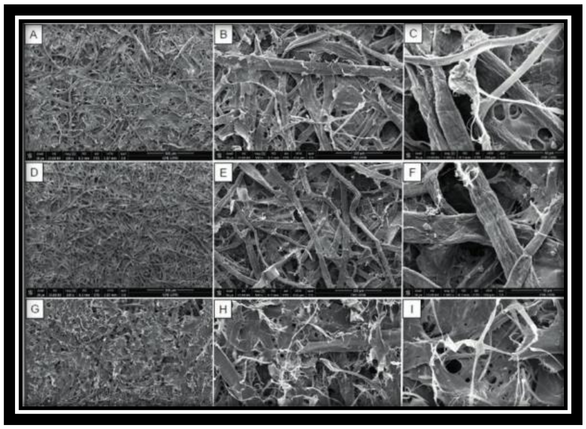
The copper sensitive material described in the previous section is one example among many of mesoporous silica's synthesized for adsorbing and sensing metal cations. Most efforts at cation sensing have relied on either optical or electrochemical sensing methods for detection.

Frequently, optical detection of cations relies on dye incorporated into mesoporous materials. Interrogation can be accomplished by absorbance or fluorescence measurements. Less commonly, phosphorescence intensities and lifetimes are employed. Some materials may exhibit vivid color changes when exposed to targets providing potential for the design of sensors for interrogation by the naked eye. The mesoporous materials provide high surface area and controlled pore sizes while limiting site accessibility. The limited accessibility can help to shield the dyes from interferents and fouling. Siliated b-diketone was used to modify pore surfaces in ordered mesostructures. The resulting materials were used for the detection of Cu^{2+}, Fe^{3+}, and U^{6+} as indicated by changes in the UV-visible absorption spectrum of the dye. A detection limit of 1 ppm was reported for U^{6+}.

PAPER

Paper is a versatile, flexible, porous, and eco-friendly substrate that is utilized in the fabrication of low-cost devices and biosensors for rapid detection of analysts of interest. Paper-based sensors provide affordable platforms for simple, accurate, and rapid detection of diseases, in addition to monitoring food quality, environmental and sun exposure, and detection of pathogens. Paper-based devices provide an inexpensive technology for fabrication of simple and portable diagnostic systems that can be immensely useful in resource-limited settings, such as in developing countries or austere environments, where fully-equipped facilities and highly trained medical staff are absent. Paper based sensor makes it even easy for a analyst to work in field areas without any laboratory setup or equipment.

FIG:6 Surface image of paper



Advantage of paper based sensor

Paper based sensor are eco-friendly, no professional skills analyst are required to perform the analysis, Paper-based sensors offer users the possibility to produce simple, mass-scalable devices at an affordable cost. However, in order to create an analytical device, suitable transduction methods are necessary which may require additional reagents, materials and instrumentation at further cost and complexity. In order to maintain simplicity, affordability and portability, low power techniques such as optical and electrochemical methods are well suited as transducers. The five most commonly reported techniques for quantitative analysis on paper are colorimetric electrochemical, chemiluminescence, electrochemiluminescence and electrical conductivity

Applications

Colorimetric detection has been widely used in paper-based microfluidic devices This is perhaps the simplest of techniques as a change in colour may be visualized by eye due to an enzymatic or chemical interaction. Martinez et al. first demonstrated paper-based microfluidic devices for the colorimetric detection of glucose and protein. The investigation was based on a change in colour when introduction of the sample filled the reaction zone. For the glucose assay, a positive result was observed when the colour shifted from clear to brown which was mainly due to the enzymatic oxidation of iodide to iodine whereas for the protein assay, a positive result was indicated by a colour change of tetrabromophenol blue from yellow to blue. Recently, some scientist demonstrated the colorimetric detection of copper using silver nanoparticles (AgNP) on paper devices. The paper-based devices were fabricated by immobilising AgNPs functionalised with homocysteine (Hcy) and dithiothreitol (DTT) in the test zone. Once the sensor was fabricated, the copper solution was dropped onto the loading zone and the liquid was transported to the test zone. A colour change was observed upon copper-induced aggregation of Hcy-DTT-AgNPs through binding of copper to the carboxyl and amino functional groups on Hcy and DTT. Here the limit of detection by the naked eye is 7.8 nM.

Electrochemical techniques often require a three-electrode system, that is, a counter electrode, reference electrode and working electrode. In creating a paper-based electrochemical sensor, a three-electrode system is replicated on paper. This means that such a sensor could replace the traditional electro analytical method where expensive solid state electrodes are required.

Chemiluminescence and electrochemiluminescence are analysis methods that have also been successfully performed on paper-based sensing devices. These techniques have gained attention due to their simplicity, low cost and high sensitivity. Yu et al. [7] demonstrated a microfluidic paper-based device for the detection of glucose and uric acid based on the chemiluminescence reaction between a rhodamine derivative and hydrogen peroxide. The paper device consisted of an injection hole for introducing the sample to the filter paper, two bioactive channels where the enzymes (glucose oxidase and urate oxidase) were immobilised and two chemiluminescent detection areas containing the rhodamine derivatives. All the components were integrated between two water impermeable single-sided adhesive tapes. Interaction of a sample containing glucose or uric acid with the oxidase enzymes, produced hydrogen peroxide, which in turn interacted with the rhodamine derivatives to produce chemiluminescence.

IMMOBILIZATION TECHNIQUES

It is a method where the indicator is either coated on the surface of the material or doped or chemically bonded to the supporting material via any bonds. It is important to do this since it sometimes play an very important role in influencing the sensing characteristics.

i. Impregnation: the indicator is immobilized on supporting mesoporous material by either physical adsorption, chemisorption or electrostatic holding. This can be achieved by simply agitating the mixture containing the supporting mesoporous material along with the indicator. This is not a stable sensor since the indicator can leach out easily. That is it can lose some of the indicator.
ii. Covalent bonding: in this case the indicator and the supporting material can be chosen very carefully which is having functional groups which can then chemically bond together. These have good stability towards leaching. But this technique may lower the sensitivity of the technique.
iii. Doping: in this case the indicator is added during the initial stages of supporting material synthesis. This technique works well in holding the indicator material from initial stage.

Chapter3: Experimental Work and Results

EXPERIMENTAL WORK AND RESULTS

3.1 SYNTHESIS OF SUPPORT MATERIAL: MCM-41 AND CHARACTERISATION

Procedure:

1.922g of CTAB was weighed and dissolved in 89.2mL of distilled water. 5.3mL of 25% of ammonia solution was added to it after 5minutes. The mixture was kept on magnetic stirrer for 30minutes for homogenized mixture. 7.4mL of TEOS was added to this mixture after 30minutes. And it was kept for stirring for 4hours. Ones the 4hour stirring was over it was kept for aging for 24hours. And then it was filtered and residue was washed with 150mL distilled water. The residue was than kept for drying for 24hours at 100^{o}C. The dried residue was then calcined at 550^{o}C.This synthesized MCM-41 was characterized by IR spectroscopy. **MCM-41 was synthesized multiple times when required.**

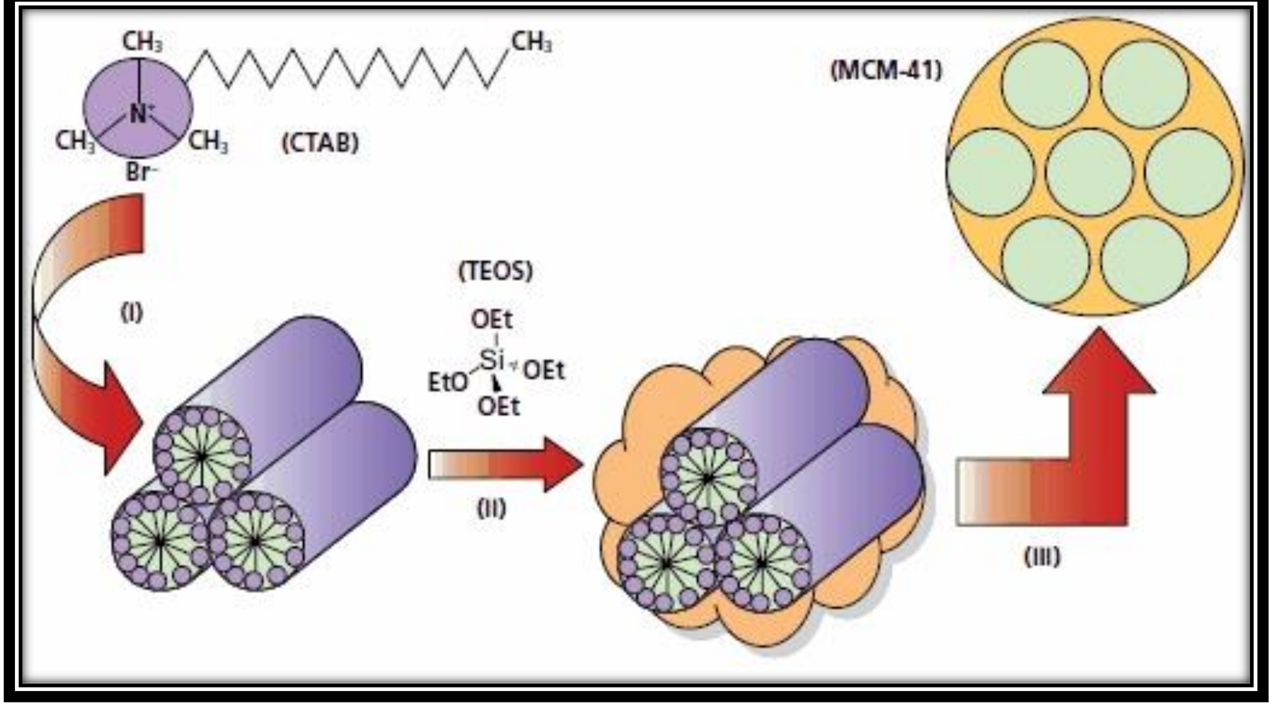


FIG:7 Synthesis of MCM-41 represented in form of figure

Results

11 batches of MCM-41 was synthesized by this sol gel method.

- Weight of MCM-41 obtained for batch 1= 1.982g approx.
- Weight of MCM-41 obtained for batch 2= 1.997g approx.
- Weight of MCM-41 obtained for batch 3= 2g approx.
- Weight of MCM-41 obtained for batch 4= 1.902g approx.
- Weight of MCM-41 obtained for batch 5= 1.988g approx.
- Weight of MCM-41 obtained for batch 6= 2g approx.
- Weight of MCM-41 obtained for batch 7= 1.974g approx.
- Weight of MCM-41 obtained for batch 8= 1.882g approx.
- Weight of MCM-41 obtained for batch 9= 1.644g approx.
- Weight of MCM-41 obtained for batch 10=1.990g approx.
- Weight of MCM-41 obtained for batch 11= 2g approx.

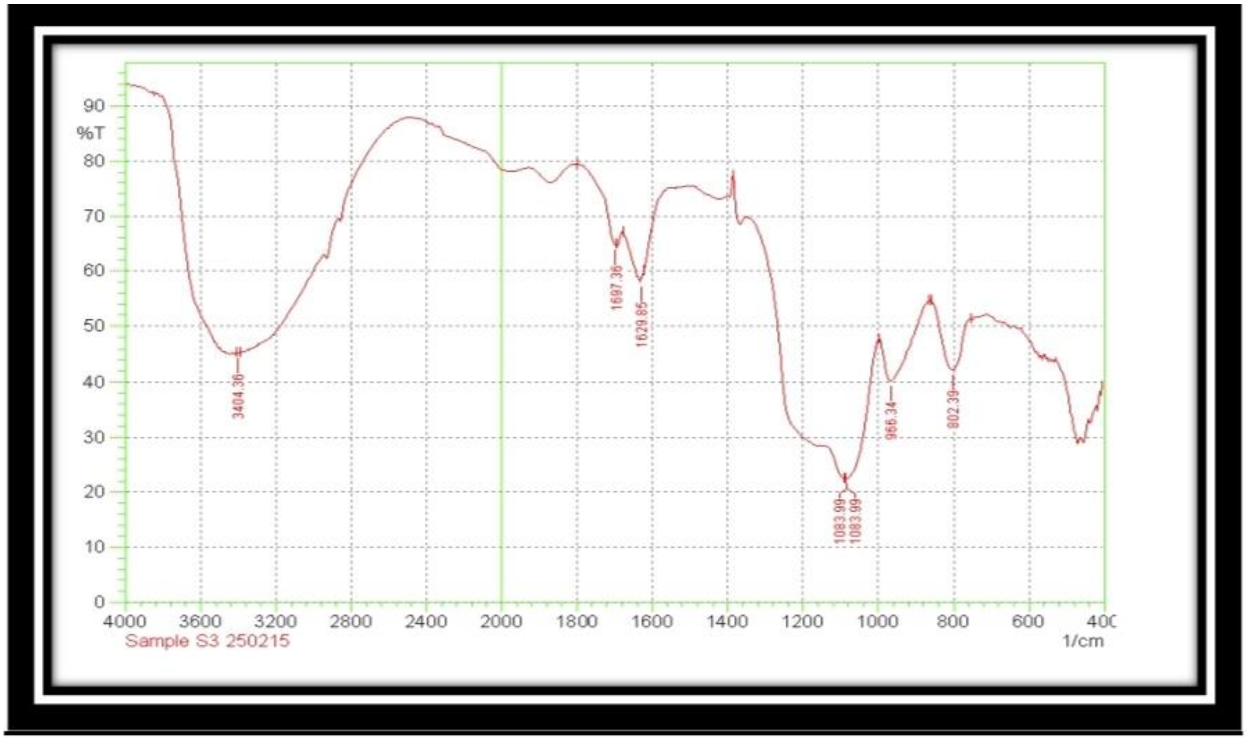


FIG:8 IR spectra for MCM-41.

Inference: IR 3404.36cm-1broad: -OH stretch

3.2 FUNCTIONALISATIONOF MCM-41.

HCl FUNCTIONALISATION

- 1g of mesoporous silica was weighed and taken in 500mL round bottom flask.
- To it 100mL 0.1N HCl was added.
- It was refluxed for 12 hours.
- It was than filtered and washed with distilled water.
- It was then air dried.
- It was characterized by IR

FIG:10 HCl FUNCTIONALISATION.

Reaction:- $SiO_2 + HCl \rightarrow SiCl_4 + 2H_2O$

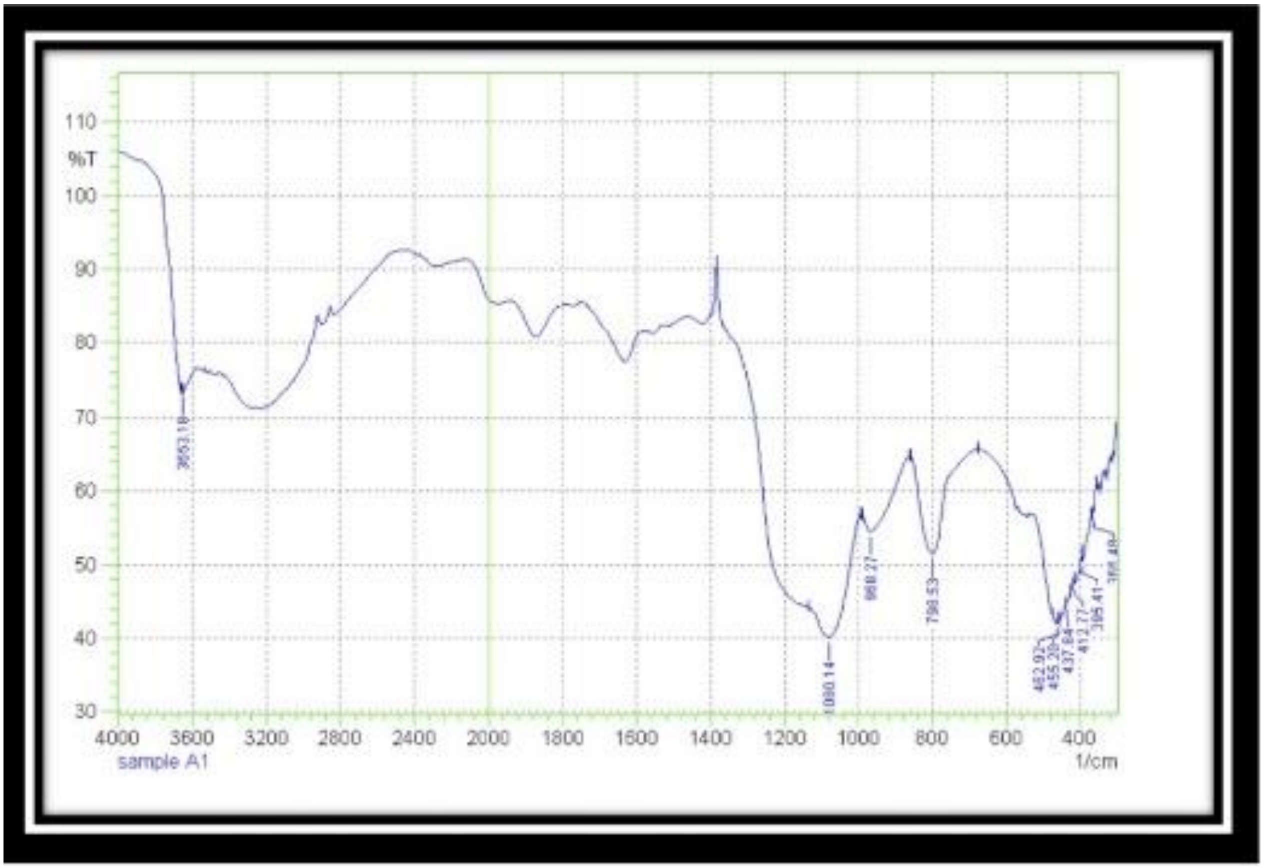


Fig:11. IR spectrum of HCl functionalized MCM-41

3.3 APTES FUNCTIONALISATION

- 1g of mesoporous silica was weighed and taken in 250mL round bottom flask.
- To it 25mL of dry toluene along with 16mmol APTES was added .
- It was stirred and heated at 110oC for 12 hours.
- It was then filtered and washed with isopropyl alcohol
- It was characterized by IR

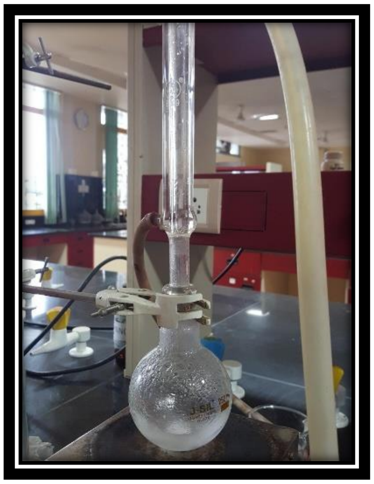


FIG: 12. APTES FUCTIONALISATION

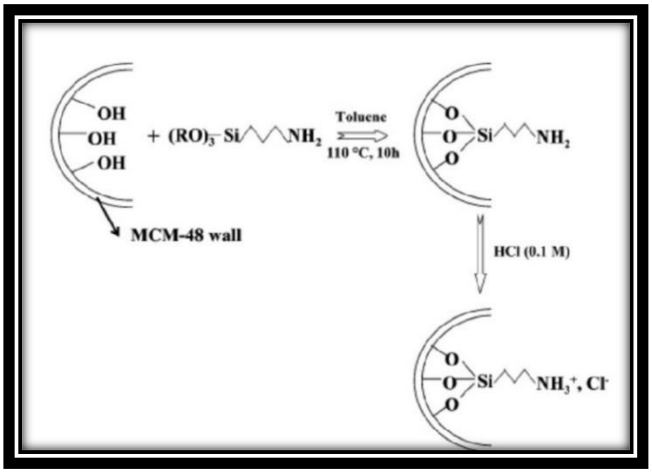


FIG:13 fictionalization of MCM-41

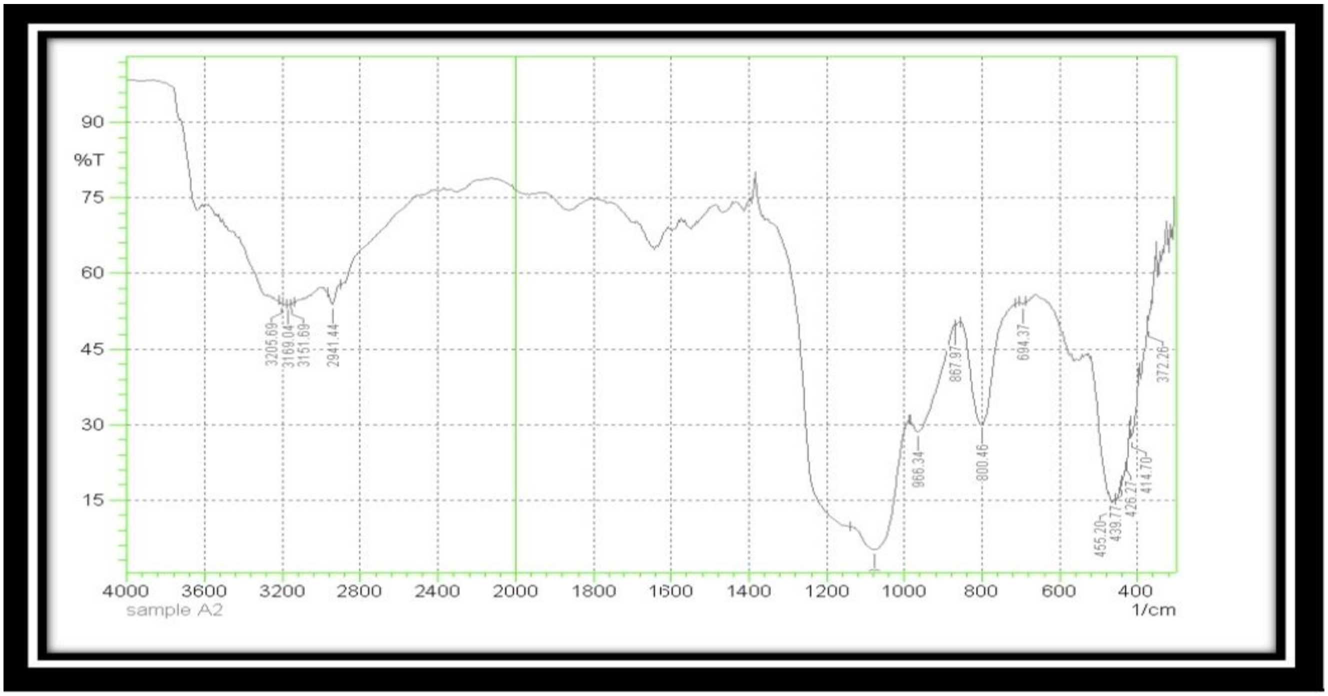


Fig: 14 APTES functionalized MCM-41

3.4 MESOPOROUS SILICA USED AS OPTICAL SENSOR

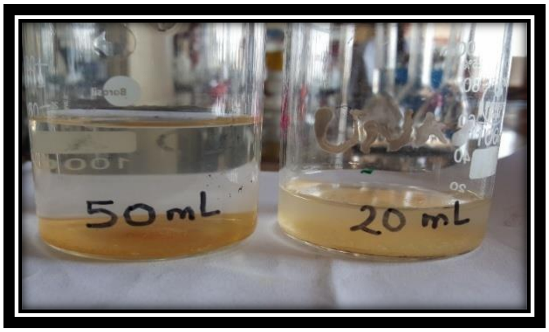
Since mesoporous silica MCM-42 has high porosity, exceptional adsorption capacity, they can be used as chemical sensor since we can immobilize the indicator on the porous MCM-4

SENSOR FOR IRON IN LIQUID MATRIX.

REQUIREMENTS: 40%KSCN , breakers, conc HCl.

2g of functionalised MCM-41 was taken in a beakers. To this 100 mL of potassium thiocyanate solution was added. This content was kept for 24hrs. The silica was filtered and dried. In two different beaker ,20ppm and 50ppm FAS solution was taken respectively. The pH was adjusted to 1 by adding few drops on concerned HCl. Now to each of this beaker 1g of silica previous coated with ligand KSCN was added. The color of the silica changed from white to orange ensuring the detection of iron. The intensity of the color was determined by the software imageJ.

ImageJ: It supports standard image processing functions such as logical and arithmetical operations between images, contrast manipulation, intensity of color, convolution, Fourier analysis, sharpening, smoothing, edge detection, and median filtering. It does geometric transformations such as scaling, rotation, and flips.



Result:

Weight of silica (in g)	Concentration of Iron (in ppm)	Color intensity
1g	20ppm	133.54
1g	30ppm	140.1

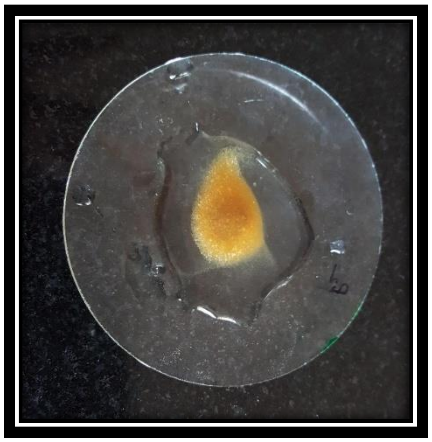


Fig:16 Silica indicating presence of iron(50ppm)

3.5 CALIBRATION CURVE FOR ANALYSIS OF IRON(III)

CHEMICALS: 10ppm iron (III) solution (FAS), 40% potassium thoicyanide solution, 4N nitric acid.

INSTRUMENT: UV-Visible spectrophotometer.

PROCEDURE:

Different concentrations of Fe(III) solution were prepared by pipetting out different volumes of the FAS solution in standard volumetric flasks.

To this thiocyanate solution and 4N HNO_3 was added using a micropipette.

The solutions were diluted unto 1mL with distill water.

The absorbance was recorded at 480nm using the UV-Visible spectrophotometer.

REACTION: $Fe^{+3}_{(aq)} + 6SCN^{-}_{(aq)} + HNO_3 \rightarrow FeSCN^{+2}_{(aq)}$

Result:

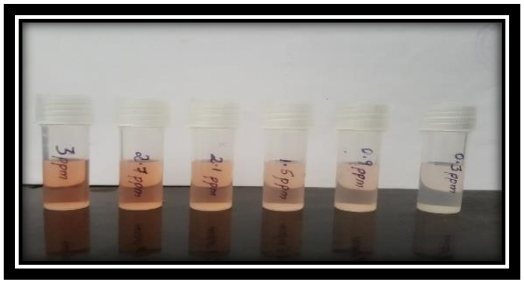
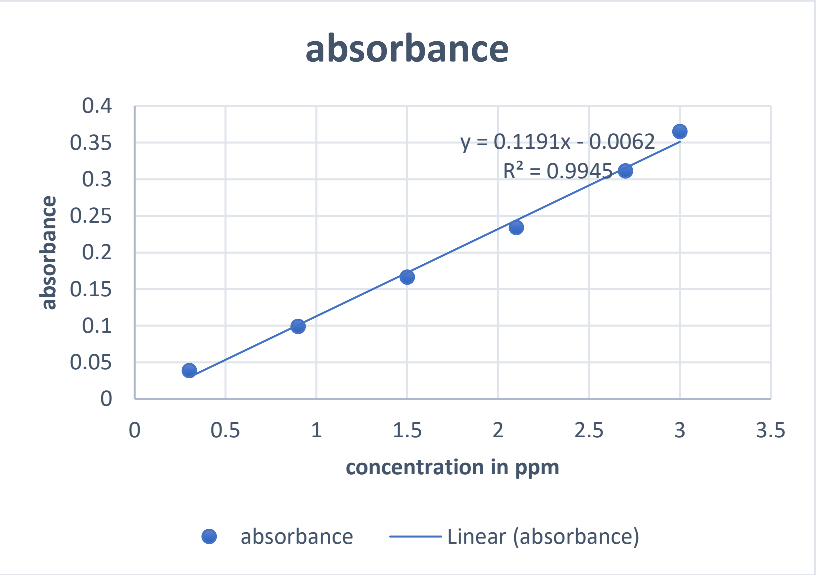


Fig: 17 color change observed in solution



GRAPH 1: CALIBRATION CURVE OF Fe^{+3}

3.6 DEVELOPMENT OF PAPER INDICATOR STIPS

Fig:18 Paper reagent stripes

Procedure: paper strips of appropriate length were cut and placed on a glass slab. With the help of fusion tube impression was created to prevent the reagent spot spreading out. 50 microliter of 40%KSCN was added with the help of capillary by spotted pattern and kept for drying in oven at 50^0 C in between addition of KSCN. In similar manner 50 microliter of 8N nitric acid was added. Dried completely .31 batches of paper indicator strips were prepared ,and the indicator strip were used in further analysis.

CALIBRATION CURVE FOR ANALYSIS OF IRON(III) USING PAPER INDICATOR STRIP

Requirements: previous prepared paper reagent strips ,100ppm of FAS solution, beakers, distilled water.

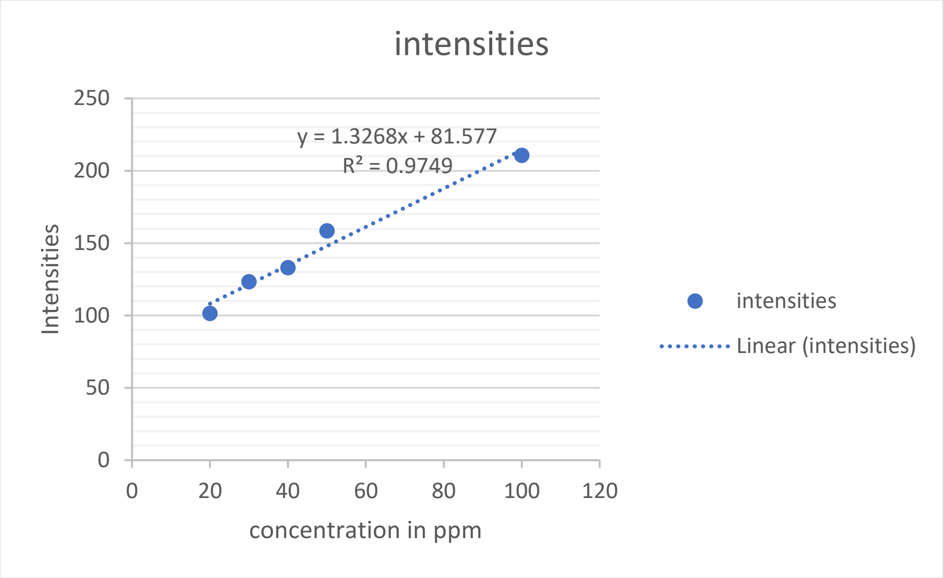
edure: Different concentration of FAS solution's were prepared (20ppm, 30ppm, 40ppm, 50ppm, 100ppm) and added to a beakers. The pH of these solution was adjusted to 1 by adding few drops of concentrated nitric acid. The reagent strips were dipped into the each of the breaker containing standard analyte solution. The color of the reagent spot on paper strip changes from white to red.

Fig:19(a, b, c, d, e)Paper reagent strips showing presence of iron.

Result:

of Iron in ppm	Intensity of the red spot
20ppm	101.3
30ppm	123.1
40ppm	133
50ppm	158.4
100ppm	210.53

The intensity of the spot on the paper reagent strips increases with increasing concentration of iron standard solution.



Graph:2 calibration curve for indicator strip

3.7 Analysis of the artificially prepare mine waste using paper sensor strip to study interference of other heavy metals.

Procedure: series of solution's of lead, copper, manganese, zinc, cadmium, Iron, chromium were prepared. 20mL of 20ppm of each solution was pipetted out in 500mL breaker. This solution was acidified to adjust the pH to 1 by adding few drops of concentrated nitric acid. This solution was then analyzed using paper sensor strip.

Fig:20(a) Artificially prepared mine waste.

Color: yellow color on addition of 20ppm iron solution.

Fig:20(b) Artificially prepared mine waste

color: red color on addition of More 10mL of 20ppm iron solution

Result: it was observed that the color of the spot on paper reagent strip of standard iron solution matches with that of the spot obtained after dipping reagent strip in artificially prepared mine waste in laboratory. The intensity of red spot does not show variation of color indicating no interference of other heavy metals present in the solution.

Concentration of solution	Intensity of mine waste	Intensity of standard
20ppm	100.2	101.9
30ppm	121.3	123.1

Fig:20(c) 20ppm mine waste and 20ppm of standard iron solution

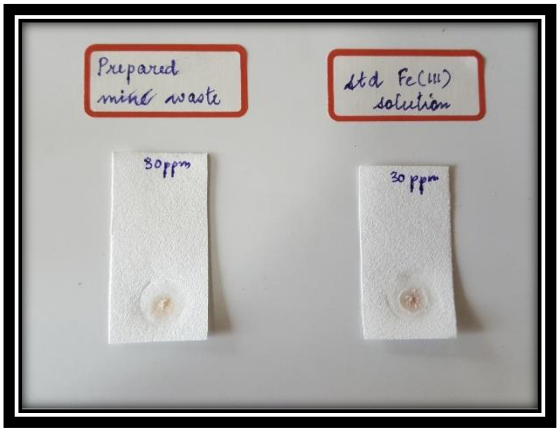


Fig:20(d) 30ppm mine waste and 30ppm of standard Iron solution

3.8 APPLICATION OF PAPER REAGENT STRIPS

Real sample analysis

Analysis for mine water

Water from Bicholim mine pits was collected for analysis. The solutions was spiked with 20 ppm iron standard solution. This solution was then analyzed using paper strip

Mine water	Distilled water	Fe(III) spiked
10mL	-	20ppm
8mL	2mL	20ppm
6mL	4mL	20ppm
4mL	6mL	20ppm
2mL	8mL	20ppm

Fig:21(a, b, c, d, e)paper strip showing presence of iron

Result:

Mine water in mL	Intensity	20ppm standard intensity – intensity on paper strip
10mL	101.9	0.6
8mL	101.72	0.42
6mL	101.63	0.33
4mL	101.51	0.21
2mL	101.42	0.12

3.9.Detection of iron in Food sample

Sample: Moong, spinach

Moong as sample

Procedure: **part 1**:- 200 g of moong was kept in 100mL of 50ppm iron solution for 24hrs. After 24hrs a paste of this moong was made and the liquid medium was filtered. 125mL of this solution was acidified to adjust the pH and evaporated to dryness. This was then diluted in minimum amount of water and analysis of this solution was carried out using paper reagent indicator.

Part 2:- 200 g of moong was kept in 100mL of water for 24 hrs. Paste of this. Moong was made and the liquid medium was filtered. 125 mL of this solution was acidified to adjust the pH and evaporated to dryness. This was then diluted in minimum amount of water and analysis of this solution was carried out using paper reagent indicator

Fig:22(a)Moong soaked in 50ppm of iron Solution.

Fig:22(b) moong socked in distilled Water.

Result:-

Part I

Moong socked in Fe(III) give a dark spot of intensity =159.6.

Intensity of red spot obtained from 50ppm of standard iron solution=158.4

Therefore amount of iron in moong after spiking of it with 50ppm iron solution is =50.3ppm

Spinach

Procedure:200g of spinach was digested in 100 mL of 4N nitric acid. Solution was filtered and evaporated to dryness and the resulting mixture was diluted in minimum amount of water. This solution was then analyzed using paper sensor strip

Fig:23 paper strip showing presence of iron in spinach

Result:-

Sample	Intensity of spot
Spinach	78

3.10.ANALYSIS OF ENVIROMENTAL SAMPLE

Procedure:- water sample from well located in field ,from well located near River and well located in a city was collected. To each sample few drops of concentrated nitric acid was added to adjust the pH to 1. These water samples were then analyzed with paper sensor strip.

Fig:24(a) Indicator strip used to detect presence of iron in water collected from well near river.

Fig:24(b) Indicator strip used to detect presence of iron in water collected from well near field

Fig:24(c) Indicator strip used to detect presence of iron in water collected from well in the city.

Result:-

Water collected from different areas.	Color of strip
Well water near river	Light red coloration
Well water from city	Light red coloration
Well water near field	Bright red

It was observed that high amount of iron was present in the water collected from well situated next to field then the water collected from Well in city or close to river. The probable reason for increased amount of iron content in well situated in field can be the excessive use of fertilizers by the farmers which contains iron in large amount. Fertilizers seep into the soil and mix with the ground water which then in turn reaches to well.

Analysis of water from different sources

FIG:25(a)TAP WATER

FIG:25(b) DAM WATER

FIG:25(c) WELL WATER.

FIG:25(d) RIVER WATER

PROCEDURE: water samples from different sources were collected (river water, tap water, dam water and well water). Samples were analyzed using paper indicator strip to detect presence of iron. The pH of water samples was adjusted by adding few drops of concentrated nitric acid.

Result:

It was observed that the paper sensor used for analysis of river water showed a red spot indicating presence of iron in the water where as the paper sensor used for water samples of well, tap and dam showed negligible change in the color of the spot. There for it can be concluded that River water contains presence of iron in some amount.

3.11 ANALYSIS OF IRON IN AYURVEDIC IRON SUPPLEMENTS

Loha bhasma powder(ayurvedic iron supplements) of 3 different brands (Patanjali, Dhatapeshwar, Baidyanath). The amount of iron content in the powder was not specified on the brand.

PROCEDURE: The powdered samples were labelled respectively. 1g of each sample was digested in 25mL concentrated HCl and 25mL of double distilled water. Solution was allowed to stand for 24 hours . The mixture was filtered using whatman filter paper and the solution was then analyzed using paper sensor.

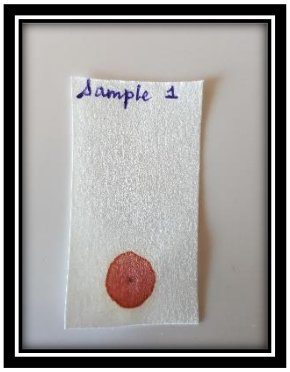


Fig:26(a) Sample 1

Fig:26(b) Sample 2.

Fig:26(c) Sample 3

Result:

Sample	Brand name	Mean Intensity of colored spot
Sample 1	patanjali	202.11
Sample 2	Dhatapeshwar	191.5
Sample 3	Baidyanath	189.7

It was observed that the supplement of Patanjali brand show red spot of highest intensity among the 3 sample analyzed. This indicates that Patanjali Loha bhasma iron supplement contains highest amount of iron.

Conclusion

Optical chemical sensors are novel analytical devices and have gained popularity as they are portable, economical, Environmental friendly and does not require any skilled professional operator to use them. These sensor does not require laboratory set up therefore they are very effective in field work analysis. Detection of heavy metal is made easy as change in the color of the sensor can be seen by naked eyes which is one of the significant features of the developed sensor.

The supporting Materials such as paper and mesoporous silica used in the sensor have multiple advantages over the routine analytical iron detection method. They don't require extensive sample pretreatment, laboratory set up, they are inexpensive, reusable, easy to handle, effective in field work, power consumption is not needed.

During the study extensive experiments were carried out using different immobilized matrix such as commercially available silica, Synthesized MCM-41, HCl functionalized MCM-41, APTES functionalized MCM-41. Characterization of above materials by and IR also supports experimental data. The presence of iron was detected by change in Color of silica from white to orange .

Paper sensors developed were successful to detect presence of iron in different materials. The sensor was proved to be inexpensive and environment friendly.

In experiment conducted it was observed that artificially prepared mine waste consisting of various heavy metals gave a red spot of same intensity as that of the standard solution. Indicating that the there was no interference of other heavy metals in the solution. The sensor is successfully works and not interference is observed.

The sensor was able to detect presence of iron in natural samples such as moong and spinach.

In experimental work conducted to check influence of the location and Environmental conditions on amount of iron in water showed that the water from the well situated in or in close proximity of fields should high amount of iron content by giving an intense red spot on the indicator strip then the water from Wells in city and next to the river. Probable reason for this can be the fertilizers use in field which contaminate ground water.

Water from different sources were analyzed to detect presence in iron .it was found out that River water from a river close to mining belt had detectable amount of iron then tap, well or dam water

In analysis of ayurvedic iron supplements from different brands. It was observed that each sample gave red spots on indicator of different colors. Patanjali brand Loha bhasma powder showed the spot of high intensity.

The intensity of the red spot was measured using imageJ software.The paper sensor worked excellently in detecting presence of iron in different samples. By giving a red spot which was visible to naked eyes.

Appendix

ANALYTICAL INSTRUMENTS USED AND THEIR PRINCIPLE

Analytical instruments are used to characterize the synthesized supporting mesoporous silica, to analyze the solutions for their concentrations and to know their λmax i.e. at which particular wavelength the absorption is maximum, to know the particle size of the samples and so on.

Infra Red spectrometer

Principle: IR radiations are part of electromagnetic radiations which lie in 4000cm-1-200cm-1. Above 4000cm-1it is known as near IR region and below 200cm-1its far IR region. For a chemist the mid IR i.e. 4000- 200cm-1 is important. For a molecule to absorb IR there should be change in net dipole moment due to vibrations and rotations of bonds or around bonds. The altering electric field radiations interact with the fluctuations in the dipole moment of the molecule. If frequency of radiations of the IR source matches with vibration frequency of the molecule then the radiations will be absorbed which then causes change in amplitude of molecular vibrations. Software used: IR solution

UV-Visible spectrophotometer

Principle: UV-Visible spectrophotometer works on the principle of Beer Lamberts' law. It says that a radiation absorbed by the analyte is directly proportional to path length and the concentration of analyte. Ultra Violet light is a part of electromagnetic radiations which lie in 200-400nm region. And visible light falls in 400-800nm region. In case of UV-Visible spectroscopy the molecule absorb radiations, the electrons from lower energy levels absorb radiation and move to higher energy level.

Colored complexes absorb sometimes in visible as well as ultra violet region and they can be analyzed using simple colorimeter. Whereas colorless analyte absorb only in ultra violet region. i.e. compound having conjugations absorb in ultraviolet region.UV-Visible .

Spectrophotometer used: UV-2450; UV-Visible Spectrophotometer; Shimadzu

Software used: UV probe

Software used

Imagej:-Java-based processing program developed at the National Institutes of Health and the Laboratory for Optical and Computational Instrumentation (LOCI, University of Wisconsin). Its first version, ImageJ 1.x, is developed in the public domain, while ImageJ2 and the related projects User-written plugins make it possible to solve many image processing and analysis problems, from three-dimensional live-cell imaging to radiological image processing, multiple imaging system data comparisons to automated hematologysystems. ImageJ's plugin architecture and built-in development environment has made it a popular platform for teaching image processing. ImageJ can be run as an online applet, a downloadable application

Bibliography

1. G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney. Vogel’s textbook of quantitative chemical analysis fifth edition.
2. Qiang M, Xingguang SU, Silica nanobead based sensing system for analytical and bioanalytical application, TrAC trends in Analytical chemistry, vol 74, 2015:130-145.
3. Sarupriaa M., Manjare S D, Girap M. Environmental impact assessment studies for mining area in Goa, India, using the new approach, Environmental Monitoring and Assessment , 2019, 191 : 1-18
4. Skoog, Holler, Niemen Principles of Instrumental Analysis, 5th edition, Saunders College Publishing, Fort Worth, TX 1997, Ch. 10.
5. Adam Hulanicki, Stanislaw Glab and Folks Ingman ,Chemical Sensors Definitions and Classification; Pure and Appl. Chem; Vol.83, no.9, pp.1247-1250.
6. Tautkus S, Steponeniene L ,Kazlauskas. R. Determination of iron in natural and mineral waters by flame atomic absorption spectrometry. Department of Analytical and Environmental Chemistry, Vilnius University, Naugarduko 24, 2006: 393-402.
7. 1. Elinder C-G. Iron. In: Friberg L, Nordberg GF, Vouk VB, eds. Handbook on the toxicology of metals, Vol. II. Amsterdam, Elsevier, 1986:276-297.
8. Determination of iron in natural and mineral waters by flame atomic absorption spectrometry S.Tautkus, L.Steponeniene and R.S Kosciusko.
9. Background document for development of WHO Guidelines for Drinking-water Quality,Originally published in Guidelines for drinking-water quality. Health criteria and World Health Organization, Geneva, 2nd ed. Vol. 2. 1996.
10. International Organization for Standardization. Water quality—determination of iron. Geneva, 1988 (ISO 6332:1988).

11. Weaver LC et al. Comparative toxicology of iron compounds. American journal of medical science, 1961, 241:296-302.
12. Kyung Beom Kim, Gyeong Park, Hyun Kim, Eun Joo Song, Jeong Mi Bae, Cheal Kim .A novel colorimetric chemosensor for multiple target ions in aqueous solution: simultaneous detection of Mn(II) and Fe(II). Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul 139-743,
13. Xavier L.Pascual, Miriam Pablos Cascallar, Mireia Planell Calle, Eloi Puigdollers Rodés, C. IRONIRON MINING IN GOA (INDIA), An interdisciplinary study Degree in Environmental Sciences, Autonomous University of Barcelona, 2013
14. Singh R, Lantigua D , Meka A, Taing S, Pandher M , Gulden Up, Paper-Based Sensors: Emerging Themes and Applications. University of Massachusetts Lowell, One University Avenue, Lowell, MA 01854, US
15. Won Seok Han, Hye Young Lee, Sung Ho Jung, Soo Lee, Jong Jung, Silica-based chromogenic and fluorogenic hybrid chemosensor materials, *Chemical Society Reviews 38 (7), 2009: 1904-1915.*
16. Afshani, Alireza Badiei, Negar Lashgari, Ghodsi Mohammed Z. AA simple nanoporous silica-based dual mode optical sensor for detection of multiple analytes (Fe 3+, Al 3+ and CN−) in water mimicking XOR logic gate, *RSC advances 6 (7), 2006:5957-5964*
17. Giancarla , Giovanni Emma, Roberta C, Maria P, Valeria Marina N, R bizer. Novel DFO-functionalized mesoporous silica for iron sensing. Part 2. Experimental detection of free iron concentration (pFe) in liquid matrix (urine samples) *Analyst 139 (16),, 2014:3940-3948*
18. Raffaela Biesuz, Maria Amelia Santos, Valeria M Nurchi, Giancarla Alberti. Development of a sensor for trivalent iron: AHP fixed on mesoporous silica. *New Journal of Chemistry 42 (18), New Journal of Chemistry 42 (18), 2018:15237-15244.*
19. LF Capitán-Vallvey, E Arroyo, C Beleaguer, MD Fernández-Ramos, R Avidad. Single-use optical sensor for the determination of iron in water and white wines. *Fresenius' journal of analytical chemistry 369 (2),, 2001:139-144.*
20. Clemence S, Chad Glen, Brandon , Dan Wallace, Sana , Kevin Pennings, Glen T Diggers, Robert Pelton, John D Brennan, Carlos DM Filipe. Tools for water quality monitoring and mapping using paper-based sensors and cell phone, *Water research 70, 2015:360-369.*
21. Aleksandra Lobnik, Matejka Turel and Spela Korent Urek. Sensors: Design and Applications, University of Barcelona, 2002.