Utilization of Green Synthesized Iron Oxide Nano Particles for the Removal of Arsenic from Aqueous Solution

Athira Asokan*, Ayisha Sithara[1], Niveditha RM[1], Reshma Raju[1] and Veena SK[1]

*Assistant Professor, Department of Chemical Engineering, MVJ College of Engineering, Bangalore, India.
[1]VII Semester Students, Department of Chemical Engineering, MVJ College of Engineering, Bangalore, India.

ABSTRACT

Arsenic poisoning has become one of the major environmental worries worldwide, as millions of people, who have been exposed to high arsenic concentrations (through contaminated drinking water), developed severe health problems. The utilization of iron oxide nanomaterials has received much attention due to their unique properties, such as extremely small size, high surface-area-to-volume ratio, surface modifiability, excellent magnetic properties and great biocompatibility. The present investigation focuses on various studies with respect to the novel routes for biosynthesis of iron oxide nanoparticles by plant resources along with utilization of these nanoparticles for the removal of Ar(V) from waste water. The SEM analysis reports showed the size of synthesized nanoparticles as 63 to 96 nm for betel leaf extract, 90 to 110 nm for neem leaf extract and 500nm for cucumber seed extract. FTIR analysis also confirmed the presence of functional groups in the synthesized iron oxide nanoparticle. It was observed that the Arsenic removal efficiency was 99% for 5mg/l of initial concentration of Arsenic solution, at 30 minutes contact time, pH 7 and iron oxide nanoparticle dosage of 0. 5mg.The equilibrium data was fitted with Langmiur and Freundlich adsorption isotherm. This study is suggesting the utilization of superior adsorption performance of iron oxide as a promising approach to deal with a variety of environmental problems.

Keywords: Biosynthesis, Iron oxide nanoparticles, Arsenic removal.

1. INTRODUCTION

Water being an abundantly available natural resource but surprisingly its scarce availability for human consumption is a major concern to be taken care (Grey et al., 2013; Adeleye et al., 2016) .The major trouble faced by people today is water contamination. The reason for this is suspended heavy metals like arsenic, lead, cadmium, nickel etc from the rising industries(Karim H Hassan., vol4 2016).exposure to these heavy metals can be lethal to human beings as it causes kidney failure, cancer, liver damage, insomnia, chronic asthma and dermatitis (Vinod kumar Gupta., vol7 2017). Nano technology is recently being explored for the removal of these heavy metals from industrial waste water. Nano technology is a science that deals with particles varying in sizes from 0-100 nm. The interesting and unique properties of nanoparticles such as high surface area to volume ratio and rapid adsorptions are used for treating water at high depths which is failed by other technologies (Prachi.,vol5 2013). A wide range of application in wastewater treatment focuses on properties of nanomaterials like nano sorbents, nano catalyst, nanotubes, nanowires, nanofluids, nanomembranes, bioactive nanoparticles.

Nanosorbent: Nanoparticles having sorption property is termed as nanosorbents. These are proven to be more efficient than the conventional sorbents.

Nanocatalysts: It has high surface area and shape dependent property because of which it increases the catalytic activity on the surface. Due to this the reaction is enhanced and degradation of contaminants. It has good selectivity and activity. Most common nanocatalysts used are zero-valence metal, semiconductors and bimetallic nanoparticle for the breakdown of environmental contaminants like organochlorine pesticides, azo dyes, herbicides.

Nano tubes: Nano tubes were discovered in the year 1991. It possesses properties such as magnetic, electric and mechanical properties. The strength of carbon nano tubes are 100 times stronger than steel, so it could strengthen almost all material. It shows good conductivity and used for anti-static packing. Carbon nanotubes are unique

because of their very strong bonding and it is as thin as few nanometer (10000 times thinner than hair) and vary in length and thickness. They are classified as single-walled and multi walled carbon nanotubes.

Nano wires: Nano wires are made out of nanotubes having diameter less than 100 nanometer. It has various applications especially in small electronic circuits, tansistors, biomolecular nanosensors, optoelectronics, field emitters. Manufacturing of nanowire include vapour liquid solid synthesis, vapour deposition and suspension methods.

Nano fluids: It consists of nanoparticles put in a base fluid. The base fluid can be water or any other solvent. It has good application in energy transfer processes, in automobile industry, it can also be used as a coolant because of its better heat conductivity properties compared to other coolants.

Nano membranes: These are widely used for treatment of waste water. It has good applications in uniformity of catalytic sites, limiting catalyst contact time and optimisation. It also includes deactivation of microorganisms, fouling actions, and physical separation techniques done under the nanostructured TiO_3 films under UV spectroscopy.

Bioactive nanoparticles: Water contamination causes various diseases due to contaminating pathogens.

Nanosorption has been proven to be the most efficient adsorption than the prevailing methods in waste water treatment. Experiments were done using nanomaterials such as carbon nanotubes (CNTs), manganeseoxide (MnO2), ferric oxide (Fe3O4) in treatment processes for water

Green synthesis: bio reduction is an important mechanism to understand plant mediated nanoparticles synthesis. It is easily available , cost effective , nontoxic and environmental friendly. It eliminates the use of toxic chemicals consume less energy ,produces safer products and bi-products. Since there is no involvement of any harmful chemicals, biosynthesis of nanoparticles is considered as a green technology. Green nanotechnology is a major attention seeking topic due to its wide range of processes that eliminates toxic substances to restore the environment. Greensynthesis of nano particles is a bottom up approach which mainly involves iron oxide reduction reaction.

Arsenic: Arsenic is naturally found in earths crust in its trivalent(III) and pentavalent(V) forms anthropogenic generated ions and also due to erosion on surface of rocks, smelting of nonferrous ores. Pentavalent is less toxic than trivalent form. When the ground water penetrates through these rocks they carry these different forms of arsenic along with them and causes water pollution along with the chemicals disposed in water bodies from different industries. It is classified under metalloids or semi-metals. It has a garlic like odour when grounded. It is available in white red and bright yellow forms (S.M.Aronson.,vol77 1994). Arsenic is one of the major trace metal observed in ground water in the form of arsenate($HAsO_3^{2-}$) and arsanite($HAsO_4^{2-}$), which causes high risks in liver, lung, bladder and kidney cancer when consumed via drinking water. Low levels of arsenic may also cause some acute diseases. The allowable limit of consumption of arsenic in drinking water is 0.05 mg/L according to WHO standards. Certain places in China, India, Mongolia, Vietnam, Italy, Taiwan and Iran ,the concentration of arsenic in ground water is exceeded by 1mg/L (K. Deepa.,vol7 2015). It is also being used as a preservation for wood in the form of chromated copper arsenate as it prevents organisms from growing on the wood (S.M.Aronson., vol77 1994). Arsenic removal techniques are being practiced and various methods have been adopted to reduce the

arsenic concentration in wastewater, which includes membrane exchange processes, ion exchange, chemical oxidation , chemical coagulation, dissolved air floatation, surface adsorption, nanosorption . Studies show that zero valent metals like iron is the effective method for decreasing the contaminants present in water in recent years. It is been given more attention because of its properties like having high efficiency to break down the contaminants and has a good adsorbing factor. Since it has good properties as mentioned above it is used as an adsorbent in treating arsenic from ground and industrial waste water, which is obtained from green synthesised nano particles (Abooalfazl azhdarpoor., Vol 3 2015).

2. MATERIALS AND METHODS

2.1 Preparation of extract

200g of plant material sample (neem leaf, betel leaf and cucumber seed) was taken and washed with sterile distilled water and keep the samples for drying. After drying, it is finely crushed with the help of a blender. The powders were transferred into 3 different 500ml round bottom flask.300ml of triple distilled water was added to all flasks. The mixtures were heated for 10 minutes at 65^0C.Then it was decanted and filtered using Whatman No.1 filter paper. The three different filtrates obtained were centrifuged at 5000rpm for 5 minutes. After centrifuging the supernatant (of 3 plant extracts) was collected for further processing.

2.2 Synthesis of iron-oxide nanoparticle

To the supernatants (i.e., plant extract) and 0.001M ferric chloride($FeCl_3$) precussor was added in 1:1 proportion in a clean sterilised beaker. The mixture was continuously stirred for 1 hour at 50^0C. After stirring the mixtures were allowed to cool 20 min and then centrifuged at 5000rpm for 5 minutes by means of an ultracentrifuge. Throw the supernatants and wash the sediments (nanopowders) two to three times with deionised water.

2.3 Removal of arsenic from waste water

2.3.1 Spectrophotometric determination of Arsenic using safranine O as a reagent

Different concentrations of sodium arsenate (0.0001g, 0.0002g, 0.0005g, ……0.001g) solution was taken in a 1000 ml volumetric flask. 1ml of this sodium arsenate solution was taken in a test tube. To this 1 ml potassium iodide solution(2%) and 1 ml of 1M hydrochloric acid was added and shaken well. Then 0.5 ml of safranine O and 2ml of sodium acetate was added. This was shaken well and kept for 2 minutes. Then, distilled water was added and the solutions were made up to 10 ml. Blank solution without sodium arsenate was also prepared and the absorbance value at 490nm was noted down using a UV-spectrophotometer. Then the absorbance of solutions with different concentration was noted.(B Narayana et al., 2006).

2.3.2 Adsorption procedure

To the 50 ml of the prepared arsenate solution, 0.05g of synthesised iron oxide nanopowder was added to it and kept it in shaker for 2 hours at 180 rpm. The nano particle obtained from betel leaf extract was used for the study.1 ml of this solution was taken in a test tube and added all reagents with respect to the standard spectrophotometric

procedure with safranine O. Using UV spectrophotometer absorbance of each solution was checked. A graph of absorbance v/s concentration was plotted and found out the concentration of arsenic being absorbed.

%Removal=$((C_o-C_f)/C_o)*100$

C_o-initial concentration

C_f- final concentration

2.4 Analysis

SEM analysis is done to check the morphology of the nanopowder and FTIR analysis is done to check the compounds present in it before absorption and after absorption.

3. RESULTS AND DISCUSSION

3.1 Characterization of Iron nanoparticles using Scanning Electron microscope (SEM)

SEM analysis gives the morphology of the surface of prepared ironoxide nanoparticles through SEM images. The synthesized iron oxide nano particles were analysed by Scanning Electron Microscopy (SEM).
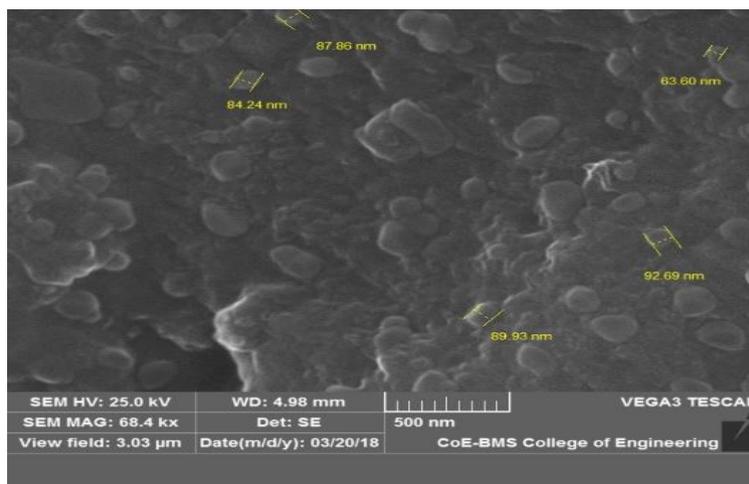
Fig 3.1.1: SEM analysis image of Iron nano particle from Piper betel sample
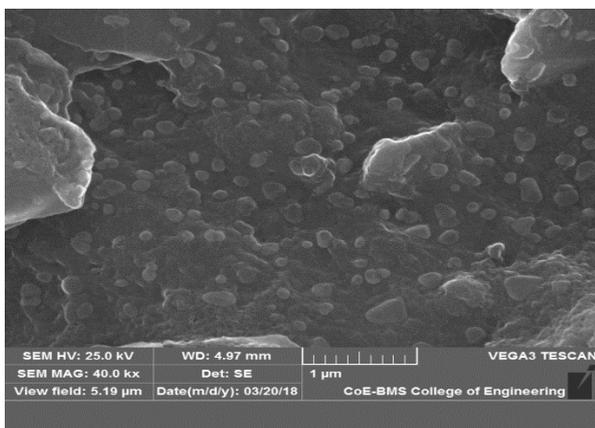

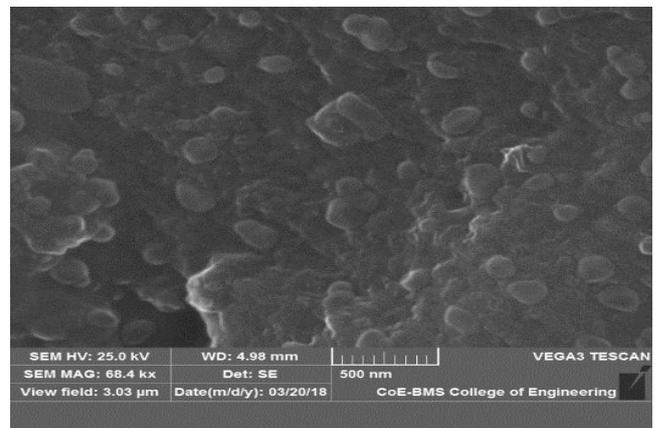Fig 3.1.2: SEM Analysis image for Azadirachta indica

Fig 3.1.3: SEM Analysis image for Cucumis Sativus

The average particle size of nanoparticle obtained from Piper betel fig 3.1.1 was found in the range of 63.60-92.68nm. The shape of the nanoparticle was found to be spherical and rod shaped. The SEM images for the average particle size of nanoparticle obtained from of Azadirachta indica (fig 3.1.2) was in the range 90-110nm and the shape was observed to be spherical. The SEM images for the average particle size of nanoparticle obtained from Cucumis Sativus (fig 3.1.3) was in the range of 500nm and spherical in shape.

3.2 Fourier Transform Infrared (FTIR) ANALYSIS

3.2.1 FTIR for Azadirachta indica

Fig 3.2.1. Shows the FTIR Analysis for Azadirachta indica shows that, the spectrum with wave number 3243,2927,1574,1398 and 1029 corresponds to O-H,CH3 and CH2 stretching, C=O,C-N AND C-O stretching respectively. The obtained bands are similar to those reported to iron oxide nanoparticle.
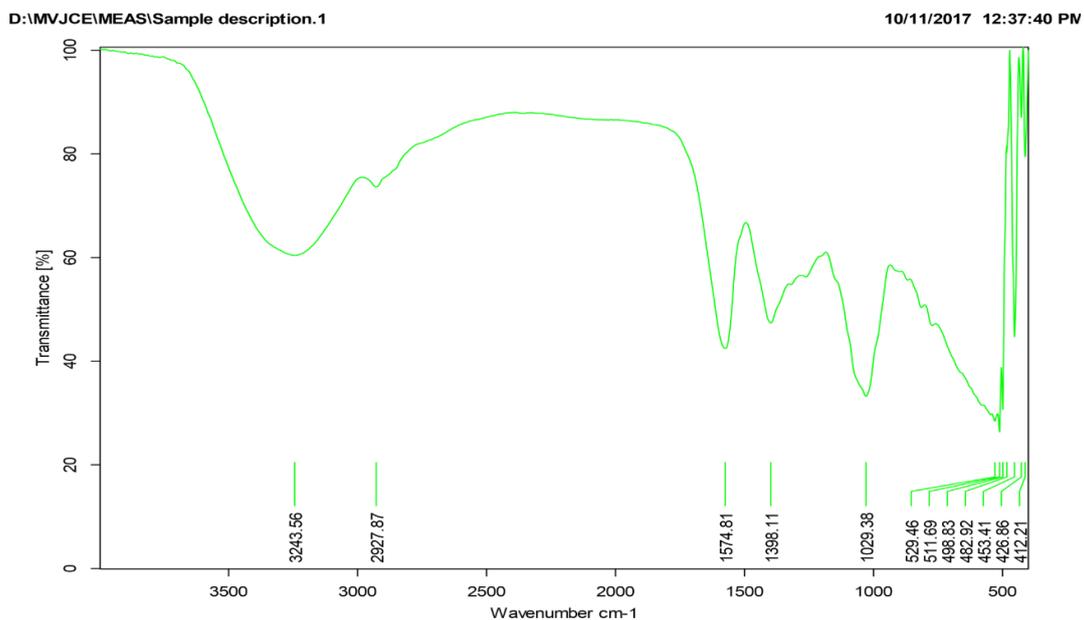

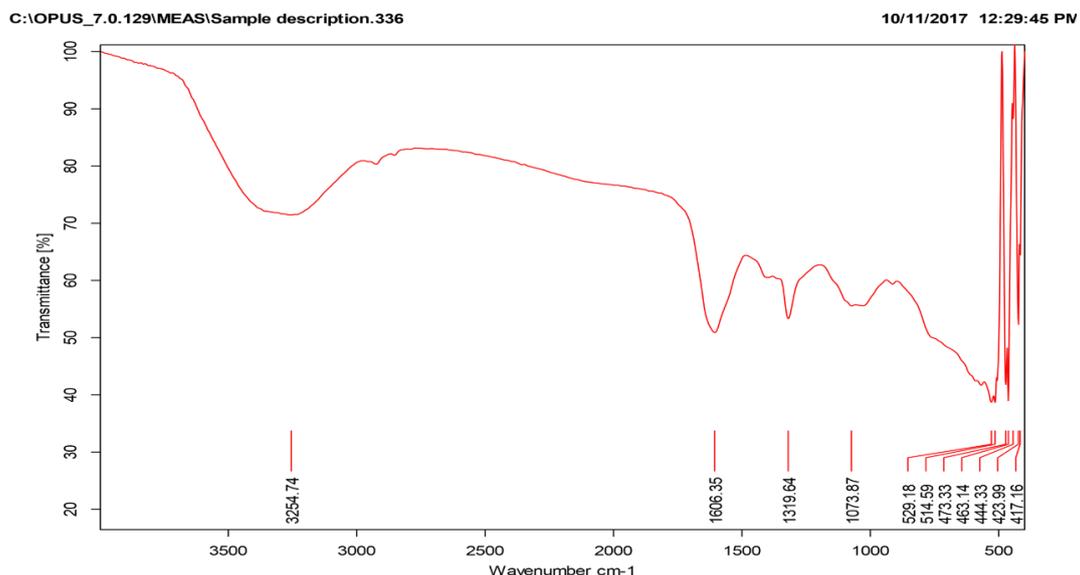Fig 3.2.1: FTIR Analysis for Azadirachta indica

Fig 3.2.2: FTIR Analysis for Piper betel before adsorption

3.2 FTIR for piper betel

Fig 3.2.2. FTIR Analysis for Piper betel confirmed the presence of iron nano particle. The FTIR spectrum showing wave number 3254,1606,1319,1073 corresponds to O-H stretching for alcohols and phenols carbonyl stretching, N-H bond stretching of amines, C-N stretching of the aromatic amino group and C-O stretching of alcohols and ethers respectively. After adsorption it can be seen that some of the functional groups are merged (Fig3.2.3).
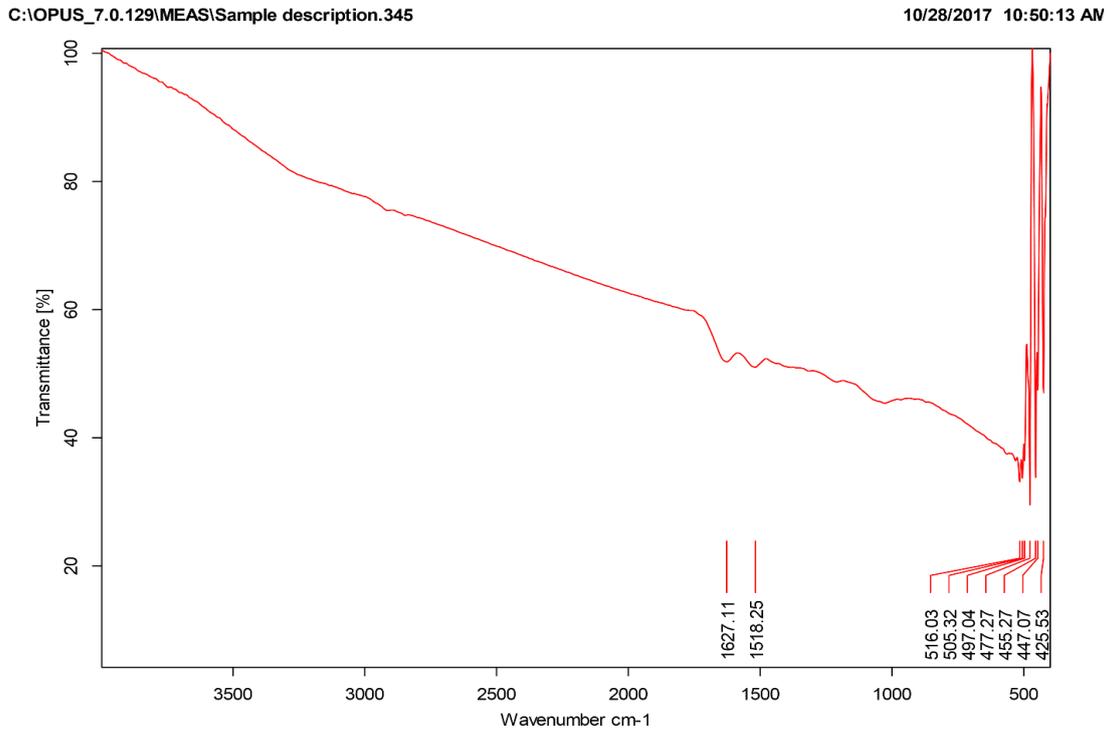
C:\OPUS_7.0.129\MEAS\Sample description.345   10/28/2017 10:50:13 AM

Fig 3.2.3: FTIR Analysis for Piper betel after adsorption

3.3 Effect of initial concentration on Arsenic

Fig 3.3.1. shows the percentage arsenic removal with respect to change in initial concentration of arsenic. The plot shows the increase in removal efficiency of As(V) against the increasing concentration.
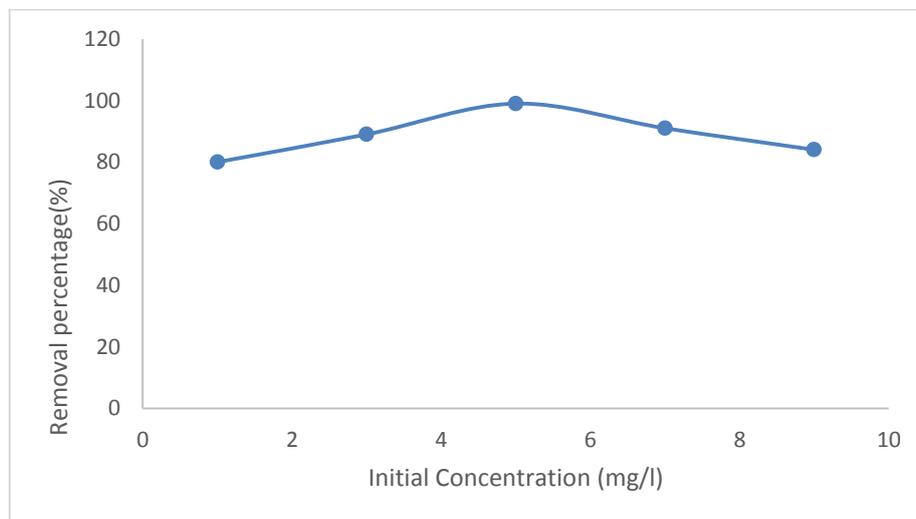

Fig 3.3.1: Effect of initial concentration of Arsenic removal percentage (pH 7, Adsorbent dose 0.05g,Time of contact 30 minutes)

The adsorption of arsenate for a brisk stirring time interval of 30 min showed a maximum removal efficiency of 99% (5mg/l) for Piper betel. By increasing the concentration of adsorbent larger sites are available for the adsorption. Due to some factors, that contributes to the adsorption concentration like the adsorption sites are unsaturated while adsorption reaction as the weight of adsorbent increases, there is less equivalent increased in adsorption which results from less adsorption capacity use of adsorbent(Mohamed hiban, Fouad inan, oct 2011).

3.4 Effect of initial pH on Arsenic removal efficiency

This is one of the most crucial parameters in adsorption studies of arsenic ions in an aqueous solution. The pH for the adsorption medium shows the mechanism of adsorption on the adsorbent surface from solution because of physicochemical interactions between the adsorbing sites of adsorbent and species in solution. The pH for drinking water is between 6.5-8.5, thereby, complete study for the effect of pH on arsenate is required. The effect of pH on Piper betel based nano particle was studied under normal room temperature. The pH ranged from 2 to 11 for 5mg/l of initial As(V) concentration. A graph of As(V) removal efficiency vs pH was plotted .From the fig4.4. graph it is clear that at initial acidic pH studies and basic pH adsorption studies, the arsenate removal efficiency was less. It was seen that the adsorption of arsenate by adsorbents (ironoxide nano particles) is maximum for the removal of As(V) at the optimum pH of 7 with a removal efficiency of 96% and after pH 7 the adsorptivity gradually decreases, it is due competition between hydroxyl ions at high pH and arsenic species in adsorption sites. The carboxyl ,amide groups have negative charge in basic conditions because of which there is a repulsion between adsorbent and anionic species of arsenic resulting in less adsorptivity efficiency (Mohamed hiban, Fouad Sinan,oct 2011).

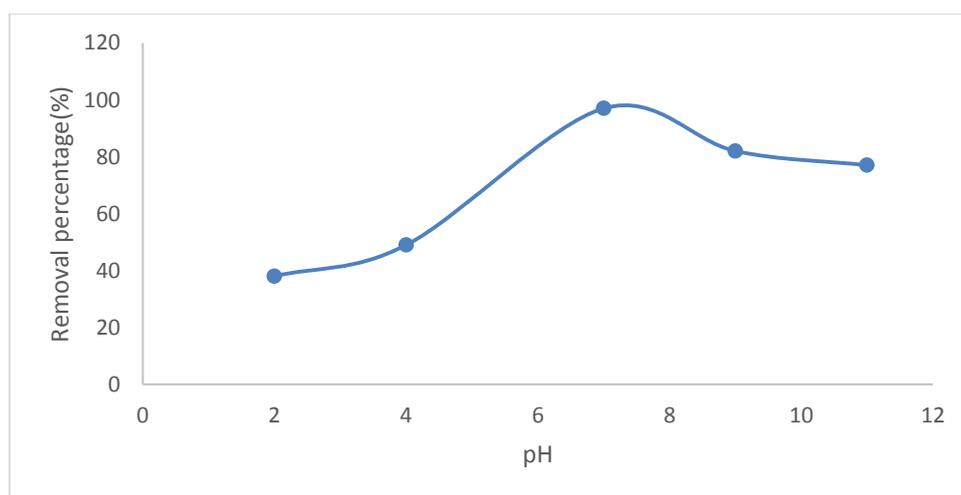$$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+ , pKa=7$$

Fig 3.4: The effect of initial pH on Arsenic removal percentage (Initial concentration 5000µg/l, Adsorbent dose 0.05g, Time of contact 30 minutes)

3.5 Effect of time of contact

Time of contact of adsorbate on adsorbent has great significance in adsorption. Fig4.5. shows the plot of removal efficiency versus different concentrations of arsenate ranging from 1000µg/l - 10000µg/l at room temperature for

the ironoxide nano particle synthesised from Piper betel at pH 7, there is an increase in adsorption efficiency of As(V) until 30 minutes. After that as there is increase in time of contact, the removal efficiency was decreased to 88%, 83% and 75% which implies that the equilibrium state is attained. The obtained results for the studies on the effect of time of contact on Arsenic removal efficiency showed an optimum time of 30 minutes with 98% of adsorption efficiency. For higher concentrations the free sites for adsorption is lesser therefore the efficiency of adsorption depends on concentration. If the adorbate dosage is fixed, then the adsorbing sites are limited and have the same adsorption for all the adsorbates (Mohamed Chiban, Fouad Sinan, oct 2011).
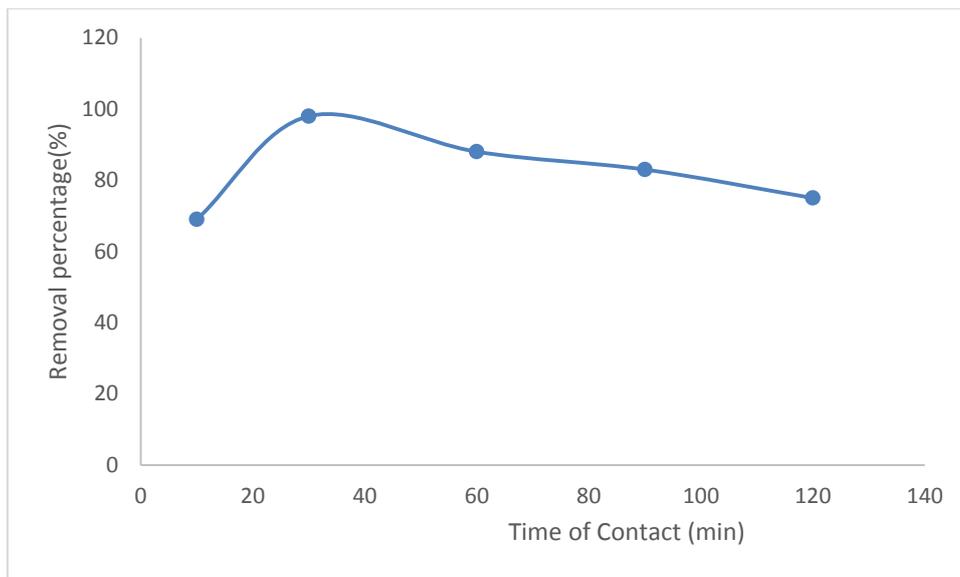
.

Fig 3.5: The effect of time of contact on Arsenic removal percentage (initial concentration 5mg/l, pH 7, Adsorbent dose 0.5g)

3.6 Adsorption isotherms

These are the mathematical models that describes the adsorption of adsorbate of solid in liquid phase and to understand adsorption mechanism. There are different models published in reference with the adsorption isotherms like Freundlich equation, Langmuir equation, Temkin equation are more often used models. These three models were used in this study to determine the arsenate adsorption from iron oxide nanoparticles synthesised from Piper betel (Mohamed Chiban, Fouad Sinan, Oct 2011).

.

3.6.1 Langmuir adsorption isotherm

From the obtained data it was fitted to Langmuir adsorption isotherm using the empirical co-relations assuming it to be monolayer adsorption on the surface for identical sites where Each site can hold only one molecule and the process involves a constant heat of adsorption. The equation is expressed as (Saikia Ananta, 2015):

$Q_e = Q_{max} (K_L C_e/(1+K_L C))$　　　　　　1

It is also expressed in linear form as

$(1/Q_e) = (1/Q_{max}) + (1/(Q_{max} K_L C_e))$　　　　2

Where Q_e is equilibrium concentration of adsorbate to adsorbent(g), C_e is the equilibrium concentration of adsorbate in solution(gMol/lt), K_L is the constant or free energy for adsorption in (l/mg). fig 3.6.1 shows the graph of Qeversus Qe/C_e , giving a straight line of intercept $1/Q_{max}$ and slope $1/Q_{max}k_L$. Regression co-efficient was obtained to be 0.8696 which fit the Langmuir adsorption model of arsenate (Le zeng., 2004).
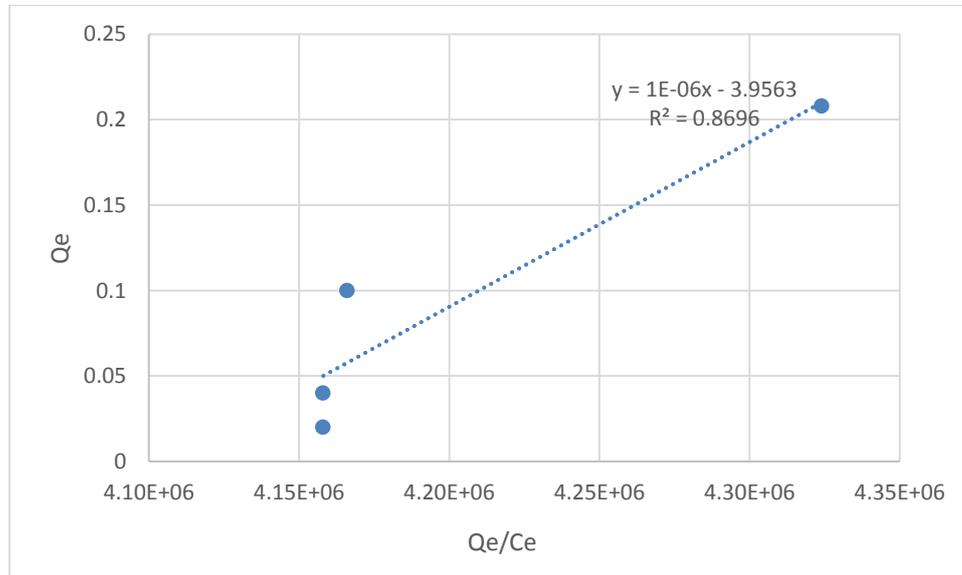

Fig 3.6.1: Langmuir adsorption isotherm

3.6.2 Freundlich adsorption isotherm

From the obtained data it was fitted to Langmuir adsorption isotherm using the empirical co-relations assuming it to be multi molecular layer adsorption (Saikia Ananta., 2015). The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
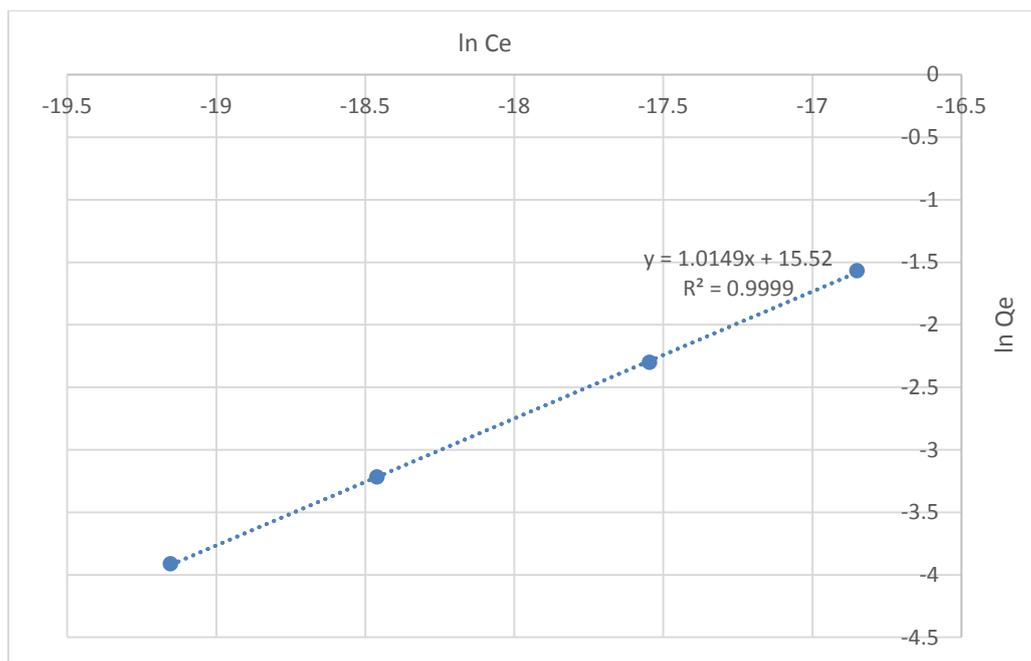

Fig 3.6.2: Freundlich adsorption isotherm

It is expressed as:

$$Q_e = K_f C_e^{1/n} \qquad (3)$$
$$Ln\ Q_e = Ln\ K_f + (1/n)Ln\ C_e \qquad (4)$$

Where k_f and n are Freundlich isotherm constants. Fig 3.6.2 shows the plot of Q_e versus C_e, a straight line is obtained, K_f is the intercept and n is obtained from the slope. The regression co efficient was found to be 0.9999.

Langmuir isotherm	
K_L	1000000 l/mg
Q_{MAX}	-3.9563 mg/g
R^2	0.8696
Fruendlich isotherm	
n	0.985
K_F	2.7421 l/g
R^2	0.999

Table 3.6: Table showing the isotherm values

4. CONCLUSIONS

According to the results of the study we can conclude that there are different green alternatives for the cheap, best and effective synthesis of iron oxide nanoparticle. In this study it can be inferred that from SEM analysis precise nanoparticles size was obtained from Piper betel extract of the range between 63.60-92.68nm and the shapes were rod and spherical. The FTIR spectra was comparable with the iron nanoparticles of previous studies, it was observed that after adsorption only the aldehyde, ester and other metal oxides compounds were present. The synthesised iron nanoparticle had significant removal efficiency for As(V) in an aqueous solution. Removal efficiency of arsenic was found to be 99% for 5 mg/l of initial arsenic concentration which was kept in rotary shaker for 30 minutes maintained at a neutral pH 7 and iron oxide nanoparticle dosage of 0.05g. According to the kinetic studies, it best fitted the Freundlich isotherm with regression coefficient 0. 9999.The study combined the unique features of iron nanoparticle for the removal of toxic As(V) from aqueous solution. Thus this is a simple, cleaner and eco-friendly procedure for synthesizing iron nanoparticle for nanotechnology and environmental engineering applications.

5. ACKNOWLEDGEMENTS

REFERENCES

[1] Monalisa Pattanayak, and P. L. Nayak.(2013), Green synthesis of zero valent Iron nanoparticles from the leaf extract of Azadirachta indica(Neem),Nano Science and Technology,volume-3,issue-1, jan-march 2013, 6-9.

[2] Prachi,Pranjali Gautam,Deepa Madathil,A.N.Brijesh Nair,Nanotechnology in waste water treatment,volume 5,July-Sep 2013.

[3] Eman Ahmed Hashem,Nanotechnology in waste water treatment,case study, Egypt, volume 2, sep 2014.

[4] Matheswaran Balamurugan and Shanmugam Saravanan, Synthesis of Iron Oxide Nanoparticles by Using Eucalyptus Globulus Plant Extract, Journal of Surface Science and Nanotechnology, Vol. 12 (2014) 363-367.

[5] Tanujjal Bora and Joydeep Dutta,Applications of Nanotechnology in wastewater Treatment,Volume 14, 2014.

[6] Karishma.K.Chorawala,Mehali.J.Mehta,Applications of Nanotechnology in wastewater treatment, Volume 2, Issue 1, 2015.

[7] R.A.CraneT.B.Scot Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology, journal of Hazardous Materials, Volumes 211–212, 15 April 2012, Pages 112-125.

[8] Praveen K. Tandon, Ritesh C. Shukla, and Santosh B. Singh, Removal of Arsenic(III) from WaLiquorter with Clay-Supported Zerovalent Iron Nanoparticles Synthesized with the Help of Tea, *Ind. Eng. Chem. Res.*, 2013, *52* (30), pp 10052–10058.

[9] B Narayana, Tom Cheriyan, Mendalin Mathew & Chand Pasha, Spectrophotometric determination of arsenic in environmental and biological samples, Indian Journal of Chemical Technology, Volume 13, January 2006, pp 36-40.

[10] Saikia Ananta,Banerjee saumen and veer vijay Adsorption isotherm, thermodynamic and kinetic study of arsenic(III) on Iron Oxide Coated Granular Activated Charcao, international research journal of environmental sciences,vol.4(1),64-77,january 2015.

[11] Mohamed Chiban, gabriela carja, gabriela lehutu, Fouad Sinan, Equilibrium and thermodynamic studies for the removal of As(V) ions from aqueous solution using dried plants as adsorbents, Arabian journal of chemistry (2016)9,S988-S999.

[12] Le zeng, Arsenic adsorption from aqueous solutions on an Fe(III)-Si binary oxide adsorbent, water qual.res. j. Canada, 2004. Vol 39, no.3, 267-275.