

Original Research Article

Synergistic Effect of Polypyrrole-Polyaniline Conducting Polymer Nanocomposite and Fe₃O₄ Nanoparticles for Arsenite (III) Adsorption from wastewater

ABSTRACT

For treatment of arsenic contaminated water, adsorption of arsenic and its reduction are there important processes. Conducting polymer efficiently show the efficient absorption but in use of it there is agglomeration of particles which make its usage difficult. To reduce this problem magnetic property material are used. In this polypyrrole and polyaniline conducting polymers were used. By oxidative polymerization of Polypyrrole and aniline in presence of Fe₃O₄ by utilizing FeCl₃ nanocomposite was manufactured. In this magnetite prevented the agglomeration of particles of polymers and also helped in separation of nanocomposite from solution. Characterization was done by FTIR, SEM and XRD. This nanocomposite removal 88% arsenide (III) from aqueous solution at adsorbent concentration 0.01g and pH=1. Colorimetric method was used which developed complex with arsenite (III) and showed the removal of arsenite (III) from aqueous solution by complex. Separation of nanocomposite became easy due to magnetic properties of magnetite. This could be isolate from aqueous solution by using of strong magnet. This nanocomposite is the promising composite for removal of arsenite (III) from aqueous solution.

Keywords: Nanotechnology, Nanoparticles, nanocomposites, Adsorption, arsenic, Wastewater

1. INTRODUCTION

Water pollution has become the major problem in the world [1]. Availability of clean freshwater is decreasing day by day. Water is being polluted by various toxic metals like chromium, lead, nickel and arsenic [2]. Arsenic pollution [3] has attracted major attention due to its toxicity and health effects [4]. There are two sources of arsenic in water i-e natural source and anthropogenic activities. There are many natural minerals which are responsible for releasing of arsenic in water [5] whose number is approximately 200. These minerals are Realgar (AsS), Arsenolite (As₂O₃), Cobaltite (CoAsS), Nicolite (NiAs) and many others. Some natural minerals in less amount release high concentration of arsenic in water [6]. In natural water arsenic is present in fewer amounts than mining and mineralization sites where arsenic level is recorded from 100-5000mg/L. Anthropogenic activities are major source which removes arsenic in water [7]. Arsenic is using as medicine, pesticides and killing agent [8]. In industry arsenic is being use for making of insecticides, pesticides and many other medicines [9]. These industries release the arsenic in their waste without treatment, due to which amount of arsenic is increased [10].

WHO Organization has recommended the tolerant arsenic level from 10ppb to 50ppb [11]. But in some countries arsenic level has reached up to 50ppb. In Asian counties arsenic level is more than 50ppb dur to which these countries are largely affecting by arsenic contaminated water [11]. Arsenic is the 20th most abundant metal in the world. Arsenic valency may be +3 or +4 or -3. Oxidation state of arsenic depends on the redox potential [12]. Many species of arsenic are found in water like arsenate As (V), arsenite (III), arsenic acid (H₃AsO₄), arsenous acid (H₃AsO₃), monomethylarsenic acid (MMA),

monomethylarsonous acid, dimethylarsinic acid (DMA) and dimethylarsinous acid [13]. Most abundant species of arsenic are arsenite As (III) and arsenate (V) [14]. Arsenate (V) is the predominant specie and less toxic than arsenite As (III) [15]. Arsenic is carcinogenic element [16]. Its exposure causes severe health issues like cardiovascular system problems, renal effects, hypertension, diabetes, respiratory issues, neurological abnormalities and cancer [17]. When regular exposure to arsenic takes place then by electrostatic interaction arsenic adsorbed in blood stream, from blood it moves towards other parts of body when it reaches into liver it metabolizes and after it some amount of it is excreted from the body by urine and it leads to detoxification [18]. When higher and chronic exposure takes place then arsenic in body is converted into intermediate species like organic intermediate form (MMA) and (DMA) [19].

Both arsenite and arsenate converts into methyl metabolites and retain in body tissues and organs like kidney, lungs, liver and placenta [20]. In these tissues and organs arsenic species start the biochemical reactions [21]. Mobility of arsenic is higher than arsenate. So, it moves fast and cross the membrane of gastrovascular tract and moves into other parts of body [22]. It reacts with fatty acids and causes oxidation by using peroxidation process. Due to oxidation reaction reactive oxygen species are formed which damage the cell structure. These reactive oxygen species alter the lipids structures, causes damage to mitochondria membrane and also damages the cell cycle and DNA structure [23]. Arsenic also produces the change into genes, it reacts with the enzyme sulfhydryl site and replaces the phosphate group due to which changes produce in genes [24]. Asian countries like Bangladesh, India, Pakistan and china are affecting more from arsenic [25]. Arsenic is causing cancer which causes death. So, removal of arsenic is compulsory to secure the health of organisms [26]. There are many methods which are using for arsenic removal. These methods are oxidation, coagulation, flocculation, precipitation, coprecipitation, membrane technologies, ion exchange process, osmosis and adsorption. Some removal processes are expensive, some are long time process, and some require large and costly instrumentation. Adsorption is the process which is costly effective, simple to handle and provides easy way for removal of arsenic. It is surface phenomenon process. In this process a solid surface adsorbent is used. This adsorbent must be cost effective, easy to handle and must has small diameter and high surface area for adsorption [27].

On this adsorbent surface ions or molecules are attached [28]. Between these ions or molecules and adsorbent attraction phenomenon takes place which may be physical or chemical [28]. There are many adsorbents which are using for removal of arsenic. These adsorbents include iron forms, clay, biomass and zeolites. There are many adsorbents which are difficult to handle and produce the sludge. Iron oxides and aluminum oxides are using as adsorbents which are very effective adsorbents [29]. These effectively react with anions or cations and replace them.

Magnetite is the iron form it has high adsorption due to high surface area [30]. It has magnetic properties which not only help in adsorption but also help in separation of nanocomposite from the water [31]. When polymers are functionalized on the nanoparticle then these increase the surface area ratio and this nanocomposite material shows the both polymer and nanoparticles properties and characteristics [32]. Conduction polymers have attracted more attention because these are cost effective, simple to use, easy to operate and separate, nontoxicity, reusability and porous structure [33]. In this polypyrrol and polyaniline are functionalized on the iron form magnetite [34]. These polymers have the ion exchange characteristics. In this nanocomposite polypyrrol undergoes into anion exchange with the counter ions and polyaniline has imine and amine groups which undergo into electrostatic or hydrogen bonding attraction and adsorb the arsenic [35]. When conducting polymers are used these produce the agglomerates of the particles due to which it becomes more difficult to separate the nanocomposite material from water solution. So, for this purpose magnetic properties materials are used like magnetite. This magnetite helps in separation of nanocomposite material from water solution by using of strong external magnetic field [36].

2. METHOD

2.1 Materials

Iron (II) chloride hexahydrate ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$) and Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were obtained from Seohaen-ro Korea. Acetone (CH_3COOH), chloroform (CH_3Cl) and polypyrrol (PPy) were supplied from sigma-Aldrich. Ammonia (NH_3) and sodium arsenite (NaAsO_2) were obtained from Merck while anhydrous iron chloride from Korea. Aniline supplied from Acros-organics. These all chemicals were of analytical grade.

2.1 Synthesis of Magnetite

0.5M solution of Iron (II) chloride hexahydrate ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$) was made in 100ml distilled water and 1M solution of Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was made in 100ml distilled water. Then these solutions were mixed with each other into conical flask and put on hot plate. The mouth of conical flask was closed by lid to ensure production of magnetic properties. This solution was heated and stirred on hot plate up to 50°C for 15minutes. After it 10ml ammonia solution was put into it, black precipitates of magnetite were formed whose washing was done with deionize water and put into oven at 90°C for overnight drying. After it grinding of magnetite was done and stored it [37].

2.2 Synthesis of Magnetite/Polypyrrol-Polyaniline Nanocomposite

In this oxidative polymerization of polypyrrol and polyaniline was done in presence of FeCl_3 oxidant to synthesize nanocomposite. In conical flask 160ml distilled water was taken and 0.1g of magnetite (Fe_3O_4) was put into water and

mixed. After it ultrasonication of it was done in water stirring ultrasonicator for half hour. Ultrasonication dispersed the magnetite particles into solution. After it this solution was cooled for some time and 12g of anhydrous Iron (III) chloride (FeCl_3) was put into it and its mixing was done on hot plate for 10 minutes. FeCl_3 used as oxidant in this reaction. For making solution of polypyrrol, chloroform solvent was used. 1g polypyrrol was dissolved into 25ml chloroform on hot plate for 1 hour to dissolve it. Some polypyrrol remained undissolved. so this solution was filtered. After it 0.8ml solution of polypyrrol and 0.8ml of aniline was put into this flask dropwise and mixed and continuous shaking was done for 15 minutes. Greenish blue solution was formed. This solution stayed overnight in order to allow the polymerization reaction to happen. After it this nanocomposite was washed with deionize water, filtrate color was brown washing was done until the filtrate colourless. Washing was done with acetone, filtrate again gave color and washed it till the time it became colourless. After it its drying was done into oven at 60 for 2 hours. After it a constant mass nanocomposite product was obtained [38].

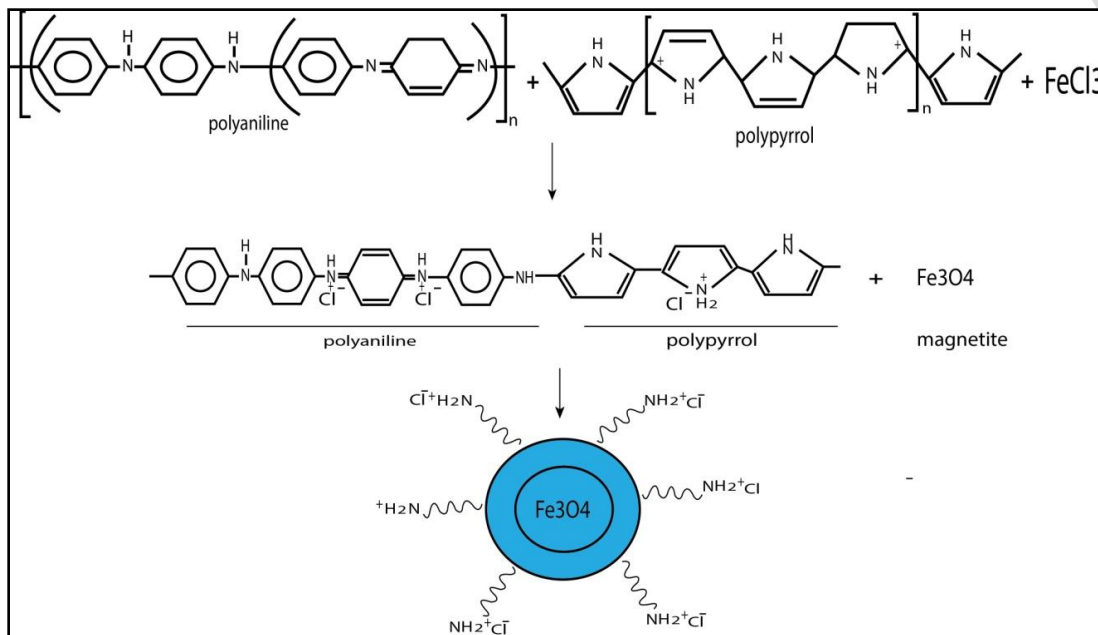


Fig. 1 Formation of magnetite/Polypyrrol-Polyaniline nanocomposite

3. RESULTS AND DISCUSSION

3.1 Characterization of (Fe_3O_4)/ (PPy)-(PANI) Nanocomposite

3.1.1 FTIR

FTIR spectrum was recorded from 650cm^{-1} to 4000cm^{-1} . Confirmatory peaks were checked in this spectrum. At 1400cm^{-1} a peak confirmed the presence of Fe-O group of magnetite. This peak showed the stretching of Fe-O group. While at 3100cm^{-1} a peak of O-H vibration was observed which also confirmed the magnetite presence in nanocomposite. For polypyrrol confirmation peaks were observed. Two peaks were observed at 840cm^{-1} and 920cm^{-1} which were due to deformation of C-H group. At 1545cm^{-1} and 1450cm^{-1} two peaks were observed one was due to stretching of ring and another peak was due to stretching of C-N group respectively. At 1044cm^{-1} one peak was due to stretching of C-H group. These were confirmatory peaks which confirmed the presence of polypyrrol. For polyaniline confirmation four peaks were observed. At 1170cm^{-1} one peak was observed which showed stretching of $\text{N}=\text{Q}=\text{N}$ group. At 1588cm^{-1} a peak was due to quinoid ring $\text{C}=\text{C}$ group. At 1274cm^{-1} and 1494cm^{-1} two peaks were observed which showed the stretching of C-N and $\text{C}=\text{C}$ benzenoid functional group respectively. These all functional groups confirmed the presence of magnetite, polypyrrol and polyaniline in the product [39].

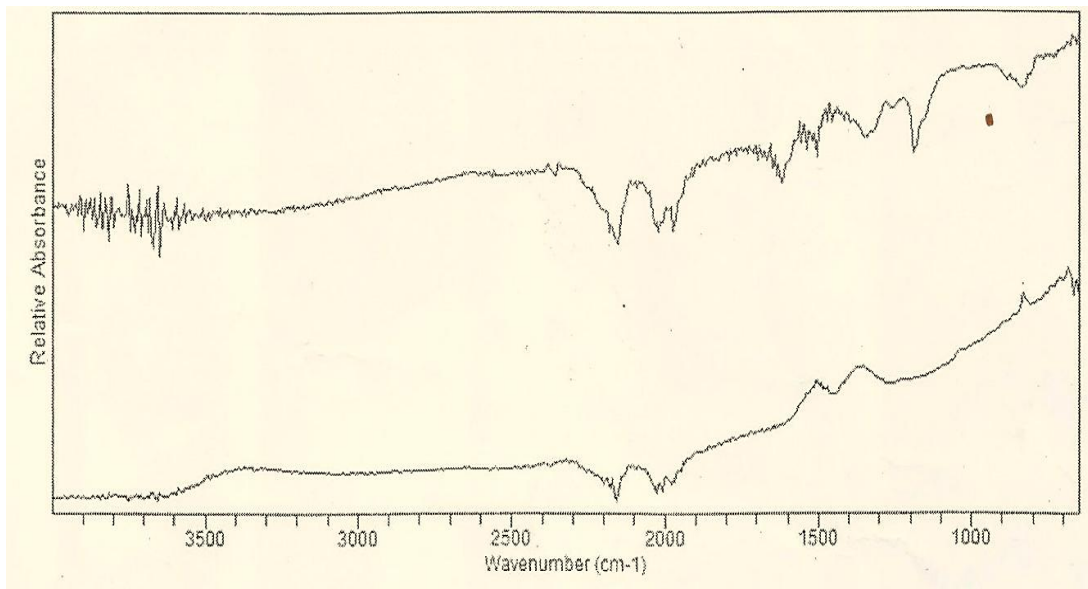


Fig. 2 FTIR spectrum of Fe₃O₄/PPy-PANI Nanocomposite

3.1.2 SEM Analysis

SEM image shows the presence of magnetite on the PANI-PPy polymer matrix. In situ polymerization method of aniline and polypyrrol leads to formation of nanofibers structure of PANI-PPy polymer matrix. In these images no nanofibers structure is shown because in this magnetite is used along with PANI and PPy which reduces the formation of nanofibers structure and leads to formation of agglomeration of particles. Magnetite shows as bright spot in these images it can be seen that magnetite bright spots are roughly spherical in shape and unequally agglomerated and distributed in the PANI-PPy polymer matrix. These images confirm the presence of magnetite in the nanocomposite [40].

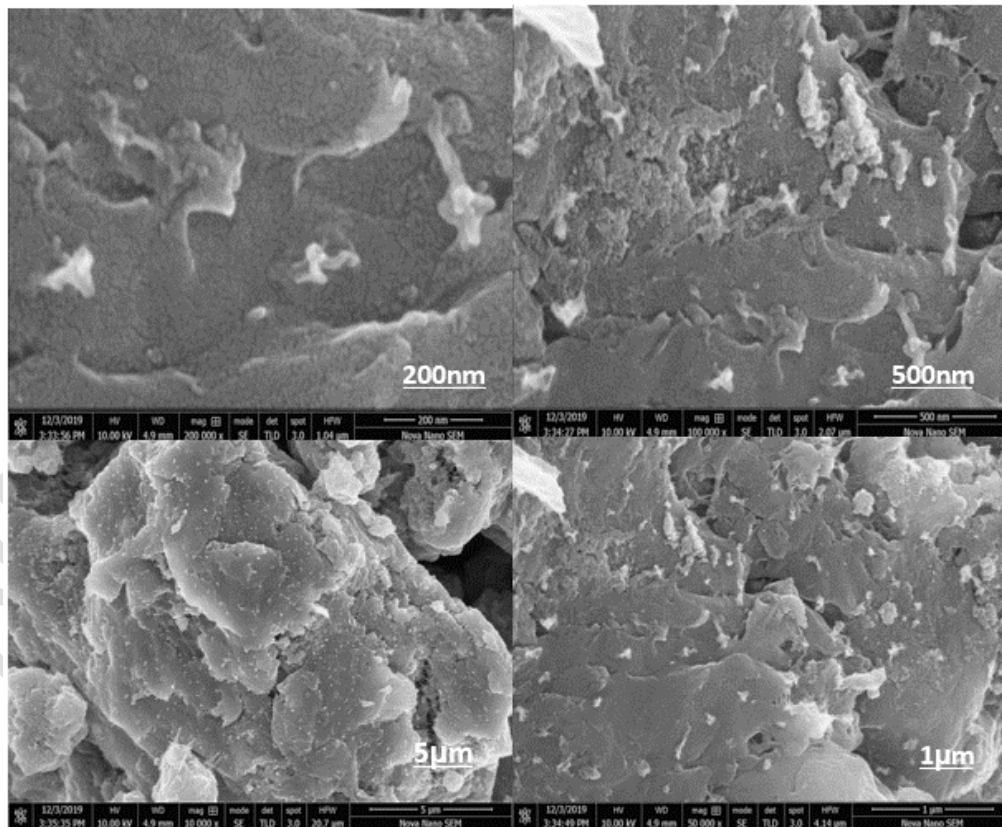


Fig. 3 SEM Images of Fe₃O₄/PPy-PANI nanocomposite at 200nm, 500nm, 5µm, 1µm resolution

3.1.3 XRD

XRD pattern is shown into given figure. At 2θ values of 14° , 21° , 25° , 26° some peaks are expected which are the characteristic peaks of PANI which has amorphous nature while at 22° a broad band peak comes which is the

characteristic peak of PPy which has mask the peaks of PANI. This broad band shows that PANI-PPy polymer matrix has low crystalline nature and PANI base form emeraldine may be present in it. XRD spectrum shows the crystalline nature of the nanocomposite. Diffraction peaks come at 2θ values of 29° , 35° , 42° , 56° , 62° which are related to intensity values which are observing for magnetite which has inverse cubic structure. XRD confirms that magnetite is entered into the polymer matrix [41].

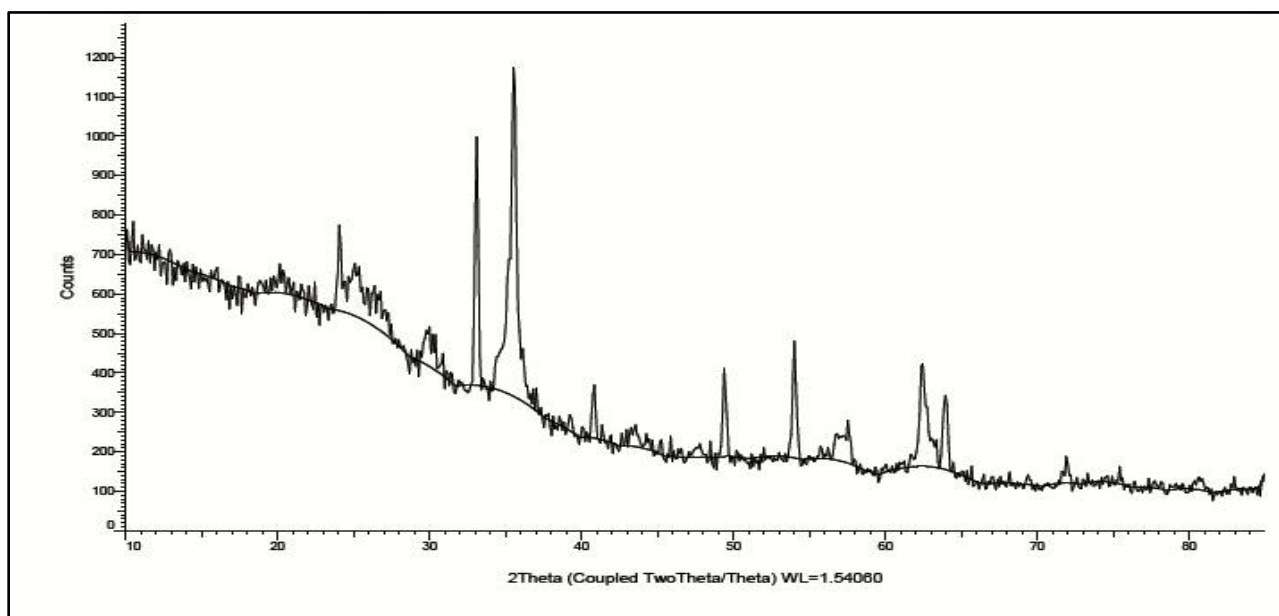


Fig. 4 XRD pattern of Fe₃O₄/PPy-PANI nanocomposite

Experimental Details

3.2.1 Optimization of parameters

Parameters including concentration and pH were checked. Concentration of nanocomposite was varied from 0.01 to 0.03g. pH was changed from 0 to 10. For adjustment of pH, 1M HCl and 1M NaOH were used.

3.2.2 Standards

250mg/L Stock solution of sodium arsenite was prepared by dissolving of 0.025g of (NaAsO₂) into 100ml distilled water. From this stock solution, different working standard solutions containing (0.025, 0.05, 0.075, 0.01μg/L) arsenic were prepared.

3.2.3 Reagent Preparation

Potassium iodate and EDTA solutions were used in colorimetric method.

- 1) 2% KIO₃ reagent solution was prepared by dissolving 2g of KIO₃ into 100ml distilled water. It was used as reagent for making complex with arsenite.
- 2) 0.01% EDTA solution was prepared by dissolving of 0.01g of EDTA into distilled water. NaOH was added into this solution for rapid dissolution.

3.2.4 Colorimetric determination of Arsenite

For removal of arsenic from aqueous solution different solutions of arsenic were formed by dissolving sodium arsenite into deionize water. In each solution 2ml of 2% potassium iodate (KIO₃) and 2ml sulphuric acid (H₂SO₄) was put into solutions and gently shaken light-yellow color appeared. After it 2ml of EDTA solution was put and shaken. Now 2ml carbon tetrachloride (CCl₄) was put then organic layer of pink color appeared. We separated the organic layer from aqueous layer and took its UV. pH of solutions was maintained to 2. After it 0.1g of nanocomposite was incorporated into solutions. Then pink layer color was turned into colourless state. After it UV readings were taken at 515nm for further confirmation of adsorption.

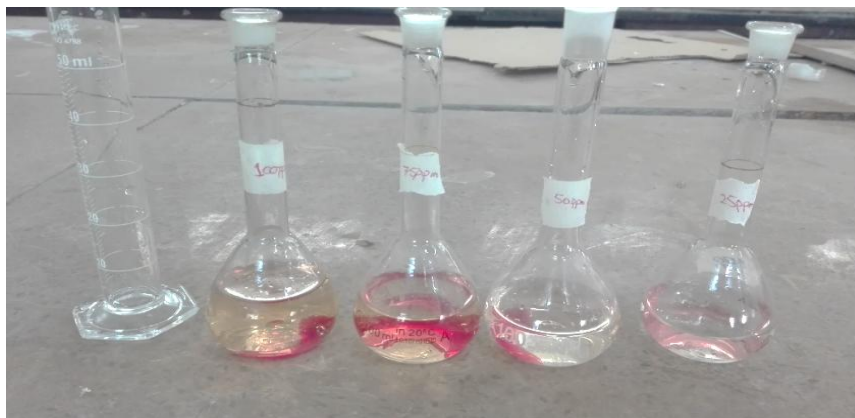


Fig. 5 Formation of pink organic layers of different concentration solutions

3.3 Effect of pH

pH was varied from 0 to 10. It was found that in acidic range nanocomposite worked best. This is because in acidic range the charge on the surface of nanocomposite was positive and more nitrogen are protonated. Due to which with arsenic species exchange of ion and adsorption took place. But in basic pH range, less nitrogen are protonated, So charge on nanocomposite was negative and adsorption was decreased because completion between hydroxyl group and arsenite. So in acidic range removal efficiency increased from 68 to 88%.

3.4 Effect of concentration of adsorbent

Concentration of adsorbent was varied from 0.005g to 0.03g. By increase, the concentration of adsorbent removal efficiency increased. 0.01g was concentration At which better adsorption took place. Minimum amount of adsorbent required for efficient removal of arsenite.

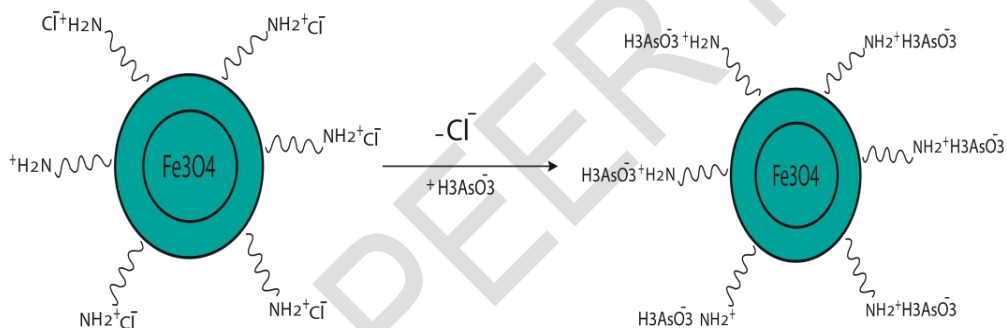


Fig. 6 Mechanism for Arsenic removal by nanocomposite

Table.1 UV Results

Concentration (mg/L)	Absorbance 1	Absorbance 2
100	0.641	0.087
75	0.469	0.08
50	0.322	0.069
25	0.169	0.06

By drawing calibration curve of all values the percentage adsorption and Q_e values are determined. This graph is given below.

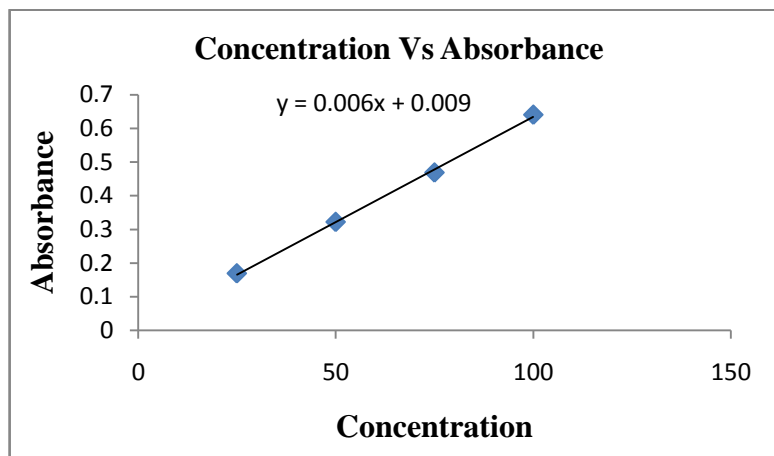


Fig. 7 Calibration graph between absorbance and concentration of solutions before adsorption

3.5 Determination of concentration of Arsenic and adsorption efficiency

Before adsorption and after adsorption absorbance values are given which show the adsorption of arsenite on the nanocomposite. %adsorbance is determined by the following formula. %Adsorbance = $\frac{C_0 - C_e}{C_0} \times 100$, C_0 is the initial concentration of adsorbate and C_e is the final concentration of adsorbate.

Q_e values are determined by the formula $Q_e = \frac{C_0 - C_e}{m \times V}$, C_0 is the initial concentration, C_e is initial concentration of adsorbate, m is the mass of adsorbent and V is volume of solution.

Table.2 Q_e values

Concentration (ppm)	Q_e
100	519
75	381.7
50	247
25	110

By using these values graph was drawn which showed the amount (mg) of adsorbate adsorbed onto the adsorbent (g). Graph is given below

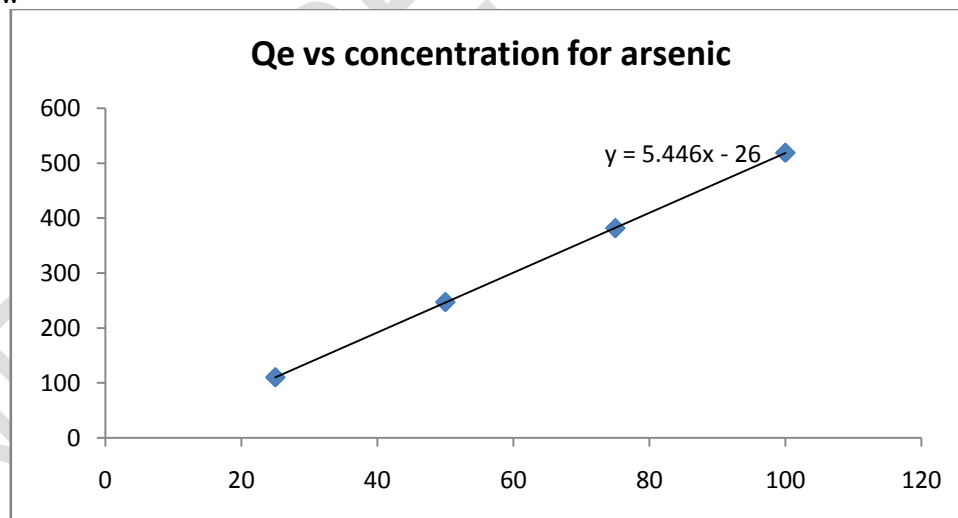


Fig. 8 Graph of Q_e values of solutions

4. CONCLUSION

We made a conducting polymer based nanocomposite for removal arsenic As (III) from aqueous solution. In situ oxidative polymerization process of polypyrrol and aniline in presence of magnetite was used for making of nanocomposite. Characterization of this nanocomposite is done to know about its properties. It was used for removal of arsenic from aqueous solution. It showed better adsorption from 1 to 3. At acidic pH condition it worked efficiently, it showed it is pH dependent. In acidic pH range positive charge was developed at nanocomposite Surface because $FeCl_3$ oxidized the nanocomposite and more nitrogen were protonated and Cl exchanged by anion exchange with arsenic speci. By using pH

1 and concentration of adsorbent 0.01g, 88% removal of arsenite (III) obtained. It showed that this nanocomposite gave the better removal efficiency in acidic pH range.

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