



## Fixed Bed Column Study for the Removal of Arsenic from Groundwater by Adsorption on Graphene Coated Functionalized Polyacrylonitrile Fiber

Waseem Abro\*, Khadija Qureshi, Imran Unar, Junaid Korai

Chemical Engineering Department, Mehran University of Engineering and Technology,  
Jamshoro, Sindh, Pakistan

\*Corresponding Author E-mail: waseemabbas4414@gmail.com

### ABSTRACT

Arsenic presence in ground water has appeared as alarming health issue in Pakistan, The majority of Pakistani people (almost 60%) live below the poverty line, with no access to safe and clean water sources. Arsenic is among the dangerous metals found not just in different parts of Pakistan, but also across the world. Above 20% inhabitants of Punjab Province of Pakistan are under the exposure of Arsenic with elevated level of above 10ppb in groundwater whereas 3% of people are under the effect of 50 ppb. The condition is worse in Sindh province with 36% and 16% of inhabitants drink arsenic containing drinking water with above 10ppb and 50ppb, respectively. Both narrow and profound sources partake arsenic contamination. Arsenic removal methods such as precipitation, membrane processes, ion exchange, and adsorption have been developed to remove arsenic from polluted water sources. Adsorption technology is appealing and widely utilized due to its sludge-free operation and possibility for regeneration. . Adsorption method is attracting and generally used for the reason that of its designing, simplicity operation, low cost and operation. Polyacrylic nitrile and its copolymers are one of them, which are studied for its commercial and technological exploitations. This column adsorption research utilizes a low-cost adsorbent named "Polyacrylonitrile Fiber (PAN)" to remove arsenic from drinking water. In comparison to other procedures for eliminating arsenic out ground water, this approach is more useful and effective. The adsorbent Polyacrylonitrile Fiber (PAN) was discovered to be an effective and efficient adsorbent for the removal of arsenic from ground water. PAN is readily accessible at a reasonable cost and may be employed as an effective adsorbent material for the removal of arsenic from water, according to this study.

### Keywords:

Fixed bed column  
Arsenic  
Adsorption  
Amine Doped Pan

### 1. Introduction

Water is essential for all life on Earth; humans and other living things cannot exist without safe and clean drinking water. Though, rapid growth in human civilization, population and industrial development become a cause of polluting the water with different chemicals including dyes, heavy metals and pharmaceuticals worldwide [1]. Arsenic is among the most toxic naturally occurring chemicals present in groundwater. Arsenic present in drinking water is an alarming issue and is at the top due to its high toxicity [2]. Lungs, Skin, kidney cancers,

and bladder are caused by long-term exposure to arsenic-contaminated water, along with pigmentation change, skin thickness (hyperkeratosis), neurological abnormalities, muscular weakness, lack of appetite, and nausea. Contamination of natural water with arsenic is a global issue. [3]. The incidence of health concerns related to high levels of arsenic has been widely described in the literature. Many major emerging and developed countries, such as Pakistan, India, Taiwan, China, Bangladesh, Malaysia, Mexico, Hungary, New Zealand, the United States, Japan, Canada and Spain have reported this problem. [4]. In Pakistan, arsenic pollution has arisen as a major public health hazard. Above 20% populations of Punjab Province of Pakistan are under the exposure of Arsenic with elevated level of above 10ppb in groundwater whereas 3% of people are under the effect of 50ppb. The condition is worse in Sindh province with 36% and 16% of inhabitants drink arsenic containing drinking water with above 10ppb and 50ppb respectively. Both narrow and profound sources partake arsenic contamination [5].

To reduce the negative health consequences of arsenic, the World Health Organization (WHO) proposed lowering the maximum contaminant limit (MCL) for arsenic in drinking water from 10ppb(parts per billion) [6]. However, a survey found that around 60 million individuals had an excess of drinking water that exceeds the 10ppb limit [7]. Although the inorganic form of arsenic including As(III) and A(V) and These forms of arsenic results in gastrointestinal, carcinogenic, dermatological, cardiorenal effects on people [8].

Arsenic contaminations in the freshwater bodies can be caused by natural activities like; erosion of soil, arsenic leaching into aquifers, weathering conditions, ecosystem activities of biodiversity, volcanos' eruption emissions [9]. There are number of anthropogenic activities like; mining, arsenic containing pesticides and herbicides, furniture preservatives chemicals and arsenic containing chemical additives can lead to increase in impacts [10]. The composition and chemical features of arsenic-contaminated water are the most important parameters to consider while removing arsenic. Arsenic removal methods that are now accessible are effective when used to remove arsenate. Arsenate is a neutrality substance with a pH of less than 9.2 (Feenstra and Erkel, 2007). The tetravalent form of a dangerous metal arsenic is treated in this approach, making it less accessible for ion exchange, precipitation, or adsorption. The two-phase method of arsenite to arsenate is shown to be an efficient operation that works on initial oxidation and also serves as an arsenate removal procedure.(Pous et al., 2015). Softening by precipitation (adding calcium oxide, calcium oxide plus sodium carbonate or sodium hydroxide to lessen hardness at acidic pH) is one of several additional treatment options available. For the removal of nitrates from surface water, bioremediation is used [11].

Ammonia removal from surface water via bio nitrification. Adsorption has been recognized as the most extensively employed arsenic removal process due to a number of benefits, including relatively high arsenic removal efficiencies, ease of operation and processing, cost-effectiveness, and the absence of sludge generation. Arsenic adsorption, on the other hand, is highly dependent on the concentration and pH of the solution. Adsorption of arsenate is preferred at low pH, but adsorption of arsenite is best between pH 4 and 9 [12]. For the removal of arsenic from water, a variety of adsorbents have already been investigated. Most traditional adsorbents, on the other hand, have irregular pore architectures and small specific surface areas, resulting in limited adsorption capabilities, Lack of selectivity, poor interactions with metallic ions, and regeneration issues may limit these sorbents' capacity to reduce arsenic levels to levels underneath the MCL [12].

Acrylic fibres are well-known for having better qualities to other synthetic fibres, such as bulk and heat insulation, and they may be used as a substitute for natural fibres like wool. DuPont developed the first acrylic fibre in 1941, which was utilised in the linings of sweaters, tracksuits, boots, and gloves, as well as in furnishing textiles and carpets. This fibre was also employed as a precursor for PAN since it contained at least 85% acrylonitrile monomer and could be made in big numbers at a low cost [13]. The nitrile groups on the PAN polymer's surface can take part in a variety of chemical processes and are easily cross-linked with polyamines. Diethylenetriamine (DETA) is a polyamine that is commonly used to raise the amount of amine groups on sorbents in order to improve their ion exchange capacity. [14]. DETA was successfully grafted onto a commercial acrylic fibre to create an ion exchange fibre in a prior work.

## 2. Materials and Methods

### 2.1. Functionalization PAN Fiber

At first the purchased PAN fiber was washed by deionized water and the filtered fiber was dried for 12 hours at controlled temperature of 50°C. The needle punched PAN fiber was cut into ~1 g sample that were then immersed in DI water overnight and dried at 50 °C. The PAN fibers were chemically modified before iron loading using diethylenetriamine (DETA) and aluminum chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) solutions.

PAN fiber 10 g and 10 g of Aluminum chloride hexahydrate (used as a catalyst) were taken in a 500mL round bottom flask and was added 250mL Diethylenetriamine (>97%). The flask was equipped with heating mantle and a reflux condenser mounted on a magnetic stirrer plate as shown in Fig. 3.4 on p. 30. PAN fiber was heated for 8 hours at 90 °C and stirred at 360 rpm. The fiber was functionalized using DETA in the presence of ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) catalyst. This

reaction in heating mantle was continuously monitored and temperature and mixing were controlled. After 8 hrs heating, PAN fiber was cooled to room temperature, then pH was checked and found 13. The PAN fiber samples were washed with deionized water (D.I) repeatedly and the pH after washing with D.I water was 10. PAN fiber samples were dried at room temperature. PAN fiber samples were dried for the iron loading by precipitation method.

## 2.2. Iron loading on Cross linked PAN fiber

Coating of Crossed Linked PAN Fiber is carried out by making a solution methanol 62.5 ml, distilled water 62.5 ml and modified PAN Fiber of 5 gram in 500ml conical flask was heated with hot plate stirrer up to 50 C for 1 hour. After then add 3 gram of Ferric chloride hexahydrate power is added in conical flask containing modified PAN Fiber along with methanol and distilled water solution, Continue stirring and heating until ferric hexahydrate were completely get dissolved in modified PAN Fiber, After then PH of modified Iron coated PAN Fiber was found 1.5. Ferric was precepted by neutralizing it by drop wise addition of 1M NAOH solution until PH will goes up to 8. Then conical flash was put on digital reprobating shocker at 150 rpm with time period of 5 hours.

After 5hour shacking PH was noted 6.5. Modified iron coated PAN Fiber was washed relatively with DI water to remove assess Precipitation. After than PH was observed 7.1. Then iron coated on Modified PAN Fiber was dried at room temperature for 12 hours.

## 2.3. Graphene Oxide coating on Iron loaded PAN fiber

The coating of the GO over the fiber was carried out by dissolving 50ml of Ethylene glycol in 450ml of distilled water. 2.5g of graphene oxide was placed in the solution at magnetic stirrer where the continuous stirring was takes place at constant temperature of 600c for 2 hours. The solvent Ethylene glycol is used for this process because it has high solubility for dissolution of GO around 5.5 Ug/ml.

After process of dissolution, the iron coated PAN fiber is mixed in solution and placed at stirrer at the rpm of 150 for four hours. The graphene oxide coated sample is then washed several times with DI water in order to normalize the pH of sample at 6.5. Then the prepared sample is dried in an oven at 500c for 12 hours.

## 2.3. Characterization of adsorbent

Adsorbent characterization was carried out using various equipment in order to examine the structure of the adsorbent at various phases and its behavior at various wave numbers. It was carryout by the following methods:

### 1. Scanning electron microscopy (SEM)

2. Fourier-transform infrared spectroscopy (FTIR)

3. Energy Dispersive X-Ray Analysis EDX

2.4. Fixed bed column study

The Fixed bed column used in this study was made of borosilicate glass with 0.5cm dia and 14cm height. The peristaltic pump was used here to maintain the inlet feed flow and fractionator was used to collect the sample at the bottom of the column. As shown in fig. 01.

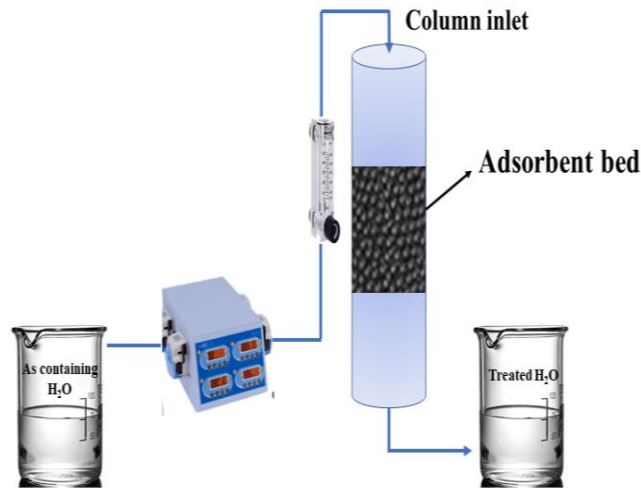


Fig. 01: Experimental setup of fixed bed Adsorption study

The effect of feed flowrate, bed height and residence time was observed whereas the initial feed concentration of arsenic was kept constant at 50ppb. The underexamined parameters are listed in table 01.

### 3. Result and discussion

3.1. Characterization of Adsorbent

#### *Fourier Transform Infrared (FTIR)*

The growth of functional groups and structure of the modified PAN fibre were studied using FTIR. N-H stretching and O-H stretching groups with alcohol, primary amine, secondary amine, amine salt, and carboxylic acid are seen in the frequency range of 3000-4000  $\text{cm}^{-1}$ . The peak at 3500 reveals N-H stretching with a primary amine compound. C=O stretching is seen at 1715.06, whereas N-O stretching is visible at 1540.66 and 1558.66 respectively. Everything to the right of 1500 is generally either fingerprint region or specific stretches of C=C, C-N.

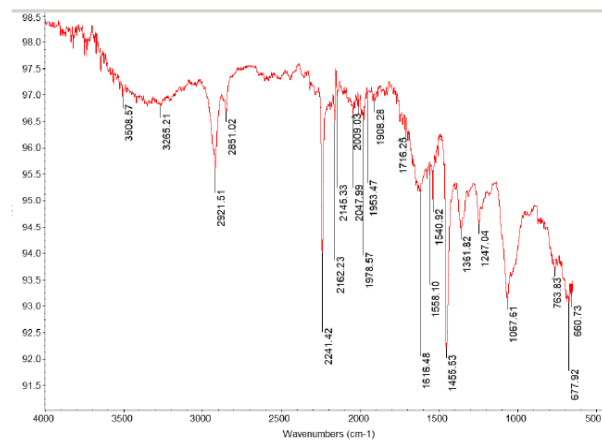
#### *Scanning Electron Microscopy SEM*

The surface morphology of the adsorbent before and after adsorption was studied using scanning electron microscopy on the modified PAN fibre. Before adsorption, the surface morphology seems smooth and uniform, however after adsorption, the surface morphology

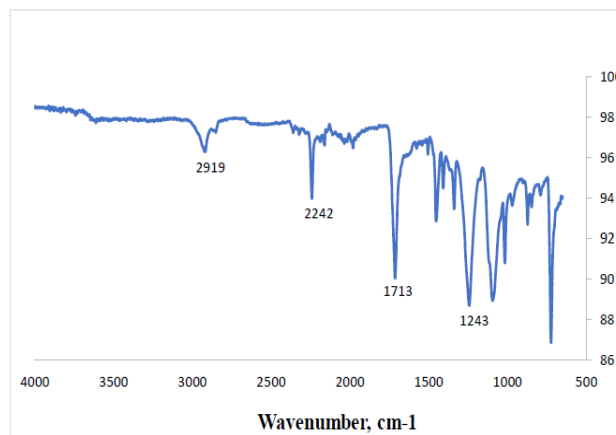
Table 01: Under examined parameters for column study

| Bed Depth (cm) | Inlet Feed Flowrate (ml/min) | Residence Time (min) |
|----------------|------------------------------|----------------------|
| 2.5            | 1                            | 30, 60, 90, 120, 150 |
|                | 2                            |                      |
|                | 3                            |                      |
| 5              | 1                            | 30, 60, 90, 120, 150 |
|                | 2                            |                      |
|                | 3                            |                      |
| 7.5            | 1                            | 30, 60, 90,120, 150  |
|                | 2                            |                      |
|                | 3                            |                      |
| 10             | 1                            | 30, 60, 90, 120, 150 |
|                | 2                            |                      |
|                | 3                            |                      |
| 12.5           | 1                            | 30, 60, 90, 120, 150 |
|                | 2                            |                      |
|                | 3                            |                      |

Table 01: *Contd.*



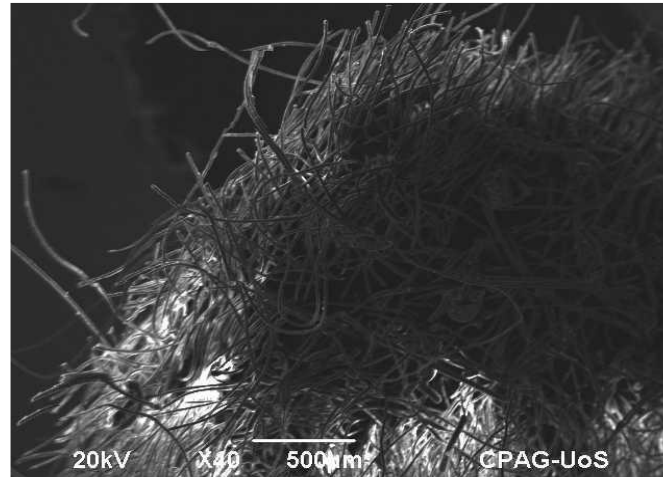
(a)



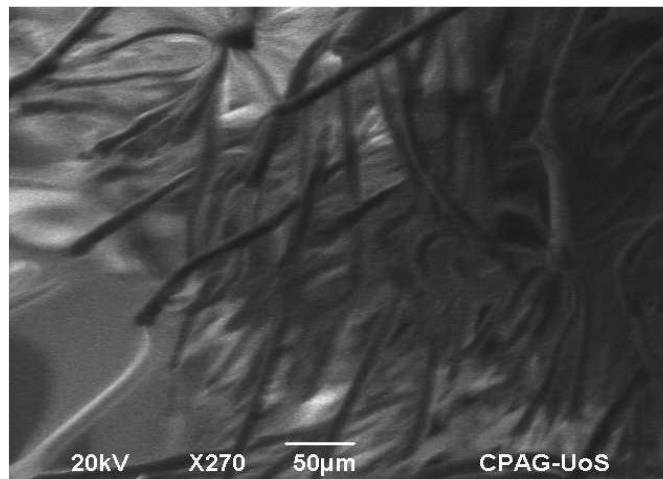
(b)

Fig. 02: FTIR results (a) before treatment (b) after treatment

changes dramatically, indicating that the adsorption process changes the surface morphology. Because the arsenic in the water sample was extracted and connected to the surface of the adsorbent during the adsorption process, the adsorbent became rough after the procedure was completed.



(a)



(b)

Fig. 03: SEM results of adsorbent before treatment at (a) 500  $\mu\text{m}$  (b) 50  $\mu\text{m}$

#### *Energy Dispersive X-Ray EDX*

Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an x-ray technique used to identify the elemental composition of materials. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed as depicted in figs. 05 (a) and (b).

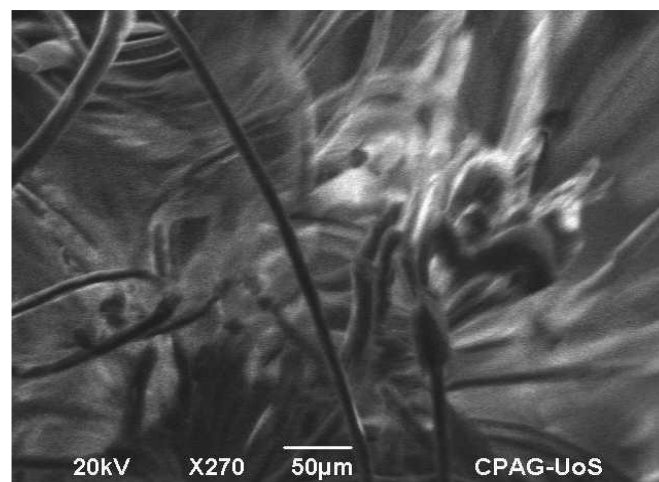
#### 3.2. Fixed Bed Column Study

The bed of coated material is used as adsorbent for arsenic removal from arsenic contaminated water. The Arsenic Contaminated water used in research is synthesized in Laboratory artificially. The bed is fixed in the absorption column and water is passed from the top of the absorption

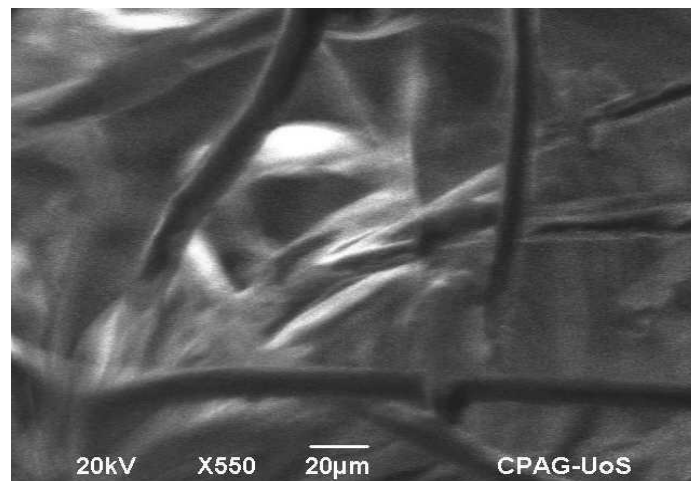
column. The effect of the bed depth and the feed flow rate were studied. The results regard experimental investigations are discussed in detail, in the following sections.

#### *Effect of Bed Depth on Arsenic Removal*

The effect of Bed depth or adsorbent height was observed at different measure as stated in Table 1. The effect was examined for three different flow rates a-e 1, 2, and 3 ml/min. Each sample was considered for different resident time the treated sample was collected at the bottom of the column at periodic intervals after that the arsenic contamination was analyzed by Atomic Adsorption and Arsenic Kit method.



(a)



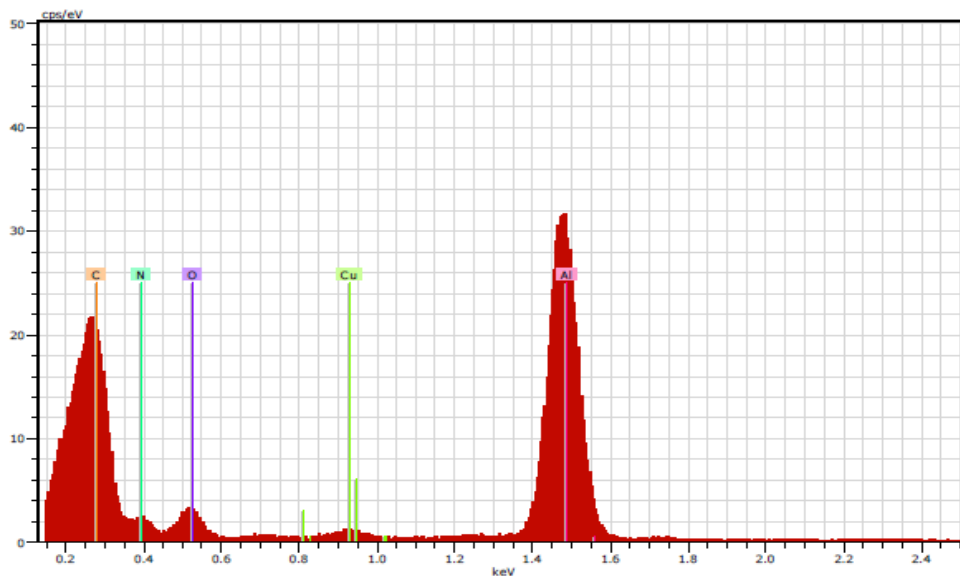
(b)

Fig. 04: SEM results of adsorbent after treatment at (a) 50 μm, (b) 20 μm

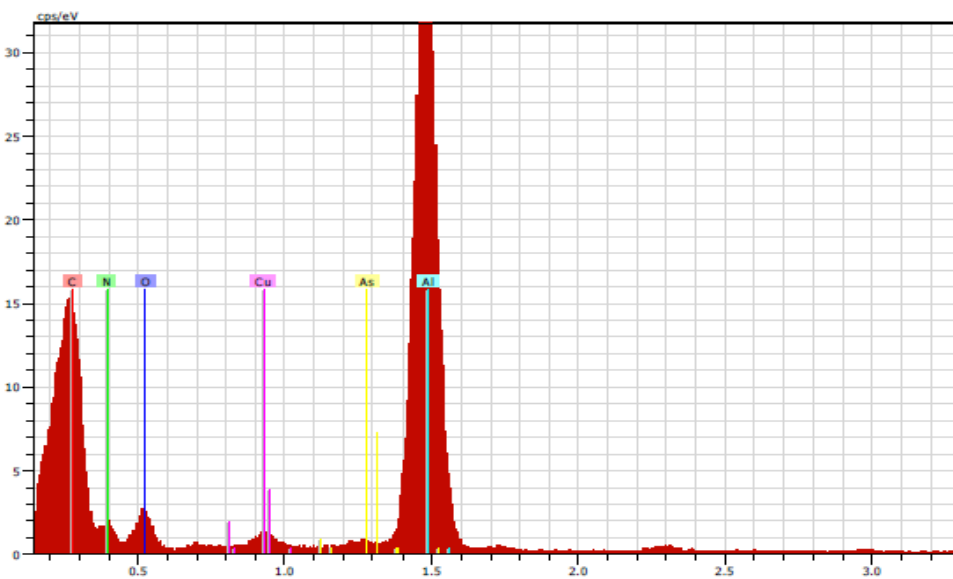
The optimum arsenic removal efficiency was obtained at low flow rate and high bed height. The removal percentage were found to be 98.8% at 12.5 cm bed height and 1 ml/min flowrate. But the minimum efficiency was also at acceptable limit which was found around



75-80% at different parameters. The effect of different bed height at different flowrates is show in fig. 06.



(a)



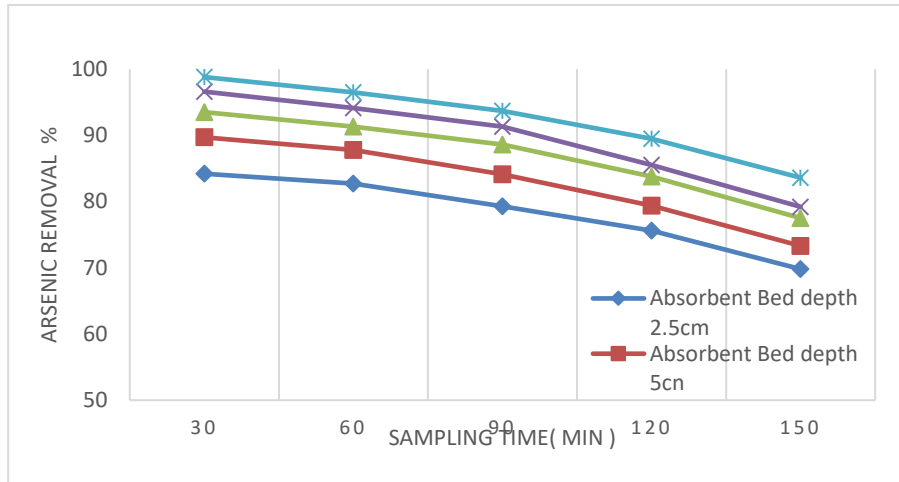
(b)

Fig. 05: EDX analysis of adsorbent (a) before treatment and (b) after treatment

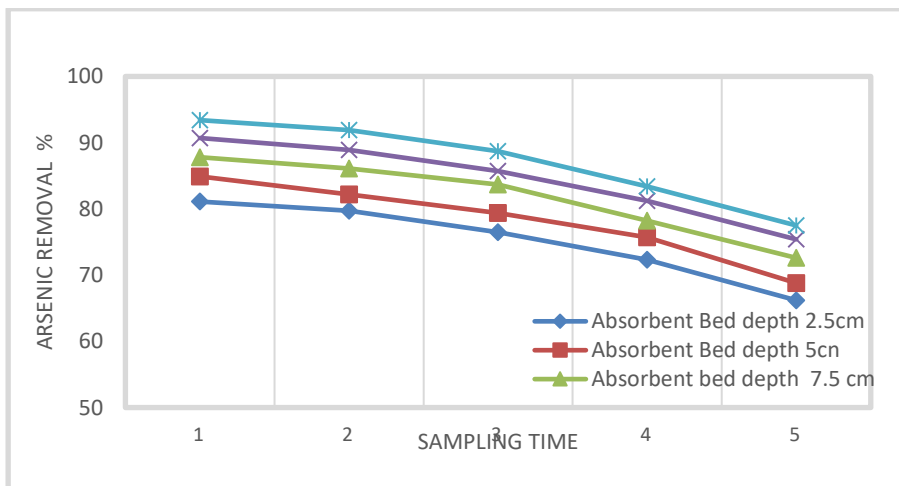
#### *Effect of Flow rate on Arsenic Removal*

The effects are shown with constant inlet concentration of Arsenic as 50ppb. The effect of feed flow rate was observed at three different flow rates of arsenic contaminated water as 1, 2 and 3 ml/min with varying bed depth of 2.5 cm, 5 cm, 7.5 cm, 10 cm, and 12.5 cm.

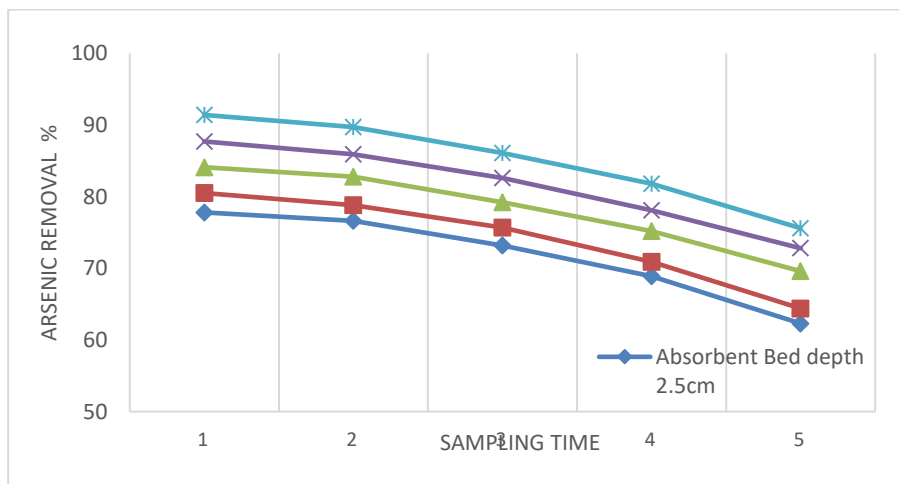
At inlet feed rate of 1, 2 and 3ml/min maximum arsenic removal was 74%, 92.4% and 91.2% respectively. It means lower feed flow rate is favorable for maximum arsenic filtration. The effects of the three inlet feed flow rates are show in fig. 7.



(a)



(b)



(c)

Fig. 06: Arsenic removal against different bed heights (a) at 1 ml/min, (b) at 2 ml/min and (c) at 3 ml/min

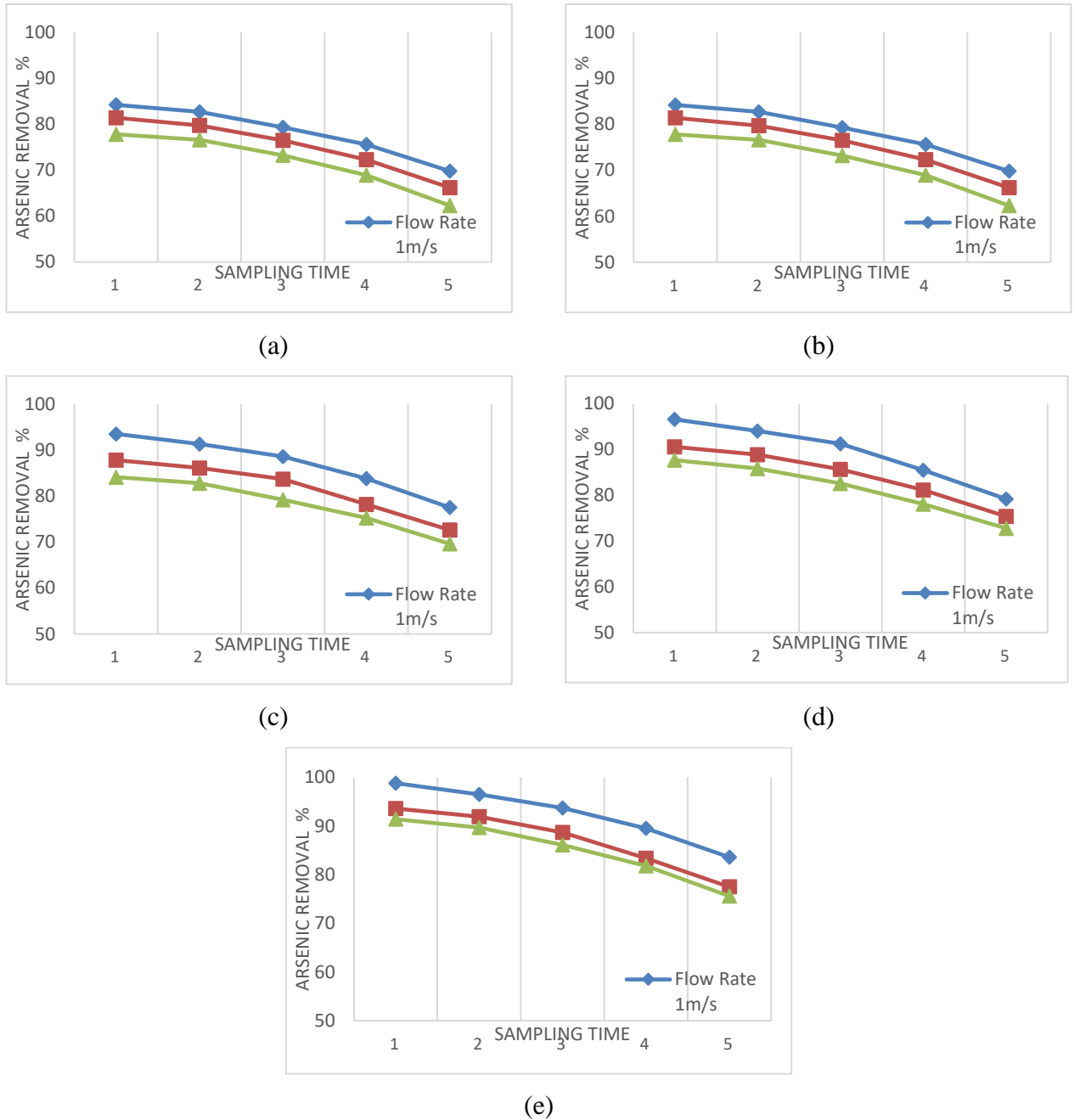


Fig. 7: Effect of flowrate on Arsenic removal @ bed height of (a) 2.5 cm, (b) 5 cm, (c) 7.5 cm, (d) 10 cm and (e) 12.5 cm

#### 4. Conclusion

Filtration of arsenic was investigated in filtration column of modified PAN fiber using aqueous solution at ambient temperature. The continuous study of the filtration system was also

conducted for finding the effectiveness of the modified fiber. The adsorption is affected by feed flow rate, contact time and adsorbent bed depth. Hence, by changing any parameter, the adsorption rate would be changed.

Flow rates were used between 1, 2, and 3ml/min and it was analyzed that by increasing flow rate decrease in removal efficiency of As was observed. So, it is concluded that at the flowrate of 1ml/min, the removal efficiency was maximum of As was maximum i-e 98%. Modified polyacrylonitrile fiber has been identified as an efficient adsorbent which can remove arsenic from aqueous solution even when its concentration is as low as 50 ppb.

The optimum conditions for the removal of arsenic from aqueous solution using modified PAN fiber as adsorbent were observed as flow rate: 1ml/min, adsorbent bed depth: 12.5 cm and contact time: 30 min. The maximum removal efficiency achieved on these optimum conditions was 98.8%. The modified PAN fiber was found to be economically efficient

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