

Adsorption of Arsenic by the Chemically Modified Polyacrylonitrile Fiber from Groundwater

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ABSTRACT

The existence of arsenic in groundwater has been reported across the world due to its highly toxic nature. It causes a serious public health issue. Various countries across the world are affected by drinking arsenic-contaminated water Pakistan is one of them. Arsenic levels have recently been found to be alarmingly high in the groundwater in the Matiari District in Sindh, Pakistan. This study focuses on rural areas of Matiari where drinking water is primarily obtained from the ground. According to WHO standards of 10 µg/L globally and 50 µg/L for Pakistan, groundwater arsenic concentrations in Matiari District have reached up to 250 µg/L. In this research, adsorbent polyacrylonitrile fiber was modified by diethylenetriamine, loaded with iron, and functionalized with chitosan. This chemically modified polyacrylonitrile fiber adsorbent is used in fixed bed column. The characterization of modified polyacrylonitrile fiber was performed by the FTIR and SEM. The removal efficiency of the fixed bed adsorption column was optimised by changing various operating parameters such as flowrates of 5 mL/min, 10 mL/min, and 15 mL/min; bed height of adsorbent of 1 cm, 2 cm, and 3 cm. The groundwater of Matiari Stop, district Matiari, Sindh, had an initial arsenic concentration of 100 g/L. The 89.3% removal efficiency was achieved at a maximum of 3 cm bed height and at 5 mL/min. The adsorbent, functionalized polyacrylonitrile fiber, was an effective and efficient adsorbent for the removal of arsenic from groundwater.

Keywords:

Arsenic,
Fixed bed column,
Polyacrylonitrile
Fiber,
Groundwater

1. Introduction

Water is a necessary element of all biological processes and life. Arsenic is a poisonous element that is found in a variety of natural environments [1]. Arsenic is mostly transferred into groundwater through weathering of pollutant rock minerals such as arsenopyrite (FeAsS), realgar (AsS), cobaltite (CoAsS), and scorodite (FeAsO₄·2H₂O) [2]. Other human activities, including mining, burning fossil fuels, and farming, can cause arsenic contamination of groundwater [3]. Arsenic is a slow toxin, and long-term exposure from food and drink can result in kidney, bladder, skin, and lung cancers, as well as pigmentation changes, neurological problems, cardiovascular illness, and other problems [4].

Stomach aches, nauseousness, vomiting, diarrhoea, and headaches are symptoms of short-term exposure [5]. Over 200 million people worldwide are exposed because 105 countries have reported arsenic concentrations in drinking water that are higher than the WHO recommendation of 10 g/L [6].

Arsenic is typically removed to tolerable levels using techniques such as precipitation and coagulation, oxidation, reverse osmosis, ion-exchange, and adsorption [7]. Adsorption is the most popular of these technologies because of its low cost, simplicity of use, and increased efficiency [8]. The effectiveness of many adsorbents for removing arsenic has been tested, including activated alumina, activated carbon, graphene oxides, clay soils, bone char, granular ferric hydroxides, and PAN fiber [9]. PAN fiber adsorbent is used to remove arsenic and other pollutants from water because of its characteristics, including chemical and mechanical stability, better cation/anion capacity, and higher surface area. Furthermore, it may be chemically modified to increase its sorption efficiency [10].

In the current study, polyacrylonitrile (PAN) fiber was chemically modified by diethylenetriamine, loaded with iron, and then grafted with chitosan, improving the fiber's characteristics and increasing its capacity for sorption. The grafted fiber, which has a high sorption capacity and is inexpensive, non-toxic, and environmentally acceptable, was successfully employed to remove arsenic from groundwater in Matiari, Sindh, Pakistan, and investigates the different treatment parameters of the adsorption column, such as flowrate and bed height to optimize the performance of the column.

2. Materials and Methods

2.1. PAN Fiber Cutting and Washing

Initially, distilled water was used to clean the purchased PAN fiber, and the filtered fiber was then left to dry for 24 hours at room temperature. The PAN fiber was divided into small pieces. Dimethylacetamide was used to chemically modify the PAN fiber before iron loading.

2.2. Chemically modification of PAN Fiber

A 500 mL round bottom flask containing 8 g of PAN fiber also included 250 mL of dimethylacetamide. The flask had a heating mantle and a reflux condenser positioned on a magnetic stirrer plate. 8 hours of 90 °C heating and 350 rpm stirring were applied to PAN fiber. Dimethylacetamide was used to functionalize the fiber. Temperature and mixing were under constant surveillance as this reaction in the heating mantle occurred. The PAN fiber samples were repeatedly washed in distilled water and dried at room temperature.

2.3. Iron loading on modified PAN fiber

To load iron onto modified PAN Fiber, prepared a solution of 65 ml methanol, 65 ml distilled water, and 5 g of modified PAN Fiber in a 500 ml flask. Heat the solution on a hot plate stirrer for 45 minutes at 60°C. In a flask containing modified PAN Fiber, methanol, and distilled water solution, 2.5 grams of ferric chloride hexahydrate power is then added. The pH of modified Iron-loaded PAN Fiber was 1.5, and the pH was corrected by adding drops of 1M NaOH solution, one at a time.

2.4. Grafting of chitosan on Iron loaded modified PAN fiber

Chitosan solution was initially created using aqueous acetic acid (CH₃COOH). 1000 ml of distilled water and 250 ml of acetic acid were added to 20 g of chitosan powder, and the conical flask was then placed on a hot plate stirrer for five hours at 45 °C and 250 rpm. The pH of the produced solution was around 3.7, and when pH was neutralized with 1.0 M NaOH, the final pH was 6.9. 400 ml of chitosan solution was then added, along with 8g of MPAN-Fe fiber, and the conical flask was then placed on a hot plate stirrer for 3 hours at 40 °C at 300 rpm. The PAN fiber was functionalized with chitosan and used for adsorption of arsenic from groundwater.

3. Result and discussion

3.1. Characterization of Adsorbent

Characterization was performed out to determine whether the surface morphologies of adsorbent and functional group development evolved.

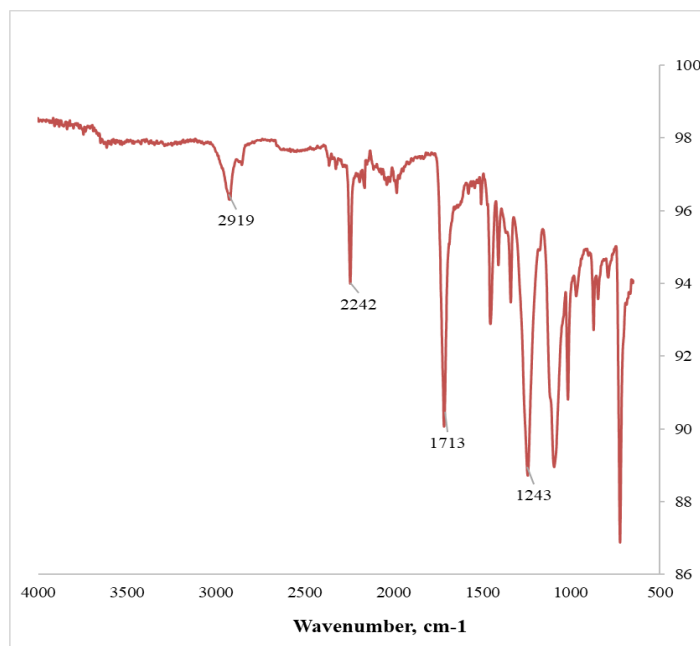
3.1.1. *Fourier Transform Infrared Spectroscopy (FTIR)*

The formation of functional groups and the structure of the modified PAN fiber were studied using FTIR. Fig.1, displays the FTIR results for virgin PAN fiber. N-H stretching and O-H stretching groups with compounds of alcohol, primary amine, secondary amine, amine salt, and carboxylic acid is visible in the frequency range of 3000–4000 cm⁻¹. As a result, the peak near 3500 shows N-H stretching with a primary amine molecule. C=O stretching can be seen in the peak at 1715.06, whereas N-O stretching can be seen in the peaks at 1540.66 and 1558.66. Generally speaking, everything to the right of 1500 is either a fingerprint region or distinct C=C, C-N, or C-O stretches.

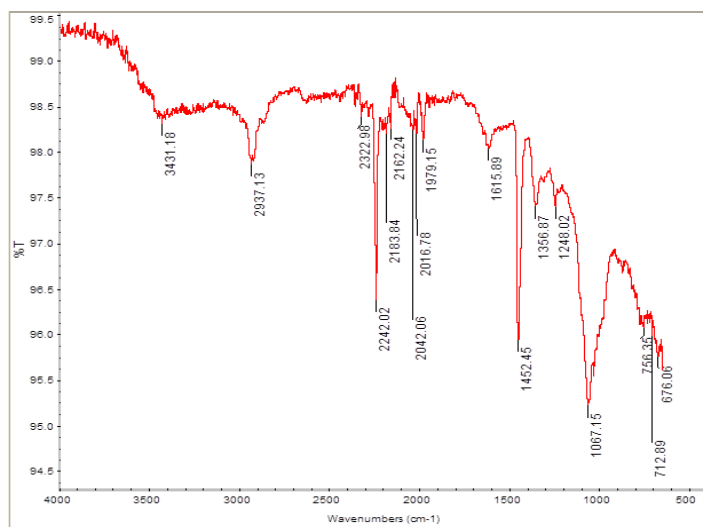
3.1.2. Scanning Electron Microscopy (SEM)

An electron microscope known as a scanning electron microscope scans a sample's surface with a concentrated beam of electrons to obtain images of the material. As the electrons contact with the sample's atoms, different signals emerge that reveal details about the

sample's surface topography and composition. SEM analysis of the modified PAN fiber was performed to determine the surface morphology of the adsorbent.

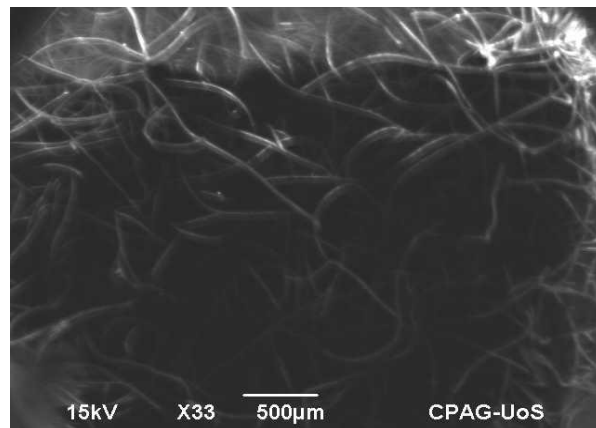


(a)

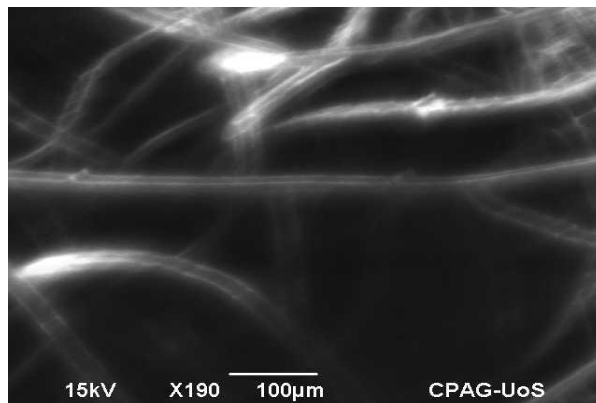


(b)

Fig.1: FTIR results (a) before treatment (b) after treatment



(a)



(b)

Fig. 2: SEM results of adsorbent (a) before treatment (b) after treatment

3.2. Parametric Investigation of Fixed Bed Column

3.2.1. Impact of Bed Height

The impact of bed height on the concentration of arsenic in treated water by using a fixed bed of arsenic ions to adsorb arsenic at varied bed heights (1, 2, and 3 cm) and varying flowrates (5, 10, and 15 mL/min) with a constant inlet concentration of 100 µg/L. The breakthrough curves, which represent the relationship between the inlet and outlet concentrations of adsorbed material (C_o/C_i), demonstrate performance. Because there are more binding sites available for adsorption as bed height is increased, breakthrough volume likewise rises. With longer service times, more intra-particle diffusion occurs into the adsorbent particle's internal pores. The amount of arsenic ions that are adsorbed increased with increased bed height and decreased flow rate.

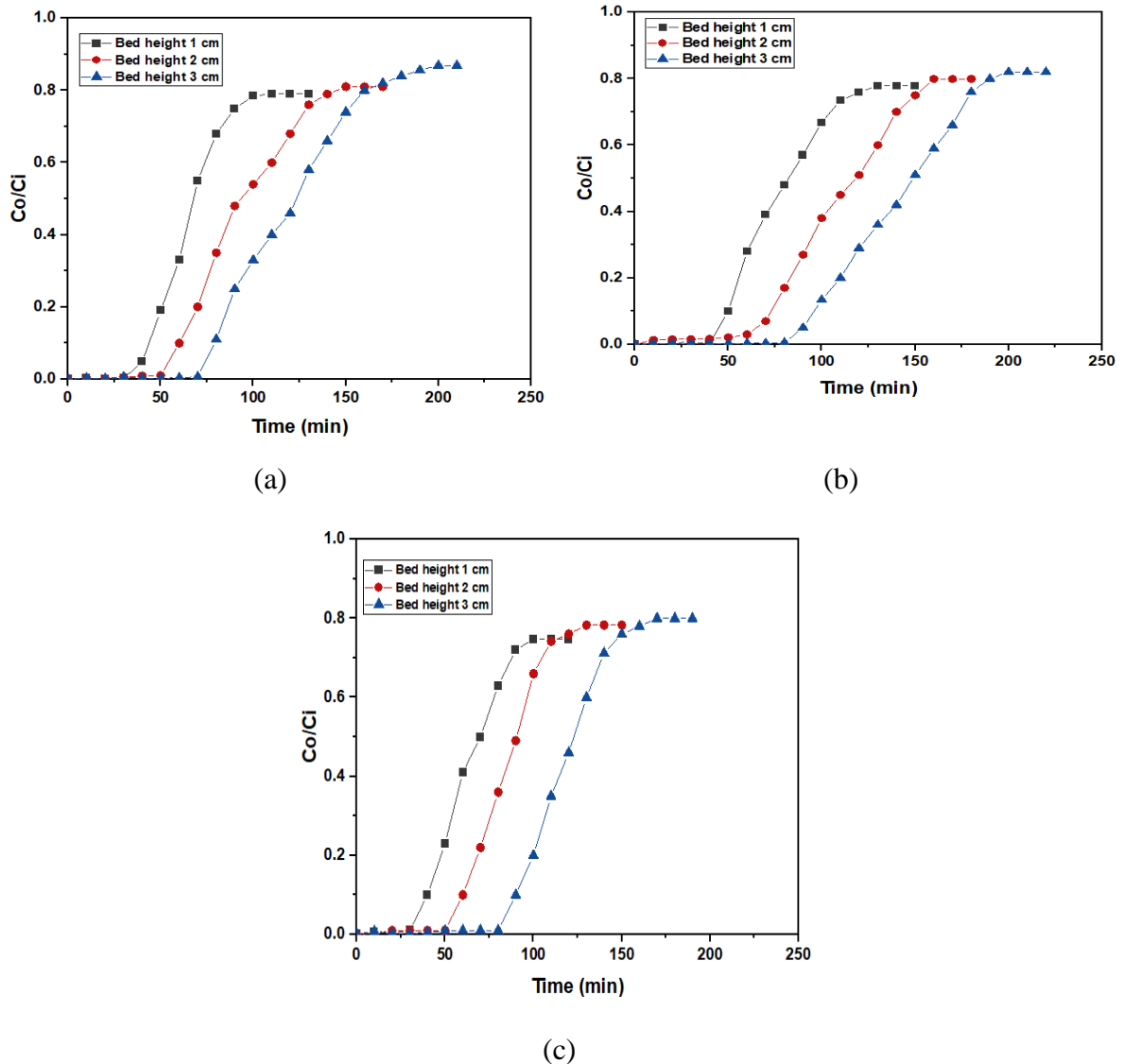


Fig. 3: Impact of bed height on Arsenic removal @ flowrate of (a) 5 mL/min, (b) 10 mL/min, (c) 15 mL/min.

3.2.2. Impact of Flowrate

The impact of flowrates on the concentration of arsenic in treated water by using a fixed bed of arsenic ions to adsorb arsenic at varying flowrates (5, 10, and 15 mL/min) with a constant inlet concentration of 100 $\mu\text{g/L}$. The impact of feed flowrate on arsenic concentration in treated water appears to be depicted in the figure, which also appears to show arsenic adsorption on MPAN at various feed flowrates (5, 10 and 15 mL/min), at various bed heights (1, 2, and 3 cm). The volume of the breakthrough decreases as the flow rate increases as a result of the arsenic ions' reduced residence time in the packed-bed column. With a decrease in flow rate, both the arsenic removal percentage and the total amount of arsenic ions adsorbed rise. Increased contact time results in improved arsenic ion absorption into the pore

structure of the adsorbent particle. Therefore, intra-particle diffusion plays a significant role in the adsorption of arsenic via the packed-bed column at a low feed flowrate.

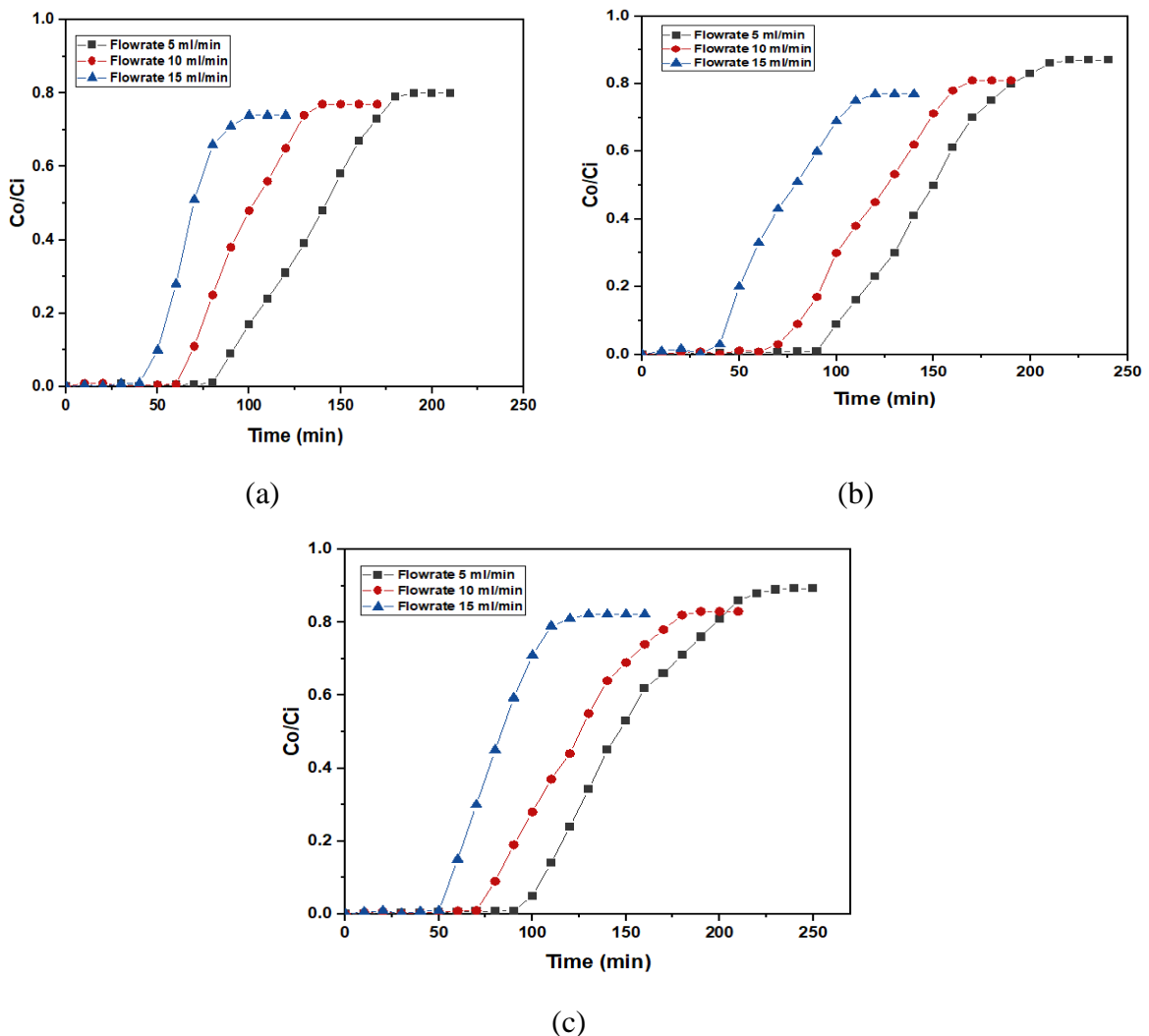


Fig. 4: Effect of flowrate on Arsenic removal @ bed height of (a) 1 cm, (b) 2 cm, (c) 3 cm

4. Conclusion

The objective of this research is to modified an adsorbent for the removal of arsenic from groundwater that is economical, simple to make, and effective in comparison to other adsorbents. For the purpose of determining the efficiency of the modified fiber, a continuous analysis of the filtration system was also carried out. The ability of modified polyacrylonitrile fiber to effectively remove arsenic from groundwater was analyzed. Feed flowrate and bed height both have an impact on adsorption. As a result, varying the parameter changed the adsorption rate. It was determined that the removal efficiency of arsenic decreased with an increased in flowrate when flowrates of 5, 10, and 15 mL/min were used. The adsorption is

affected by feed flowrate, and adsorbent bed height. Hence, by changing the parameter, the adsorption rate changed.

Flowrates were used between 5, 10, and 15 mL/min and it was analyzed that by increasing flow rate decreased in removal efficiency of arsenic was observed. The 89.3% removal efficiency was achieved at a maximum of 3 cm bed height and at 5 mL/min.

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