

| RESEARCH ARTICLE**Arsenic Adsorption on Designed Packed Bed Column using Chemically Modified PAN Fiber- A Simulation and Modeling Studies.****Muhammad suleman Memon¹ ✉ Imran Nazir Unar² and Khadija gureshi³**^{1,2,3}*Department of chemical engineering, Mehran University of Engineering and Technology, Jamshoro, Sindh, Pakistan***Corresponding Author:** Muhammad suleman Memon, **E-mail:** mohammadsulemanmemon@gmail.com**| ABSTRACT**

The efficiency of Chemically modified PAN Fiber (CM-PAN) as an adsorbent for the removal of As(III) from groundwater performed. For polluted water, many techniques have been developed recently to remove arsenic from it, such as chemical precipitation, adsorption, ion exchange, membrane processes, and others. Adsorption is the most often used technique because of its high arsenic performance and low cost. Arsenic (III) was removed from the aqueous solution in this study that use an adsorption technique with chitosan/iron oxide coated PAN Fiber as the adsorbent. In this work, Aspen AdsimV11 was used to create a steady-state model of a fixed bed column in the impact of various process factors. We created a small scale column of 2-cm-diameter and with various bed depths such as 1, 2 & 3cm. By an up-flow rate of 1, 2 & 3 mL/min and large scale column 8-cm-diameter and with various bed depths such as 8cm and by an up-flow rate of 512, 1024 & 1536mL/min. The amount of polluted water that was react towards the breakpoints where adsorption capacity was 91%of As(III) in a concentration of 0.0004004 mol/liter, 88%of As(III) in a concentration of 0.000269 mol/liter and 85% in a concentration of 0.0001335 mol/lit. By increasing starting concentration and bed depth and, total As (III) uptake decreased with increasing flow rate. Bed depth service time (BDST), mass transfer, first order kinetics, and regression analysis of equilibrium data were used to simulate the dynamics of the adsorption process and fit the Langmuir isotherms. The water quality of the treated effluent is adequate for home use, according to the findings. Ion exchange and physiosorption on the adsorbent surface appeared to be the mechanisms for As(III) removal in the CM-PAN column. For arsenic removal from groundwater, this appropriate module would be generate by using these results.

| KEYWORDS

Arsenic Removal, PAN Fiber, Modeling and Simulation.

| ARTICLE INFORMATION**RECEIVED:** 12 June 2023**ACCEPTED:** 28 August 2023**PUBLISHED:** 02 September 2023**1. Introduction**

On this planet, water is need for all life; human beings and all other breathing stuffs are incompetent to survive without safe and clean water. However, due to the swift development of human civilization, population, and manufacturing, water is becoming increasingly impacted by multiple substances, including dyes, heavy metals, and prescription drugs. [Ahmad, 2016]. Usage of water is also increasing day by day due to the growth of population in drinking purposes, industries and agriculture; in recent times, many developed and developing countries are facing high pressure to complete demand for water. Among the expanse extracted drinkable groundwater for supplies are originate arsenic contamination [Khanet al 2021]. .when ground water use for drinking purposes, agriculture, irrigation and fishery water, then wide occurrence of arsenic ground water effect human health, such as skin cancer, heart problems and skin keratinization, but nearly 150 million people are using that water above the limit[Liu 2021].

according to WHO arsenic limit in groundwater is above 10ug per liter in the form of arsenic (III) and arsenic (V); arsenic (III) occurred nearly 60-90 percent as compared to arsenic (V) [Wang et al 2021].

Arsenic contamination of drinking water bodies is of global concern. This phenomenon has been reported in a number of notable developing and developed countries, including Canada, India, Pakistan, China, Japan, Taiwan, Bangladesh, Malaysia, Hungary, the United States, New Zealand, Spain, and Mexico [Gallegos-Garcia et al 2012].

In Pakistan, the appearance of arsenic ground water has an alarming health issue, and Arsenic contamination has emerged as a serious public health concern in Pakistan. In Pakistan's Punjab Province, more than 20% of the population is at risk from arsenic at levels exceeding 10 ppb in groundwater, but just 3% of all people are affected by 50 ppb. The situation is not as good as in Sindh province, where 36% and 16% of people who live there, respectively, consume water that has more than 10ppb and 50ppb of arsenic. Both limited and deep sources are responsible for arsenic pollution [Ahmad et al 2004].

There are many different methods for arsenic removal, but Adsorption is a suitable and efficient As removal technique which is economically feasible, and it is easily available for developing countries that lack skilled personnel which remove above 95%, which mainly depend on the separation of van der Waals and the electrostatic attraction forces among adsorbed molecules [Alka et al 2021]. For the removal of arsenic from the environment, numerous conventional technologies have been investigated, which include flocculation, chemical precipitation, solar oxidation ion-exchange, bioremediation, coagulation, adsorption, and electrochemical processes. [Singh et al 2004]. Although commercial activated carbon is the most commonly utilized adsorbent, its extremely high cost is a drawback [Ihsanullah et al 2016].

PAN fiber has been the most widely used carbon in the world, so the prepared sample made from PAN fiber shows one of the largest adsorption capacities as a carbonaceous material and adsorption capacities are hardly decreased until equilibrium solution pH (pHe) changes from an acidic to neutral range. [Machida, et al 2021].

A novel idea for forecasting and optimizing the electro spun PAN process parameters was put forward in this work. First, the incompressible Navier-Stokes equation was used to develop the control equation for the electrospun PAN, and simulation software was used to solve and analyse the volume force and jet velocity during the electro spinning process. [Chen et al 2021].

Acrylic fibers are well recognized for taking recovering qualities to other artificial fibers; in place of natural fibers like wool, they can be used for functions like bulk and thermal insulation. [MENGÜÇ 2016]. they are well known for having superior qualities to other synthetic fibers, such as bulk and heat insulation. [Batchelor, 2016, Simitzis et al 2015]. The PAN polymer's nitrile groups may take part in a variety of chemical processes and are rapidly cross-linked with polyamines. [Zhang et al 2008, Chaudhary et al 2014]. A frequent polyamine used to enhance the amount of amine groups on sorbents for their ion exchange capacity is diethylenetriamine (DETA). [Kagaya, 2016, Elwakeel et al 2015]. In prior research, DETA was efficiently grafted onto a synthetic anion exchange fiber made from commercial acrylic fiber [Ko, 2011].

Then, applying the response surface strategy, the impact of simultaneous changes in several process factors on the average fiber diameter was investigated, and a prediction model was created. Last but not least, the experimental outcomes showed that the model can forecast the average fiber diameter when many process factors are concurrently altered. [Chen et al 2021]

The aim of the present study is to use modified Polyacrylonitrile (PAN) Fiber as adsorbents for the removal of Arsenic. To evaluate the performance of the adsorption column and modified PAN fiber, the dynamic simulations will be carried out in Aspen Adsim V11.

The novelty of this research is to check the modified PAN Fiber adsorption capacity of arsenic metal from synthetic water on the dynamic simulations in Aspen Adsim V11.

2. Materials and methods:

2.1 Model Development:

The Aspen ADSIM includes a variety of partial differential equations (PDEs), ordinary differential equations (ODEs), and algebraic equations to describe the total adsorption or ion exchange column collectively with the important starting and boundary conditions.

For the development of the simulation model, ASPEN ADSIM Version 11 commercial MS Window based simulator developed by Aspen-tech was used as a simulation tool. The recent literature on arsenic removal using kaolin was selected for input data. A synthetic sample with a given concentration was generated for the case study and run through a continuous column having adsorbent with known characteristics.

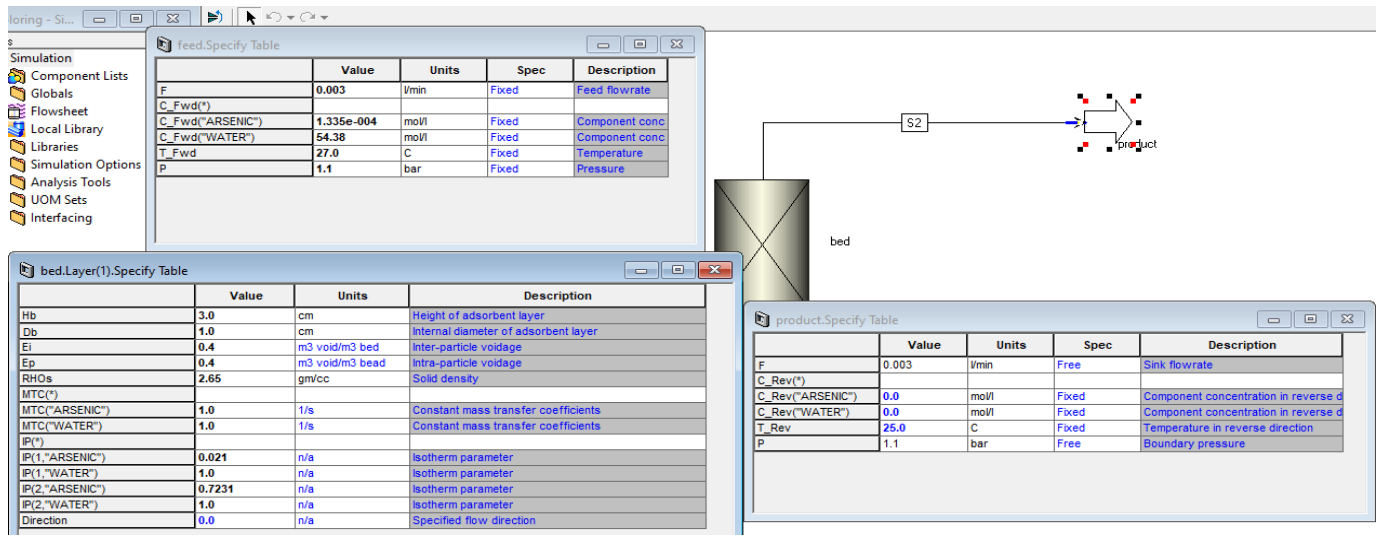


Fig:01 outlines the adsorption column model that was used for simulation. The "Feed" stream enters the column, and the initial column flow in the simulation is considered to be the ideal flow pattern where all water and arsenic molecules pass. As a result, only convective force is responsible for adsorption. For simulation, the mass transfer coefficient's default value from the model was utilized. Similarly, the model's default isotherm parameters for water were determined to be Langmuir isotherm values.

At 25°, the temperature was considered to be constant. A cylindrical column with a 2 cm diameter and a bed that was 1 cm, 2 cm, 3 cm, 8 cm, 16 cm, and 24 cm thick was allowed to run for 600 minutes. The difference technique used for calculating the model equations was expected to be the bi upward difference scheme (BUDS) with 50 numbers of nodes.

2.2 Characteristic Data for Kaolin Bed

Natural Kaolin is an effective way to remove arsenic from groundwater, and a tonne of study has already been done to determine the Kaolin's key characteristics. The main variables that were applied in this study's simulation of the Kaolin bed are shown in the table. The parameters were taken from earlier research.

S.No.	Parameters:	Used Value.
○ 1	Inter particle Porosity;	0.412/m ³ void/m ³ bed
○ 2	Intra Particle Porosity;	0.4/ m ³ void/ m ³ bed
○ 3	Mass Transfer Coefficient (MTC)	0.23/sec
○ 4	Material Density;	2.65 gram/cm ³
○ 5	(Langmuir Isotherm) IP1	0.021
○ 6	(Langmuir Isotherm) IP2	0.7231

2.3 Collection of adsorbent

PYROMEX, an air-stabilized polyacrylonitrile (PAN) fibre, was purchased by Toho Tenax, Co., Ltd., now known as Teijin Ltd., in Japan. PYROMEX was a black felt-shaped sheet that was chemically activated using aluminium chloride hexahydrate and dimethylacetamide (C₄H₉NO).

2.4 Modification of PAN Fiber

Heading Filter Material China provided the PAN fibre. Dimethylacetamide (C₄H₉NO) was used to modify PAN fiber. 10 grams of PAN fibre were placed in a 500-milliliter round-bottom flask, along with 250 milliliters of DMAC and five grams of aluminum chloride hexahydrate. The flask contained a reflux condenser positioned on a magnetic stirrer plate and a heating mantle. After 8 hours of heating, the pH of PAN fiber was calculated and found to be 13, while mixing and temperature were continually monitored and regulated. MPAN fiber samples were repeatedly washed with distilled water, and the pH after washing was 10.

2.5 Iron Loading on PAN Fiber:

MPAN fiber was loaded with ferric chloride hexahydrate (FeCl₃ · 6H₂O). For iron solution taken, 5g of FeCl₃ · 6H₂O mixed with 50 ml of methanol and 50ml of distilled water in 50 ml of Methanol and 50ml of distilled water and that flask placed on a hot plate stirrer at 60 °C, 100rpm for 1 hour. Once the FeCl₃ · 6H₂O dissolved, then was added 9g of PAN fiber in solution at 150 rpm, at 78 °C for 5 hours, and the pH of the solution was recorded at 1.53. The solution of PAN was acidic for neutralization, added drop wise of 1.0 M NaOH. After the addition pH was 5.9, MPAN-Fe fiber samples were washed with distilled water repeatedly to remove excess precipitates and were dried at room temperature overnight.

2.6 Varying Parameters In Simulations:

Several dynamic simulations with 36 variable parameters, including the column's bed height (1.2, 3, 8 cm), feed flow rate (0.001, 0.002, 0.003 lit/min), and intake concentration of arsenic (0.0001335 mol/lit), were run in order to evaluate the performance of the adsorption column.

Lab Scale Experiments was setup to conducted different experiments. To investigated the column break through and study the effects of process parameters in fixed bed columns such as Inlet flow rate, adsorbent bed height and concentration.

- Conducted various experiments to analyze the effects of the following parameters on the Arsenic removal efficiency of synthetic Arsenate water. Effect of Flow rate-0.512lit/mint, Effect of bed height-8cm, Effect of concentration- 10ppb, 20ppb, 30ppb.

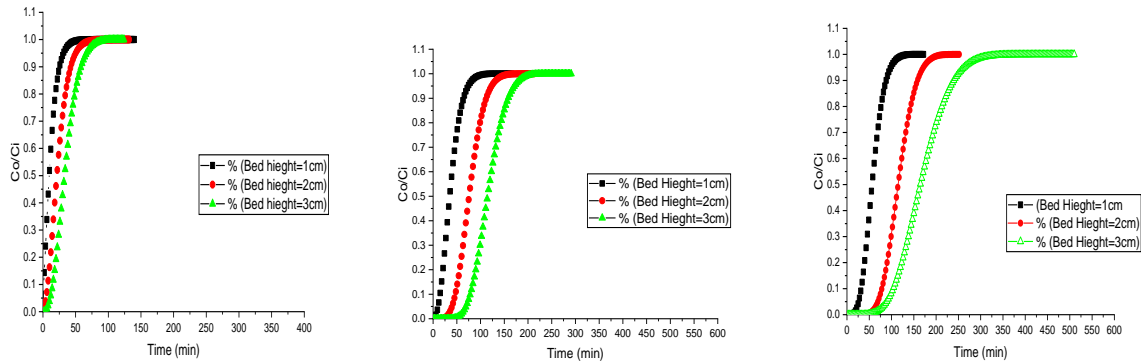
3. Results and Discussion

The comparison result has been created simulation tool ASPEN HYSYS V11 and experiment work. where the same and critical output parameters have been compared. The following figures shows a comparison of the properties of all 27 cases and one case of scaled up on simulation and lab scale experiment.

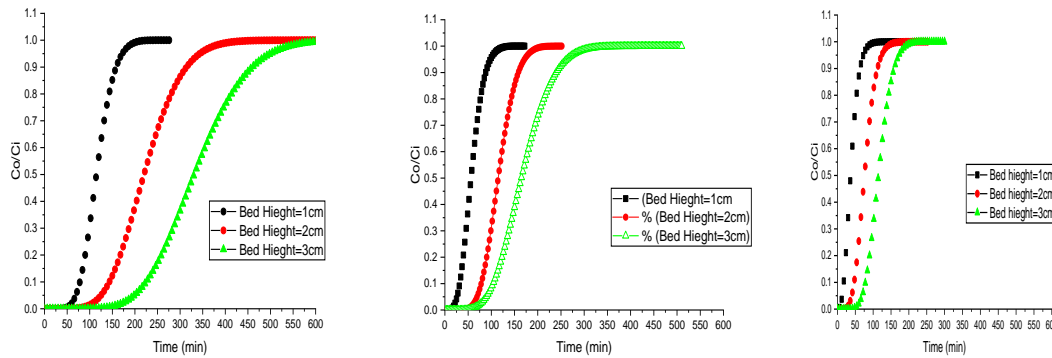
The outcome illustrates how much cheaper and environmentally friendly the modified PAN Fiber is when used as a bio adsorbent for extracting arsenic metal.

The influence of bed heights on the amount of arsenic As in treated water by using Modified PAN Fiber at varying bed depths and variable flow rates, with a constant inlet arsenic concentration.

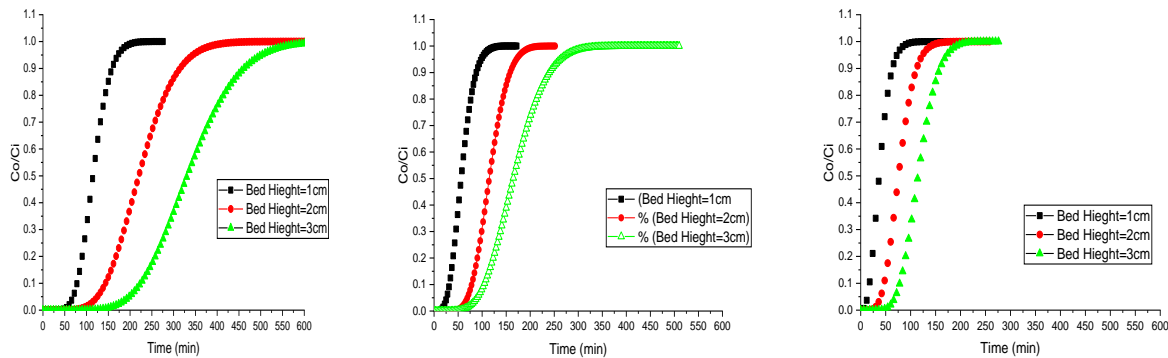
Fig: 01 Effect of bed height on Arsenic removal



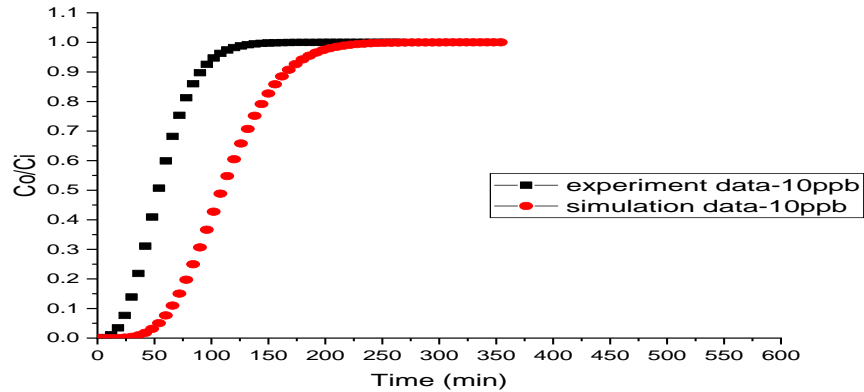
- Bed Height- 1,2,3cm Flow rate of variables- 0.01, 0.02 & 0.03 Lit/mint, Inlet Arsenic Concentration 0.0001335 mol/liter.



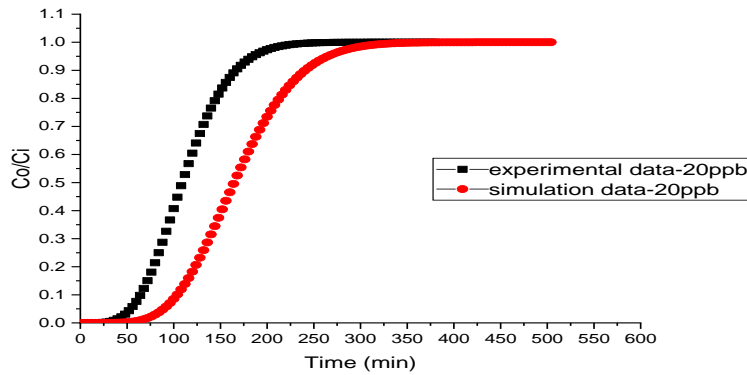
- Bed Height- 1,2,3cm Flow rate of variables- 0.01, 0.02 & 0.03 Lit/mint, Inlet Arsenic Concentration 0.000269 mol/liter.



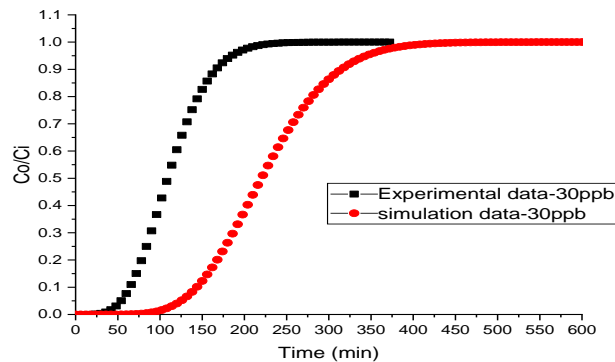
- Bed Height- 1,2,3cm Flow rate of variables- 0.01, 0.02 & 0.03 Lit/mint, Inlet Arsenic Concentration 0.0004004 mol/liter.



The Modified PAN Fiber adsorption at bed depths of 8 cm and various flow rates of 0.512 Lit/min, with a constant incoming arsenic quantity of 0.0001335 mol/Lit/10ppb, had effected the level of arsenic in the treated water.



Shows the Modified PAN Fibre adsorption at bed depths of 8 cm and various flow rates of 0.512 Lit/min, with a constant incoming arsenic quantity of 0.000269 mol/Lit/20 ppb, effected the level of arsenic in the treated water.



Shows the Modified PAN Fiber adsorption at bed depths of 8 cm and various flow rates of 0.512 Lit/min, with a constant incoming arsenic quantity of 0.0004004 mol/Lit/30 ppb, effected the level of arsenic in the treated water.

4. Conclusion

- In conclusion, the current work illustrates that given optimal modeling applications, kaolin is a highly active adsorbent for the removal of arsenic from groundwater. More specifically, the outcomes of this study allow for the following assumptions:

- From the aqueous solution, arsenic sorption was studied at 25 °Centigrade in a Kaolin packed bed continuous column. A packed bed column research was done to see how effectively Kaolin, a natural adsorbent, absorbed arsenic.
- Arsenic concentrations in treated water rise as feed flow rates increase, and contact time frame, solution pH, and adsorbent content all play major roles in removing arsenic from aqueous solutions.
- Data showed that arsenic removal on activated alumina is complicated and that the rate-determining phase includes both surface adsorption and intra-particle diffusion. The equilibrium outcomes of the regression analysis of the adsorption process' first order kinetics were fitted to the Langmuir and Freundlich isotherms.
- The breakthrough curves for the removal of arsenic from diluted solutions using activated alumina demonstrate the interaction between adsorption capacities and rates, and they offer an explanation for how the form of the breakthrough curves depends on the experimental parameters. With activated alumina, more sharper breakthrough curves have been generated at higher incoming arsenic concentrations.
- The following recommendations are made for more research based on the conclusions of the current study.
- The model should be validated using actual groundwater.
- Studying the effect of run duration on the removal of arsenic.
- Future thought has been given to this section that these findings maybe used to create an appropriate model on ASPEN HYSYS V11 for removal of arsenic from groundwater.

References

- [1] Ahmad, M., (2016) Kinetic and thermodynamic evaluation of adsorption of Cu(II) by thiosemicarbazide chitosan. *Int J Biol Macromol.* 92: p. 910-919.
- [2] Ahmad, T., et al.,(2004) Arsenic an emerging issue: experiences from Pakistan. WEDC, Loughborough University, 2004: p. 459-466.
- [3] Alka, S., (2021) Arsenic removal technologies and future trends: A mini review. *Journal of cleaner production*, 2021. 278: p. 123805.
- [4] Batchelor, B.L., (2016) , Plasticization for melt viscosity reduction of melt processable carbon fiber precursor. *Carbon*, 2016. 98: p. 681-688.
- [5] Chen, P., (2021) Prediction and optimization of process parameters of electrospun polyacrylonitrile based on numerical simulation and response surface method. *Textile Research Journal*, 2021: p. 00405175211003986.
- [6] Chaudhary, B.K. and Farrell J.,(2014) Preparation and characterization of homopolymer polyacrylonitrile-based fibrous sorbents for arsenic removal. *Environmental engineering science*, 2014. 31(11): p. 593-601.
- [7] Elwakeel, K.Z. and Guibal E (2015) Selective removal of Hg (II) from aqueous solution by functionalized magnetic-macromolecular hybrid material. *Chemical Engineering Journal*, 2015. 281: p. 345-359.
- [8] Gallegos-Garcia, M., K. Ramirez-Muñiz, and Song S (2012) Arsenic Removal from Water by Adsorption Using Iron Oxide Minerals as Adsorbents: A Review. *Mineral Processing and Extractive Metallurgy Review*, 2012. 33(5): p. 301-315.
- [9] Ihsanullah (2016) Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications. *Separation and Purification Technology*, 2016. 157: p. 141-161.
- [10] Khan, S. and Imteaz M (2021) Batch experiments on arsenic removal efficiencies through adsorption using synthetic and natural sand samples. *International Journal of Environmental Science and Technology*, 2021. 18(8): p. 2357-2364.
- [11] Kagaya, S., (2016) Chelating resin immobilizing carboxymethylated polyethyleneimine for selective solid-phase extraction of trace elements: effect of the molecular weight of polyethyleneimine and its carboxymethylation rate. *Talanta*, 2016. 147: p. 342-350.
- [12] Ko, Y.G., (2011) Removal of Cu (II) and Cr (VI) ions from aqueous solution using chelating fiber packed column: equilibrium and kinetic studies. *Journal of hazardous materials*, 2011. 194: p. 92-99.
- [13] Liu, R. and Qu J (2021) Review on heterogeneous oxidation and adsorption for arsenic removal from drinking water. *Journal of Environmental Sciences*, 2021.
- [14] Machida, M., et al., (2021) Efficient nitrate adsorbent applicable to wide pH range derived from polyacrylonitrile (PAN) fiber. *Results in Engineering*, 2021: p. 100276.

- [15] MENGÜÇ, G.S., (2016) A research on yarn and fabric characteristics of acrylic/wool/angora blends. *TEKSTİL VE KONFEKSİYON*, 2016. 26(1): p. 40-47.
- [16] Singh, T.S. and K.K. (2004) Pant, Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina. *Separation and Purification Technology*, 2004. 36(2): p. 139-147.
- [17] Simitzis, J.C. and Georgiou P.C (2015) Functional group changes of polyacrylonitrile fibres during their oxidative, carbonization and electrochemical treatment. *Journal of Materials Science*, 2015. 50(13): p. 4547-4564.
- [18] Wang, Z., et al., (2021) Enhanced arsenic removal from water by mass re-equilibrium: kinetics and performance evaluation in a binary-adsorbent system. *Water Research*, 2021. 190: p. 116676.
- [19] Zhang, X., (2008) Removal of arsenic in water by an ion-exchange fiber with amino groups. *Journal of applied polymer science*, 2008. 110(6): p. 3934-3940.