Study of PAN Fiber and Iron ore Adsorbents for Arsenic Removal

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Abstract

The main idea to conduct this study is the treatment of hazardous arsenite (As^{+3}) and arsenate (As^{+5}) from water by two efficient adsorbetns i.e. polyacrylonitrile fiber (organic) and iron ore (inorganic). Polyacrylonitrile (PAN) fibers were chemically modified prior to loading iron using a solution of diethylenetriamine and aluminum chloride hexahydrate. The characterization of PAN fibers was performed through FTIR spectroscopy, which shows the binding of functional groups on PAN fibers surfaces. Atomic absorption spectrometer (AAS) was used to analyze arsenic concentration in samples. The impact of pH, dosage, shaking (contact) time and shaking speed was studied and parameters were optimized for further study. The highest adsorption of 98% is exhibited by modified PAN fiber for As^{+5} while for As^{+3} removal is 80%. Modified PAN also showed higher adsorption capacity of 42×10 μg/g for As^{+5} which is better than the As^{+3} adsorption capacity 33×10^3 μg/g. Overall results demonstrated that MPAN adsorbent is better than the iron ore adsorbent for the treatment of both As^{+3} and As^{+5}. Comparative studies of PAN Fiber and iron ore adsorbents revealed that PAN fibers had better adsorption properties than iron ore for As^{+3} and As^{+5} in terms of percentage removal and capacity.

Keywords: Arsenic Removal; Organic; Inorganic PAN Fiber; Iron; Adsorbents.

1. Introduction

All forms of life on Earth can only be maintained with water because water is an indispensable commodity on Earth. Human development and rapid population growth have negatively affected water quality, which makes it unsuitable for drinking, and for other daily applications [1, 2]. Among the wide range of pollutants available in water, arsenic is one of the most unwanted pollutant that causes water quality to decrease [3-5]. The clean potable water is the necessity of human life on earth. Drinking water quality is affected by toxic metal contamination of As^{+3} and As^{+5}. It is reported that arsenic is a deadly factor in more than 70 countries, which causes serious health problems worldwide [6]. Higher arsenic concentrations, as recommended by the WHO, above 10 ppb can cause various diseases such as cancer and skin problems [7]. More than 150 million people worldwide are involved in arsenic-related health problems. People in Pakistan, Vietnam, Nepal, China, India, Myanmar, and Cambodia drink water contaminated with arsenic [8]. The maximum amount of arsenic in irrigation water is transported in crops grown in contaminated water [9]. The concentration of arsenic in food is another problem causing health issues in the world [10]. One of the main requirements for sustaining life on earth is clean water availability. As the world's population increases, the need for contaminated free drinking water is increasing [11].

Aware of the importance of clean water, we collected and analysed 214 groundwater samples from 24 regions of

Sindh, Pakistan [12]. Out of the 214 groundwater samples, 32 samples were gathered from the right bank and 182 samples were gathered from the left bank of the Indus River. The results showed that the content of As in 45% of the samples was greater than 10 µg L^{-1}, and the highest concentration was 200 µg L^{-1}. As was tested by the arsenic kit and the atomic absorption spectrometer in the water quality laboratory of Mehran University of Engineering and Technology. Next, we measure the effectiveness of the treatment of As^{+3} and As^{+5} by indigenous iron ore by adsorption technique. In this work, we prepared PAN fiber, which is a tremendous organic adsorbent. In the preparation process, the fibers are chemically modified before loading iron as shown in Fig. 1. The use of aluminium chloride hexahydrate and diethylenetriamine (DETA) solution ($AlCl_3.6H_2O$) was done.
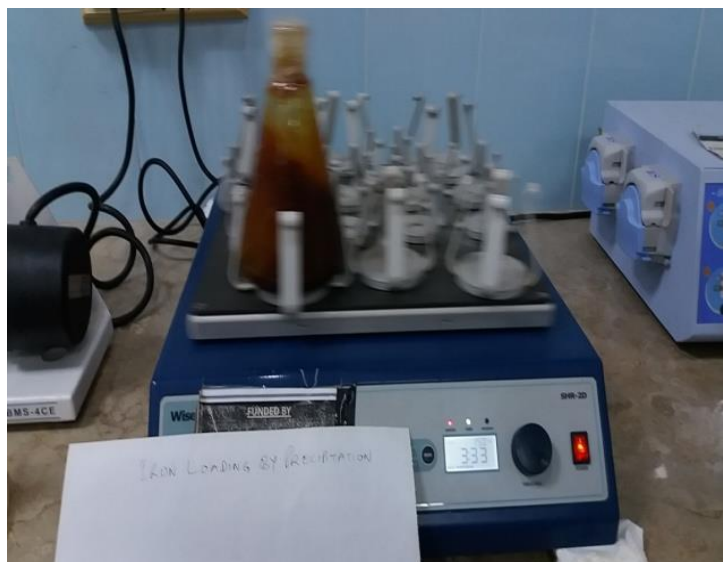

Figure 1. Iron loading by precipitation on a reciprocating shaking machine at 150 rpm

The PAN fibers were then added with ferric chloride hexahydrate ($FeCl_3.6H_2O$) via precipitation. Then neutralization was carried out with a 1M NaOH solution. At last, PAN fibers for further experiments were washed and dried as shown in Figure 2.

Figure 2. PAN Fiber after iron loading by precipitation method

The functional group successfully bound to the PAN fiber surface was characterized and confirmed by FTIR spectroscopy. The neutralization process of sodium hydroxide introduces carboxylate and carboxamide groups on the surface of the substrate. Also, the parameters were optimized i.e., contact time, pH, amount of adsorbent, and stirring speed for the removal of As^{+3} and As^{+5} by PAN fiber and iron ore adsorbents.

The main aim of this paper is to study the effectiveness of both PAN fiber (organic) and iron ore (inorganic) adsorbents for the removal of toxic arsenic. The both adsorbents which were selected for arsenic removal from water were found effective during adsorption experiments. Indigenous iron ore was collected from Balochistan and Sindh

provinces of Pakistan and checked for arsenic adsorption capacity. PAN fiber was purchased from Heading Filter Material Co., Ltd. China and tested for arsenic adsorption capacity. Both adsorbents were experimentally investigated for arsenic removal efficiency and adsorption capacity. However, PAN fiber was found more efficient having higher adsorption capacity for As^{+3} and As^{+5} removal as compared to iron ore adsorbent.

2. Materials and Methods

PAN fibers were collected from heading filter material co. Ltd. China. The tensile strength of polyacrylonitrile fiber is about ≥ 1200 psi and has tremendous alkali resistance, acid, and acid abrasion resistance, as shown in Table 1. PAN fibers have better metal adsorption properties. The PAN fibers were immersed in deionized water for one day at room temperature to clean the impurities on the fiber surface. Before use fibers were rinsed through deionized water and dried at 60°C.

Table 1. Polyacrylonitrile fiber properties [13]

Parameters	Description
Compositions	Acrylic fiber
Working temperature (°C)	≤ 140
Thickness (mm)	2
Tensile elongation (%) (wrap)	<20
Tensile strength, wrap(N/5 20 cm)	≥ 1200
Anti-abrasion	Very good
Anti alkali	Very good
Anti-acid	Very good
The stability in water solution	Good

A stock solution of As^{+3} was made via dissolving sodium arsenite $AsNaO_2$ in distilled water. A stock solution of As^{+5} was prepared by dissolving potassium arsenate H_2AsKO_4 in distilled water. The latest secondary standards were provided from stock solutions using distilled water for each test. The pH of the solution was maintained using 0.1M sodium hydroxide and 0.1M hydrochloric acid. Initially, all the glass and polyethylene bottles were dipped in a soap solution for several hours and then washed with distilled water. Subsequently, all these were immersed in 2% HCl for 24 hours and then three times washed with distilled water prior to making samples.
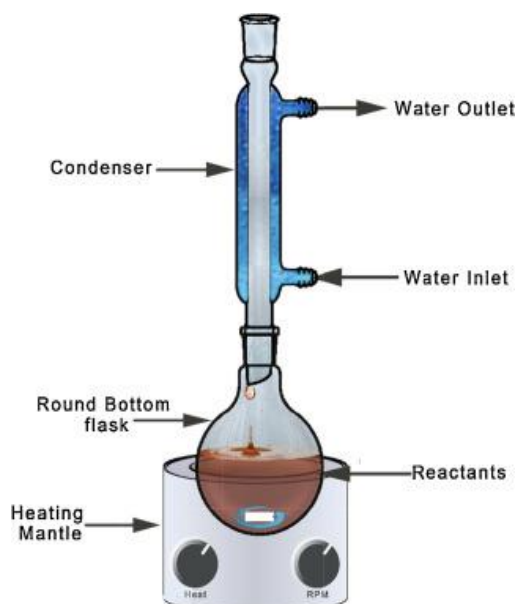

Figure 3. Schematic representation of PAN fiber modification in a reflux condenser and heating mantle

2.1. Functionalization of Fiber

PAN fibers with needles were cut into approximately 1g of sample, which was immersed with distilled water overnight and dehydrated at 50°C. Chemical modification of PAN fibers was performed using aluminum chloride hexahydrate ($AlCl_3.6H_2O$) and diethylenetriamine (DETA) solution before iron loading.
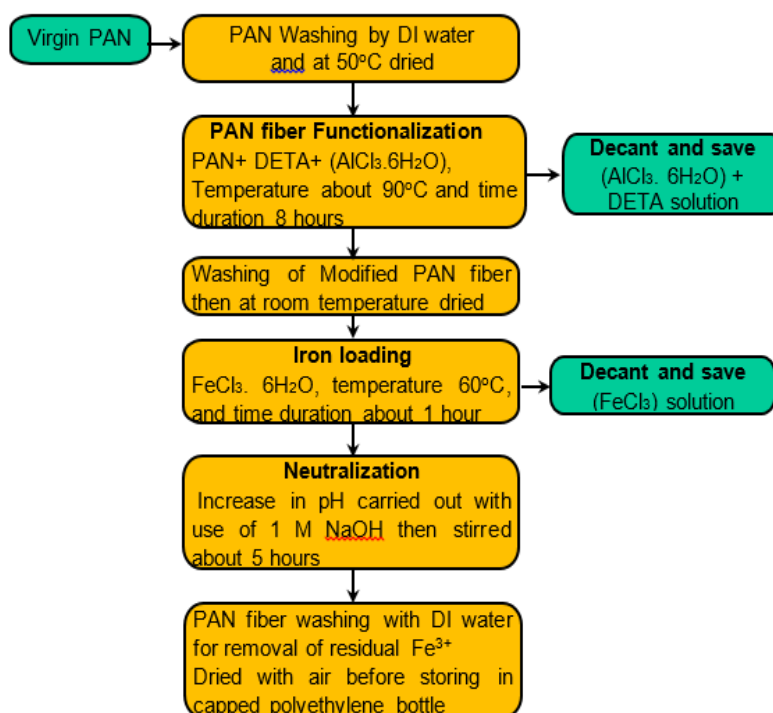
Figure 4. Diagram of functionalization of polyacrylonitrile fiber and iron loading procedures

Figure 5. PAN fiber functionalization in an isomantle and a reflux condenser attached on a magnetic stirrer plate

10 g of PAN fiber and 10 g aluminum chloride hexahydrate were placed in a round bottom flask (500 ml) and 250 ml of diethylenetriamine (> 97%) were added. As shown in Figure 5, the pot is set with a reflux condenser and heating mantle mounted on a magnetic stirring plate. The PAN fibers were stirred at 360 rpm and heated at 90°C for 8 hours. Treatment of fiber was done with the use of $(AlCl_3.6H_2O)$ catalyst through the addition of DETA and reaction in the heating jacket was monitored continuously. After heating for 8 hours, the PAN fibers were chilled to room temperature and the pH of 13 was confirmed. The washing of PAN fiber samples was done repeatedly with the use of deionized (DI) water and final pH about 10 with an aqueous solution. At room temperature samples of PAN fiber were dried.

2.2. PAN Fiber Adsorption Study

The batch study method was utilized for As^{+3} and As^{+5} adsorption in PAN. For process concerned about 0.5 g fiber of adsorbent PAN fibers were added into a clean bottle. About 50 ml volume was prepared with 2.5 ml of As^{+5} at 1000 μg/Lit and 47.5 ml. After maintaining the pH 7 of buffer solution was then added to the soup containing PAN fiber samples and pH measurement was done via pH meter (microprocessor, BANTE tool, United States). PAN fibers containing flakes were shaken on a digital replacement (Wiseshaker, Wisd, South Korea) for 2 hours at 150 rpm. For each sample, three samples were prepared using above procedure. Then, adsorbent PAN fiber was filtered with Whatman numbers, and then filtered solution was analyzed by atomic absorption spectrometer (AAS) (AAnalyst 700,

Perkin Elmer, United States) at 193.7 nm wavelengths, as shown in Figure 6.

Figure 6. Atomic absorption spectrometer

The procedure for detecting arsenic absorption consists of measuring the difference in initial concentration and the final concentration of the solution. For arsenic adsorbed percent was calculated through the application of Equation 1.

$$As\% = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

Where "C_i" is the initial As^{+3} and As^{+5} concentration in solution whereas "C_f" is the final remaining concentration of As^{+3} and As^{+5}. To confirm reproducibility, the experiment was repeated and averaged. Repeated experimental errors were observed within ± 5%. No adsorbed arsenic was detected in the blank experiment flask wall.

2.3. PAN Fiber Capacity

For analyzing the capacity of the PAN fibers to understand the adsorption mechanism first, a 1000 mg/Lit As^{+5} stock solutions was prepared. After that As^{+5} volume of 50 ml (1000 mg/Lit) was measured and placed in a single bottle. 1/2 g of Polyacrylonitrile fiber was introduced to the broth and then stirred at 150 rpm for 2 hours. After 2 hours, PAN fibers were filtered from the solution As using filter paper. 0.1 ml of a filtered solution as the solution was measured, a volume of 1 liter was dissolved with distilled water was prepared to obtain solution of As^{+5} of 100 ppb concentration. The 100 ppb As^{+5} solution was kept for the arsenic test by AAS machine.

2.4. Adsorption Parameters Optimization

The adsorption of arsenic by PAN fibers has been done in order to optimize the pH, the mass (dose), the agitation time (by contact) and the stirring speed (rpm) of the fibers.

2.5. Impact of pH

The pH of buffer solution was prepared as described in the section on iron ore. The pH of the buffer and the sample were measured using a pH meter (pH meter with microprocessor PHS-3BW, BANTE tool, USA). The pH effect was noticed in the samples of Polyacrylonitrile fiber. Testing samples were prepared by adding 2.5 ml of arsenic (1000 ppb) and 47.50 ml of beaker buffer solution, and a total of 50 ml of solution was provided at the preferred pH. The mixture was added to a round bottom hole and after that, about 0.1g of modified polyacrylonitrile (MPAN) fiber was inserted. Samples coated with Parafilm were subsequently placed on Shaker Reciprocating Digital (SHR-2D Wiseshaker, Korea) and shaken at 150 rpm for 2 hours. After stirring about 2 hours, every solution sample was separated through filter paper to extract Polyacrlonitrile fibers and separated solution, and then that was stored in polyethyle bottle. The mixture was added to a round bottom flask and after that, about 0.1g of modified polyacrylonitrile (MPAN) fiber was inserted. Sample bottles coated with Parafilm were subsequently placed on Digital Reciprocating Shaker (SHR-2D Wiseshaker, Korea) and shaken at 150 rpm for 2 hours. After stirring about 2 hours, every solution sample was separated through filter paper to extract Polyacrlonitrile fibers and then filtered solution was then stored in polyethylene bottle. The filtered solution samples were tested through atomic absorption spectroscopy.

2.6. Impact of Weight of Polyacrylonitrile Fiber on Arsenic Adsorption

Observing the ability of the PAN fibers to understand the adsorption mechanism; first, a 1000 mg/Lit of each As^{+3} and As^{+5} stock solution was prepared separately. First, a 1000 mg/Lit As^{+5} stock solutions were provided. After that, As^{+5} of 50 ml (with a concentration of 1000 mg/Lit) was measured and placed in a single bottle. MPAN fiber samples of weight 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g, 0.6 g and 0.7 g were weighed individually on electronic balance. Then these MPAN were added separately in As solution sample and stirred at 150 rpm for 2 hours. Polyacrylonitrile fiber was inserted to the broth and later stirred at 150 rpm for 2 hours. Polyacrylonitrile fibers were separated from a solution of As using filter paper after 2 hours 0.1 ml of filtered solution As the solution was measured, a volume of 1 liter was supplied with distilled water to obtain a solution of As^{+5} of 100 ppb. Maintains the 100 ppb As^{+5} solution for the AAS As test.

2.7. Shaking Time Optimization

Optimization of contact time carried out for test of arsenic adsorption test with modified PAN fibers. A sample was prepared via taking 2.5 ml of As^{+3} 1000 µg/Lit and 47.5 ml of pH 4 buffer to prepare a volume of 50 ml in a round bottom flask. For As^{+3} samples, 0.3 g of MPAN was taken and inserted in the round bottom flask. The round bottom flask was stirred at 150 rpm. Samples were prepared by varying the mixing times of 10, 20, 30, 40, 50, 70, 100 and 120 minutes. A sample of As^{+5} was prepared, 2.50 ml of As^{+5} and 47.50 ml of buffer 5.50 were mixed, and volume of 50 ml was prepared in a flask. Likewise, samples prepared via varying the mixing times of 10, 20, 30, 40, 50, 70, 100 and 120 on Digital Reciprocating Shaker. Subsequently, the sample was cleared with a filter paper to disperse the PAN fibers, and clean solution was saved for analysis of As^{+3} and As^{+5} by atomic absorption spectrometer.

2.8. Shaking Speed Optimization

The impact of stirring speed was measured through adsorption on modified PAN fibers. About 50 ml volume was prepared with 2.50 ml of As^{+3} and 47.5 ml of buffer 4.0. Later on, 0.3 g of adsorbent Polyacrylonitrile fiber was introduced to the sample bottle. Samples were shaken for 2 hours. Different samples were prepared at speeds of 50 rpm, 100 rpm, 150 rpm, and 200 rpm.

Then As^{+5} samples were prepared with only changing by taking 0.1 g of MPAN and shaking time of 70 min. Samples were prepared at 50 rpm, 100 rpm, 150 rpm, and 200 rpm. The polyacrylonitrile was separated out of the sample solutions and the clean solution was tested by the AAS machine.

3. Results and Discussion

3.1. Classification of PAN Fibre

It has been experimented that polymeric fibers are effective adsorbents for arsenic treatment present in water. A study was carried out to pay special attention to the optimal conditions for As^{+5} treatment. It is believed that the anion exchange beads have a worse kinetic nature than anion exchange fibers. The anion exchange fiber exchanges a sequence of connections to reduce wastewater contamination [14]. PAN is a very good polymer material with many benefits such as solvent resistance, abrasion, and mechanical resistance. The nitrile reactive group (C≡N) present in PAN could be changed into a plurality of functional groups by a typical reaction Aminated PAN fibers are utilized to treat lead (Pb), copper (Cu) and chromium (Cr) ions from polluted solutions [15].

The researchers [16], have performed studies on MPAN fibers for potable water treatment. Various researchers have investigated the absorption capacities of MPAN fibers by reaction with hydrazine, NaOH and ferric chloride. The current study is related to Polyacrylonitrile fibers, which facilitate with catalysts ($AlCl_3.6H_2O$) and (DETA) subsequently, the PAN fibers were added with iron for adsorption to eliminate the As^{+3} and As^{+5} from the water. The current study is related to Polyacrylonitrile fibers, which chemically reacted with catalysts ($AlCl_3.6H_2O$) and (DETA) subsequently. Then, the PAN fibers were loaded with iron for adsorption to eliminate the As^{+3} and As^{+5} from the water. Furthermore, the results collected were according to the expected outcome and this was confirmed through the comparison of current study with published results.

3.2. PAN Fiber FTIR Analysis

PAN fibers were characterized by the presence of functional groups by FTIR spectroscopy at High tech laboratories (IARSCS), Sindh University, Jamshoro. Polyacrylonitrile fiber samples with 4000-60 cm^{-1} were analyzed using an FTIR model with total attenuation reflectance (ATR) (Thermo Fisher Scientific, United States) as shown in Figure 7.

Figure 7. Fourier-transform infrared spectrometer

Water vapour were removed from polyacrylonitrile samples by heating them in a lab oven (Daihan Labtech, Korea) at 70 °C for 5 hours and were constantly monitored during this process. Fourier-transform infrared spectroscopy (FTIR) is performed on unmodified and modified PAN fiber. Different spectra of the PAN specimen were taken at 25°C temperature.

PAN fibers are chemically reformed to bind functional groups and are later loaded with precipitation iron as described in Section 2. Polyacrylonitrile raw material (R-PAN), modified polyacrylonitrile fiber (M-PAN), Polyacrylonitrile FTIR spectrum Modified after (Fe) loading (M-PAN-Fe after arsenic adsorption) and Polyacrylonitrile fiber. The FTIR peaks were assigned chemical groups with the help of a correlation chart [17].
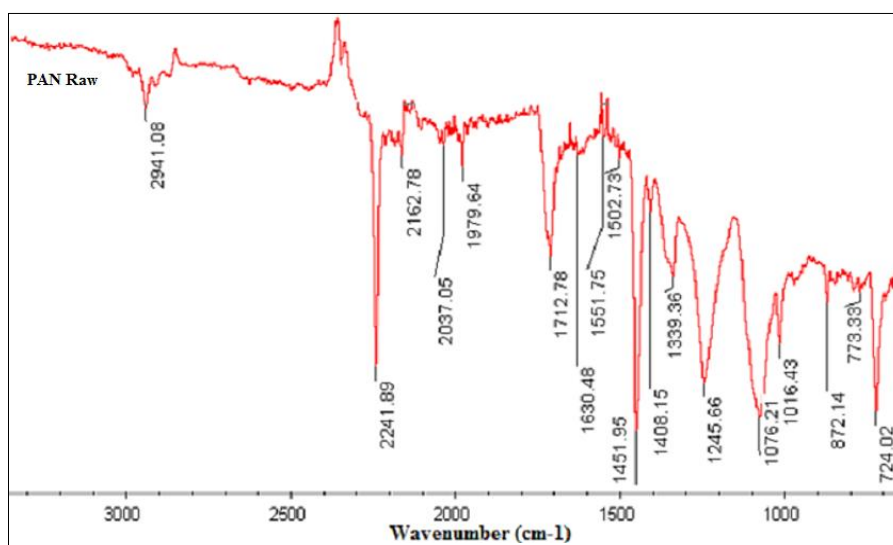

Figure 8. FTIR of Raw PAN

The raw PAN-FTIR spectra Figure 8 are represented at 1245.66 cm^{-1} (C-O), 1339.36 cm^{-1} of methyl (CH$_3$) group, 1451 cm^{-1} of methylene (CH$_2$), 2241.89 cm^{-1} nitrile (C=N), carbonyl (C=O stretching) at 1712.78 cm^{-1} and 2941.08 cm^{-1} aliphatic (CH). It indicates that the polyacrylonitrile fibers are copolymers of methacrylate and acrylonitrile. The sharp peak observed at 2241.89 cm^{-1} is the spectrum of PAN fibers recognized and associated with the group (C≡N). This result is consistent with the FTIR study performed on the implanted polyacrylonitrile nanofiber membrane [18]. Figure 9 shows the modified FTIR spectrum of polyacrylonitrile (8 hrs and 90°C). The 1452 cm^{-1} peak relates to (bending CH$_2$). The spectrums at 1562.92 cm^{-1} and 3394.83 cm^{-1} are called imine (NH) and hydroxylamine (NH/OH). The spectrum at 1658.65 cm^{-1} is defined as the amide (C=O) group. This result proves the chemical attachment between Polyacrylonitrile and Di-ethylene triamine.
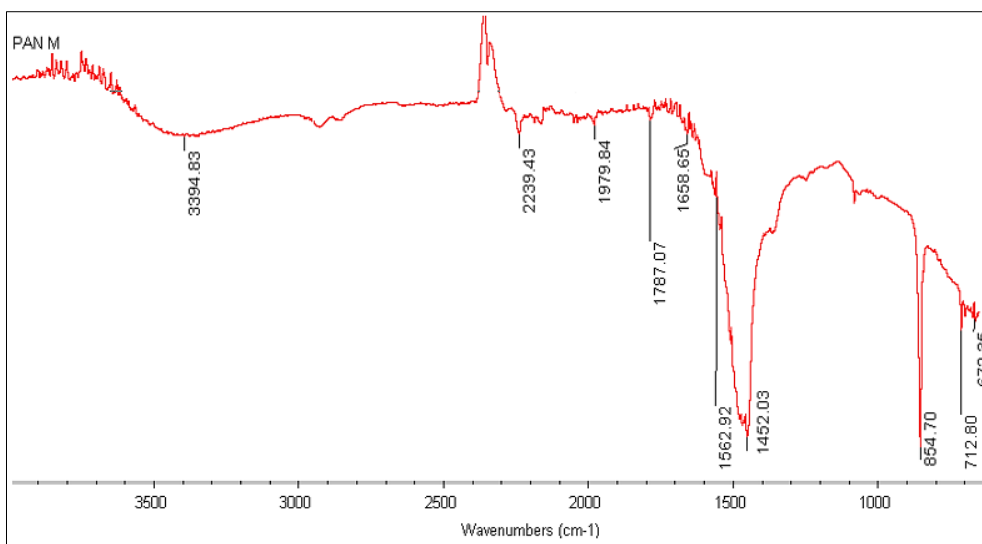
Figure 9. FTIR of Modified PAN

Figure 10 shows the PAN spectrum modified by the iron load and the spectra at 1451 cm^{-1} is determined by (CH$_2$ Curve). Furthermore spectra were visible at 1602.92 cm^{-1} (C = N), 2241.29 cm^{-1} (C≡N), CH-aliphatic at 2922.59 cm^{-1}, 1658.07 cm^{-1} (NH) and 3326.32 cm^{-1} (NH/OH). At 1658 cm^{-1} the spectra correspond to the NH group in carboxamide, indicating NaOH deposit in iron. The NaOH treated fibers had a small volume of 3100 to 3600 cm^{-1} in combination with the hydroxyl (OH) groups in the carboxylate, confirming the development of cationic carboxylic exchange groups [18].
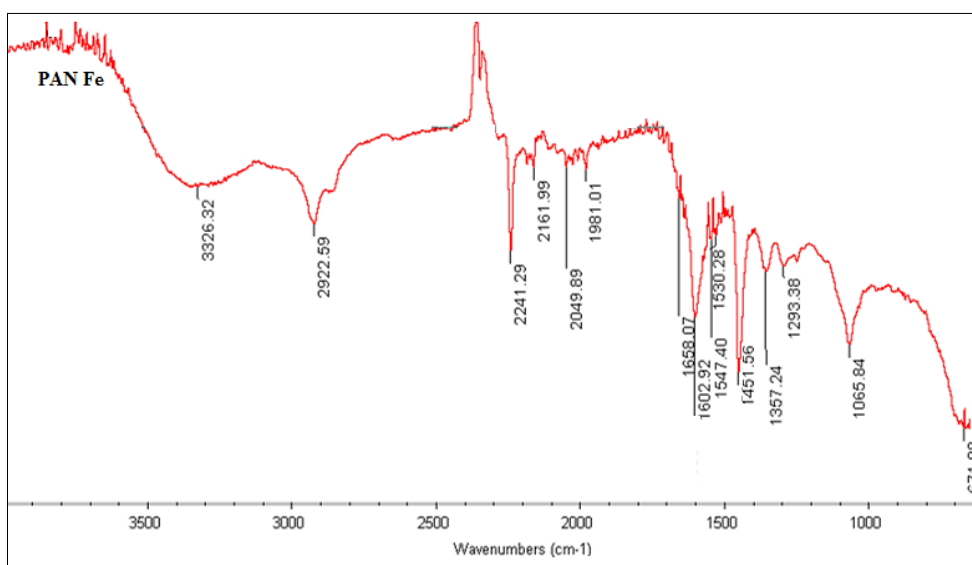

Figure 10. FTIR of modified polyacrylonitrile fiber with iron loading

4. Optimization Study of PAN Fiber

4.1. Impact of pH

The pH effect was observed by the adsorption of As^{+3} and As^{+5} by the modified polyacrylonitrile fibers (MPAN), as shown in Figure 11. It is clear that the MPAN adsorption rate increased for As^{+3} was 78.40 %. The adsorption of As^{+3} decreased with increasing pH as demonstrated in Figure 11.
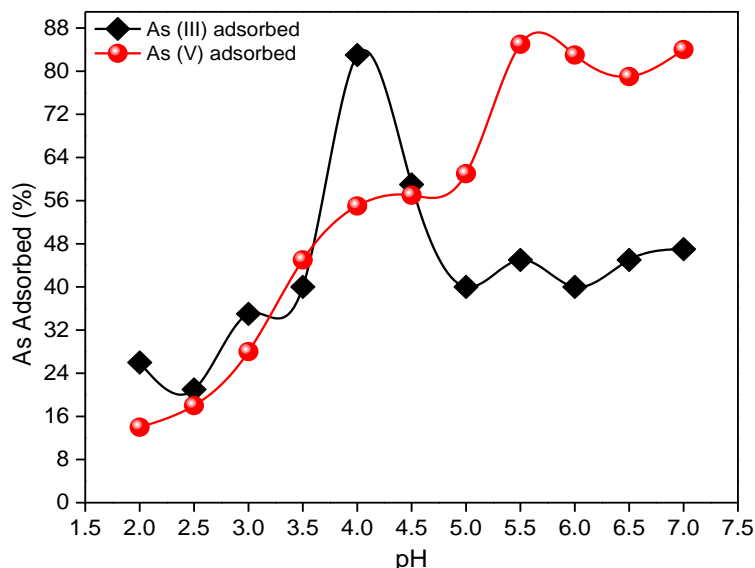
Figure 11. Impact of pH on As+3 and As+5 adsorption by modified polyacrylonitrile fiber

Amine functional groups on the surface of modified polyacrylonitrile fibers are protonated to generate (NH_3^+) at low pH [19]. Therefore, the highest sorption of As^{+3} by modified PAN was at pH 4.

Due to the adsorption of As^{+5} by MPAN, the elimination of As^{+5} increased from pH 2, reached the highest of 81.60 % at pH 5.50 and gradually decreased with increasing pH increased to 7.0. It indicates, that the MPAN has the greatest removal capacity of As^{+5} at 81.60 % and for As^{+3} is 78.40 %. It indicates, that the change in NAP has the greatest removal capacity of As^{+5} is 81.60 % and As^{+3} is 78.40 %. Hence, pH 4.0 and pH 5.50 were optimized for As^{+3} and As^{+5}, respectively, for additional tests on modified PAN adsorption. One of the potential reasons for increased removal of As^{+3} and As^{+5} is the bonding of ($FeCl_3$ $6H_2O$) with polyacrylonitrile fiber as compared to the raw fibers. In addition to iron loading, the surface chemistry of PAN fibers also influences the adsorption of As^{+3} and As^{+5} [20]. The MPAN creates a (+ve) charge at a pH less than 8.0 and a high electrical resistance prevents As^{+3} and As^{+5} ions from touching the surface of MPAN Fiber when the pH is below pH 4 [21]. Electric revulsion force becomes slow and the arsenic ions can be transferred to the surface due to van der Waals force and the metal complexes can be replaced by chelation or ionization, as the pH of the solution increases [22].

4.2. Effect of Adsorbent Dose

As shown in Figure 12, the effect of the adsorption (mass) dose on the adsorption of As^{+3} and As^{+5} on MPAN fibers was analyzed. It is obvious that in the case of adsorption of As^{+3}, the elimination rate increased by 63% at a dose of 0.1 g and reached a maximum of 100% with a dose of 0.3 g of MPAN. Then adsorption was stable at elevated dosages of 100% MPAN to absorb As^{+3}.
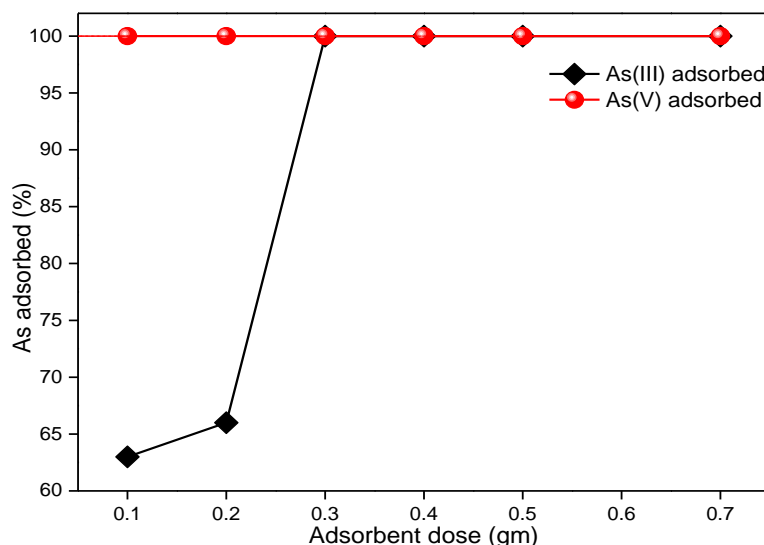

Figure 12. Impact of adsorbent dosage (mass) on As+3 and As+5 adsorption by modified polyacrylonitrile fiber

For As^{+5} MPAN, the 0.10 g dose exhibited 100% adsorption and was kept the same for greater doses of MPAN. It indicates that modified polyacrylonitrile can effectively eliminate As^{+5} at a dose lower than As^{+3} which is comparatively tougher to eliminate. Therefore, a 0.30 g modified polyacrylonitrile dose was adjusted for other As^{+3} adsorption tests. However, for As^{+5}, a 0.10 g MPAN dose was augmented for subsequent experiments. Treatment of carcinogenic Cr(VI) by nanofiber PAN/Fe Cl$_2$ material showed that at a pH of 5, the dose was 3.5 g / L and the maximum elimination rate was 95% [23].

4.3. Impact of Shaking (Contact) Time

As shown in Fig. 13, the impact of shaking time on adsorption of As^{+3} and As^{+5} by MPAN fiber observed. The influence of the shaking time was observed at a time variation of (10 minutes, 20 minutes, 30 minutes, 40 minutes, 50 minutes, 70 minutes, 100 minutes and 120 minutes). The removal of As^{+3} elevated from 53% in 10 minutes and approached to highest of 100% at 120 minutes. Thus, for further studies of adsorption of As^{+3} by MPAN, 120 min shaking time was selected. As^{+5} adsorption achieved 100 % removal at 70 min shaking time though it started from 69% in the beginning at 10 min time. Therefore, the 70-minute contact time was optimized to eliminate As^{+5} by MPAN in further experiments. A study of fibers covered with amine to eliminate As^{+5} found that the sorption reached at equilibrium state after 1 hour and revealed adsorption efficiency of 98.0 %. Rapid sorption is a classic property of PAN fiber sorbents and is attributed to the surface location of readily available fibers [18]. A scientific work addressed that the adsorption of As^{+5} by ion-exchange fibers showed 93% elimination and reached equilibrium after 30 minutes [24].
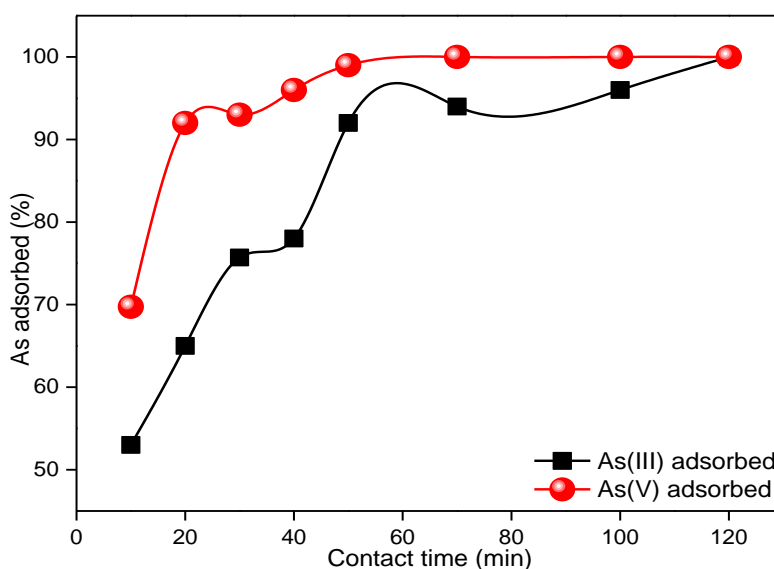

Figure 13. Impact of Shaking (contact) time on adsorption of As+3 and As+5 via MPAN

4.4. Impact of Shaking Speed

As illustrated in Figure 14, the mixing rate was developed by studying the samples at 50, 100, 150, and 200 rpm. For As^{+3}, the removal was raised from 67% at 50 rpm and gained the highest 96.5% at 150 rpm. Then, when the stirring speed was increased to 200 rpm, further removal was reduced to 94%. For As^{+5} samples, adsorption was upraised from 75% at 50 rpm and attained 100% at 150 rpm. Then, as the speed reached 200rpm, the adsorption of As^{+5} remained stable at 100%. Hence, the ideal shaking speed of 150rpm was set for As^{+3} and As^{+5} removal by modified polyacrylonitrile. These findings demonstrate that the functionalized polyacrylonitrile fiber has good removal capacity for As^{+3} and As^{+5} from toxic water.
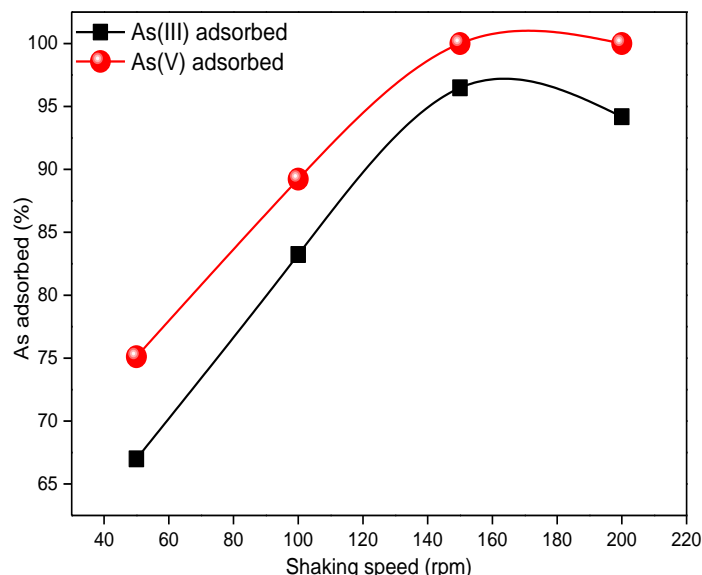
Figure 14. Impact of shaking speed on adsorption of As+3 and As+5 by modified polyacrylonitrile

4.5. Polyacrylonitrile Fibre Adsorption Capacity (Loading)

As shown in Fig. 15 (a), adsorption studies were performed on raw and modified PAN fibers. The results show that with raw PAN the As^{+3} removal is comparatively low 72%, and whereas with the MPAN, the amount of As^{+3} adsorption increases to 78%. It should also be noted that the raw PAN had shown adsorption of 76% As^{+5}, while the modified PAN fibers exhibited removal of 100% As^{+5}. The results show that the PAN fiber chemically bonded with diethylenetriamine (DETA), aluminum chloride hexahydrate ($AlCl_3.6H_2O$) and $FeCl_2$, performed a higher elimination percentage of As^{+5} as compared to raw polyacrylonitrile and As^{+3}.
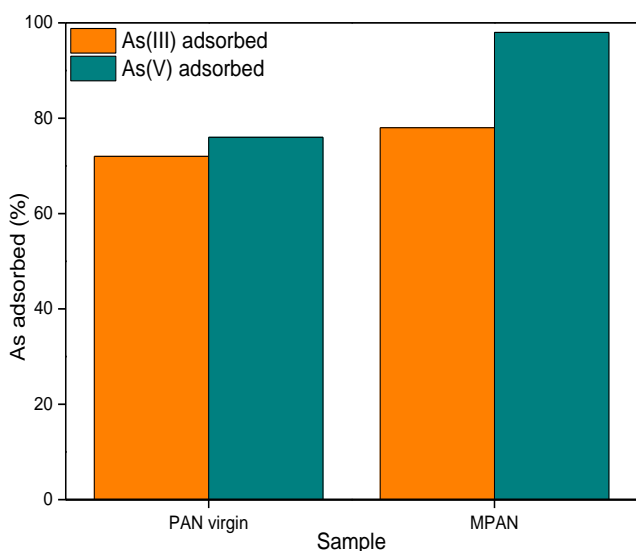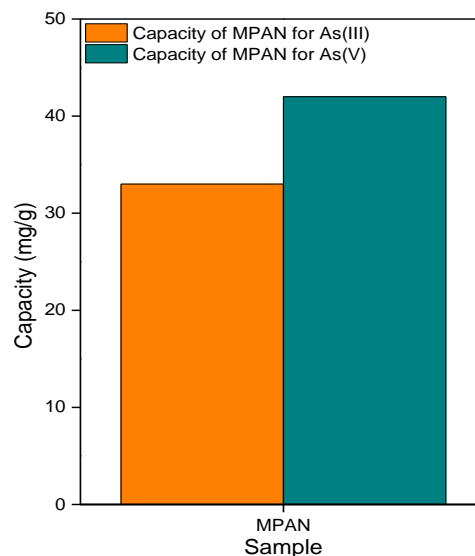

Figure 15 (a). PAN fiber for arsenic adsorption

Figure 15 (b). The ability of modified PAN fiber

DETA functionalization with catalyst ($AlCl_3.6H_2O$) and iron increase capacity of adsorption of PAN fibers. The MPAN loading in μg/g to remove As^{+3} and As^{+5} were analyzed, and it was concluded that for As^{+3} loading was 33×10^3 μg/g. As shown in Fig. 15 (b), the modified PAN loading for As^{+5} removal was analyzed at 42×10^3 μg/g. This result indicates that MPAN has better capacity in μg /g for adsorption of As^{+5} as compared to As^{+3}. These outcomes are matching with the study of the absorption capacity of amine covered acrylic fibers of 41 μg/g [19]. Due to the short transport distances and the quantity of different functional groups attached to the fibers, the PAN fibers have a high sorption capacity and high adsorption rates of the ion exchange resins. Nitrile groups on the surface of PAN fibers can be easily cross-linked with polyamines and undergo many chemical reactions. Polyamine DETA can increase the number of amine groups in the adsorbent to increase its ion exchange capacity [25].

4.6. Relative Study of Organic (PAN fiber) and Inorganic (Iron ore) Adsorbents

Table 2 presents a comparison of iron ore absorption and PAN fibre. Obviously, the adsorption of the PAN fibre showed a better 80% removal for As^{+3} as compared to that of iron ore adsorbent which is 77%. In the case of the performance of the PAN fibre adsorption for As^{+5}, the removal is 98% that is greater than the iron ore adsorbent having low adsorption of 82%. The PAN fibre loading in ($\mu g/g$) is also greater than that of iron ore adsorbent. PAN fibres illustrated the loading of 33×10^3 $\mu g / g$ for As^{+3}, which is greater than the iron ore capacity which is just 13.7 $\mu g/g$. The capacity of PAN fibres for As^{+5} is (42×10 $\mu g/g$) which much greater than that of iron ore i.e. just (67.1 $\mu g/g$). These findings demonstrate that PAN fibres are comparatively efficient adsorbent for As^{+3} and As^{+5} removal in comparison with iron ore adsorbent and PAN can be economically developed at the laboratory scale.

Table 2. Comparative study of iron ore and PAN fibre adsorbents

Adsorbent	Adsorption of As^{+3}	Capacity of As^{+3}	Adsorption of As^{+5}	Capacity of As^{+5}
Polyacrylonitrile fibre modified with DETA+AlCl$_3$.6H$_2$O)	80%	33×10^3 $\mu g/g$	98%	42×10^3 $\mu g/g$
Iron ore	77%	13.7 $\mu g/g$	82%	67.1 $\mu g/g$

4.7. Arsenic Removal from Water Sample

Actual samples of groundwater were collected from the Hala area of Sindh province since the groundwater in the area was contaminated with arsenic. A study reported that the higher arsenic levels were observed in ground water samples of Hala i.e. 10-180 $\mu g/$ L. Table 3 shows the removal rate of As^{+3} and As^{+5} from actual groundwater samples in the Hala region using iron ore and MPAN. Due to the presence of anions in the actual groundwater sample, the adsorption % is slightly lower than the synthetic water results shown in Table 2. Therefore, MPAN has excellent potential to be used as adsorbent for carcinogenic arsenic water treatment in Hala district, and other parts of Sindh and Pakistan. MPAN and iron ore have proved as efficient and economical adsorbents for arsenic contaminated water which can save lives of millions of common people from Cancer and other deadly diseases.

Table 3. Arsenic removal from a water sample

Adsorbent	Adsorption	
	As^{+3}	As^{+5}
Iron ore	75%	81%
Polyacrylonitrile fibre (modified with DETA+AlCl$_3$.6H$_2$O)	78%	95%

Table 4. Comparison of results with other literature

Treatment Method	Adsorbent	Capacity of As^{+3}	As^{+3} Conc./ removal% after treatment	Capacity of As^{+5}	As^{+5} Conc./ removal% after treatment	References
Adsorption	PAN fibre	33×10^3 $\mu g/g$	80%	42×10^3 $\mu g/g$	98%	This study
Adsorption	Iron ore	13.7 $\mu g/g$	77%	67.1 $\mu g/g$	82%	This study
Adsorption	Chitosan zerovalent Iron Nanoparticle	94 mg/g	5 $\mu g/L$	119 mg/g	5 $\mu g/L$	[26]
Adsorption	Magnetite nanoparticles	23.8 mg/g	82%	-	-	[27]
Adsorption	Zeolite with iron	2 $\mu g/g$	50%	6 $\mu g/g$	60%	[28]
Adsorption	Aluminum-loaded Shirasu-zeolite	-	-	64$\mu mol/g$	99%	[29]
Adsorption	Pine wood char	1.2 $\mu g/g$	70%	-	-	[30]
Adsorption	Iron oxide-coated sand	0.5 μg g^{-1}	0.4 $\mu g/cm^3$	-	-	[31]
Adsorption	Manganese Green sand	0.5 μg g^{-1}	0.4 $\mu g/cm^3$	-	-	[31]
Adsorption	Granular ferric hydroxide	-	-	8 μg As/mg	50%	[32]

Table 4 shows that the MPAN and iron ore adsorbents used in this study have great potential to be employed in continuous water treatment plants for arsenic removal as compared to other adsorbents which have less removal efficiency. The indigenous iron ores are present in huge amounts in Balochistan and Sindh provinces of Pakistan making it an economical and efficient adsorbent for common citizens of the country. PAN fiber can be also produced locally by using PAN fiber with spinning technology which make it also economical and more efficient for toxic arsenic polluted water.

5. Conclusion

Adsorption studies were performed on raw PAN fibers and the modified PAN. The results demonstrated that when As^{+3} was initially used, the raw PAN showed a 72% elimination, but As^{+3} adsorption was enhanced with MPAN adsorption to 78%. It should also be noted that the raw PAN had adsorption of 76% for As^{+5}, while the modified PAN fibers exhibited 98% As^{+5} removal. The capacity of MPAN for As^{+3} and As^{+5} was analyzed and found that for As^{+3} the capacity was 33×10^3 µg / g. At the same time, the modified PAN capacity for As^{+5} was analyzed at 42×10 µg/g. This result shows that MPAN has a better response to adsorption of As^{+5} than the adsorption of As^{+3}. It is suggested that arsenic treatment filters should be installed in the arsenic affected areas with MPAN and iron ore adsorbents. Modified PAN fiber prepared by chemical functionalization and iron loading procedure was observed to be an effective method because of its enhanced As^{+3} and As^{+5} removal, adsorption loading (µg/g) and simple method. PAN fiber prepared by chemical modification and iron loading procedure was observed to be an efficient method because of its improved arsenic removal, adsorption capacity, one-step method, affordable cost, wider availability and absence of hazardous chemicals. So, the organic adsorbents like PAN fiber could be developed in developing nations where the expensive commercial products may not be available. PAN fiber adsorbent was imported from foreign country, then chemically modified in the laboratory for As(III) and As(V) removal from water. However, PAN fiber can be prepared from PAN powder locally by spinning method to make it more economical. Column study should be investigated with the iron ore and PAN fiber adsorbents separately to check the effectiveness of continuous system.

6. Funding

7. Conflicts of Interest

The authors declare no conflict of interest.

8. References

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