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Arsenic (V) removal from aquatic media by electrospun alumina nanofiber

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Today, it is believed that the world population is encountered with water crisis and some solutions should be presented for this challenge. New technologies are one of the requirements to eliminate these problems. The present study aims to use Nano technology to make a fiber filter called alumina nanofiber by which arsenic-a heavy and toxic metal- is removed via adsorption.

The technology applied in this study is electrospinning and it is the most effective method to produce Nano with fiber structure and it is cost effective as it is recovered to be used in nanofiber filter production. This study differs from other studies given that arsenic (V) removal is aimed and polyacrylonitrile (PAN) is used instead of polyvinylpyrolidone (PVP) and it is due to the high thermal resistance of polyacrylonitrile (PAN) and maintenance of leaf structure of nanofibers during sintering process (injection) and deterioration of aluminum precursor. The results show that arsenic (V) removal is examined based on the effect of pH, contact time, initial metal concentration, solution volume and adsorbent dosage parameters. The optimal conditions are pH=2, contact time=60 min, metal initial concentration of 5 mg L^{-1}, solution volume of 50 mL and adsorbent dose of 0.05 g and this removes about 90% of arsenic (V).

Keywords: Electrospinning, Alumina nanofiber, Removal, Arsenic, Heavy metals

INTRODUCTION

With the growth of communities and different industries around the world, water resources are encountered with industrial and agricultural wastes. These wastes include some pollutants such as heavy metals, organic compounds, dyes, etc. Large amounts of these hazardous materials damage the environment and human health [1].

Heavy metals are harmful to the environment. They enter nature via water, soil, air and natural and anthropogenic resources and create hazardous long and short-term effects. With the accumulation of heavy metals in plants and animals, they can be consumed by humans [2]. With the presence of heavy metals in the food chain, severe toxicity can occurred [3].Geological and anthropogenic activities are two main sources of metals in the environment. The geological activities include natural phenomena such as weathering and volcanic eruptions which significantly contribute to heavy metal pollution [4]. Human resources are dependent upon human activities such as industry, agriculture, mining and urban development infrastructures which emit pollutants into water via river etc [5].

Arsenic is a metalloid and widely distributed in the earth’s crust. The three allotropic forms of arsenic are grey, black, and yellow. Arsenic and its compounds are used as pesticides and herbicides. Arsenic concentration ranges from 2-5 mg.L^{-1} [6].This element can flow through arsenic-containing rocks or get into water through dissolution of mineral rocks in areas with weathered rocks. Arsenic is also emitted via fossil fuels combustion. In some regions, industrial waste water releases arsenic in water. Commercially, arsenic is used in alloys and wood preservatives. Also, this element is achieved by heating minerals containing arsenic and re-crystallization of vapors of its sublimation and industrially; it is achieved as an additional product of metal production centers.

Arsenic is naturally found in a slight quantity on earth. Arsenic is in soil and mineral materials and it gets into air or water through dust or runoff. It is difficult to convert arsenic into liquid or gas states. Arsenic is mobile naturally and it is rarely found in one place. This is a good point, but arsenic pollution mostly occurred due to its easy emission. If arsenic is immobile, it cannot move easily. Due to anthropogenic activities such as mining, arsenics can be mobile in most regions. Arsenic cycles are extensive due to anthropogenic activities and arsenic is found less in the environment and in nature. Arsenic is mostly emitted by copper producing industries but they are also distributed in lead, zinc production and agricultural activities. If arsenic gets into the environment, it will not be decomposed and

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this excess arsenic is emitted and causes diseases for humans and animals.

Arsenic is absorbed easily by plants and it has high concentration in food. High concentration of inorganic arsenic in underground water can induce genetic changes in fish and they can enter into the food chain.

WHO's provisional guideline value for arsenic in drinking water is 0.01 mg.L^{-1} (10 μg.L^{-1}), 0.01 μg.(m^3)$^{-1}$ in air for less than 15 min and 0.002 μg.(m^3)$^{-1}$ for contact time of more than 15 min . As earlier mentioned, the standard value of this element in soil is 2-5 mg.L^{-1}.

Now, there are various methods for eliminating pollutants from water such as coagulation, filtration adsorption, ion exchange, etc. Most of these techniques are costly with low efficiency. Despite the selection of coagulation and chemical precipitation synthesis, this technique is also problematic. An efficient, rapid, environment-friendly and effective system to remove pollutants is of great importance. Today, adsorption methods are taken into consideration due to their simplicity, low price, high efficiency and effectiveness. In these methods, a good absorbent is used for removal of pollutants. Nanoparticles is raised as a managerial solution. Despite the availability of other methods, this one covers a wide range of sciences. The main properties of this method are the reduction of the size of materials. Matter as a chemically inactive substance can be converted into a catalyst at Nano scale. Thus, for the treatment of heavy pollutants in water, Nanos are applied. Nano technology plays a crucial role in water treatment. Nanofiber is based on this technique and acts as a filter and pollutants are absorbed. With their interesting properties such as high surface to volume ratio (this ratio is increased thousands times for a nanofiber compared to microfiber), flexibility in surface features and great mechanical performance (e.g. stiffness and tensile strength), nanofibers can absorb the majority of pollutants and they are also used in the removal of heavy metals.

This study attempts to use alumina nanofiber for the removal of arsenic in water. Alumina nanofiber (AL_2O_3) is one of the most important materials in terms of resistance, insulation, chemical strength and catalyst strength. Alumina is available in various crystalline structures depending on the operational conditions in which it is formed. Alumina is a hard durable material that can be used as a filter. It is a good electrical insulator, has relatively high thermal conductivity, can be used as a catalyst or as a catalyst carrier, and is chemically inert [7]. The materials applied in this absorbent are of great importance and besides being the innovative aspect of any research, they can produce a filter with high adsorption quality. There are no researches on arsenic adsorption by this adsorbent in aquatic media in Iran and there are few of such researches in the world and this increases the significance of this study.

MATERIALS AND METHODS

Materials and Instruments

All the chemical materials in the present study are of the highest purity value purchased from Merck. A glass dish is submerged into nitric acid 10 (v.v^{-1}) and then washed using double distilled water. Double distilled water is used for solutions, dilution and washing. Polyvinylpyrolidone (PVP) with molar mass of 40000 g.mol^{-1}, polyacrylonitrile (PAN) (99% purity), aluminum isopropoxide (AIP) with molar mass of 204.24 g.mol^{-1}, ethanol (99.9% purity), malic acid (99% purity), dimethylformamide (DMF) (99.5% purity) were obtained from Merck. The standard solution of arsenic (V) (H_3AsO_4 in HNO_3 0.5 mol.L^{-1} 1000 mg.L^{-1} As) was purchased from Merck. The experiment solutions were prepared with the desirable concentration by dilution of stock solution with doubled distilled water. In order to determine the morphology of nanofibers synthesized from scanning electron microscope (SEM- LEO 1455vp), X-ray diffraction (XRD); PW3040 and Philips Netherlands, wavelength: cuka.5405A, depth:2-120μm were used.

FTIR spectrum was used to identify the chemical bonds and functional groups positioned on alumina nanofibers by infrared spectrometer, Spectrum 100. Also, Raman spectrometer, FT-Raman960 was applied. To measure arsenic, Narian-AAS-240 was used. IKAKS260، shaker, pH meter model 713, Metrohm, Swiss, centrifuge and scale with 4-digit accuracy were used.

Adsorbent preparation

Electrospinning is a popular method for the synthesis of nanofibers. In this method, a high voltage power supply was used to produce an electrical charge used in the polymer solution and melts. In order to produce nanofibers, high voltage power supply electrodes were used as conductive polymer solution and the other electrode was connected to ground or aggregator. By passing the solution through a capillary tube, the effect of the electric field between the tip of the capillary tube and aggregator of high voltage power supply connected to the ground, is that charged fluid from the tip of the capillary tube is pulled to the aggregator. With the impact of fluid flow, the solvent evaporates and submicron diameter strings are produced on the aggregator. Actions by electrical forces, surface charge flow, viscoelastic and surface tension forces, pregnancy-induced spiral fluid produced nanofibres for interconnected or nonwoven layers. In this method, a polymer solution is poured into the syringe at a distance of 20 cm from it and placed in a metal plate. Page is fixed to the ground and placed on the pump and syringe needle is connected to the high voltage power supply. Low charge solution discharged into the syringe when a voltage between 5-30 kW is applied. Accordingly, for jet drops pulled along and after evaporation of the solvent, metal plates collide and then the fibers are collected into a nanostructured metal plate. In this study, based on previous research study on the use of electrospun alumina nano fibers, the synthesis procedure is as follows:

Spinning solution with a concentration of 6% by weight of aluminum precursor and weight ratio of polymer to AP (6:10) is prepared by adding 0.3 g of AP to polymer solution. In this stage, PAN/DMF/AP ratio is 0.3/4.5/0.5.

By providing the solution with polymer weight of 10 AP to precursor ratio of 6, electrospinning process is performed better and nanofiber surface of this sample has high smoothness. After transferring the solution to a syringe, 10 mg.L^{-1}, positive electrode of power supply is connected to a steel needle Number 23 and negative electrode is connected to a collecting screen. The distance between the tip of the needle and collecting screen is 15 cm and stable spinning voltage is in the range of 17-20 kV and flow rate is 0.5 ml.h^{-1}.

Batch experiments

The study was investigated using batch experiments at room temperature. The experiment was performed on shakers with volume of 25, 50 and 100 ml, pH range of 2-11 and absorbent of 0.05-0.12 g and concentration of 3, 5 and 7 mg.L^{-1}. The mixture was agitated in a shaker at 30, 60 and 120 min and was placed in centrifuge for 5 min at a speed of 2500 rpm. Finally, arsenic removal was measured using atomic adsorption. The effect of each parameter on the results of arsenic removal was studied by alumina nanofiber. The absorbed material of a solution per gram of adsorbent q (mg.g^{-1}) is obtained by the following formula:

$$q_e = \frac{(V(C_0 - C_e))}{W}$$

Where, *v* is the volume of the solution (L), C_0 is the initial concentration (mg.L^{-1}), C_e is the concentration at equilibrium (mg.L^{-1}) and *W* is the adsorbent dose (g).

The percentage of metal ion removal by the adsorbent is calculated by the following formula:

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100$$

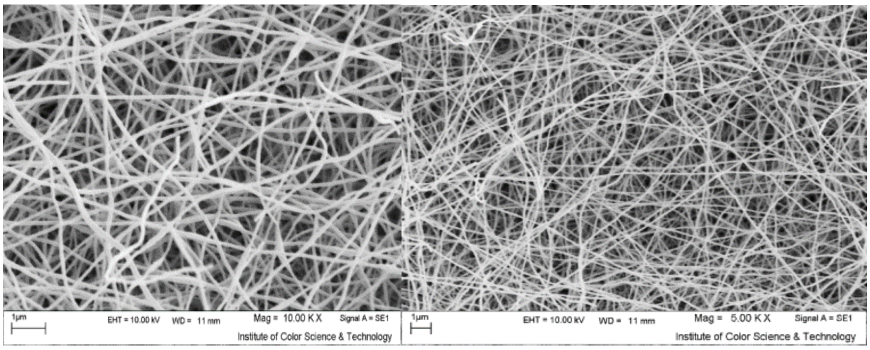
Where, *R* is the efficiency of metal ion removal, C_0 is the initial concentration (mg.L^{-1}) and C_e is the metal ion concentration (mg.L^{-1}).

Characterization of adsorbent

The nano structure including smoothness of surface or phases distribution is examined using SEM. This analysis is used in this study. SEM showed that the diameter of alumina nanofiber ranges between 10^2 nm and narrow strings with low interval are observed. The following figures illustrate these explanations (Hosseini Shekarabi et al., 2017).

XRD properties of alumina nanofiber are shown in Chart 1. As shown, two peaks are seen, the first peak is at 2θ =17.02 and distance D=5.20 and the bigger peak is at 2θ=29.38 at the distance D=3.03.

As shown in the figure, the distance between two peaks is about 1:$\sqrt{3}$ indicating PAN hexagonal chain [8].



(a) (b)

Fig. 1. SEM images of alumina nanofiber [8].

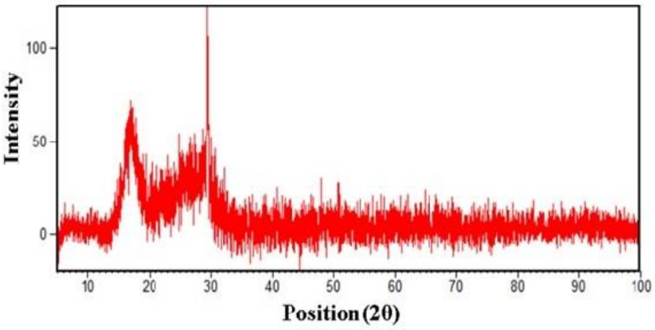


Chart 1. XRD of Alumina nanofiber [8].

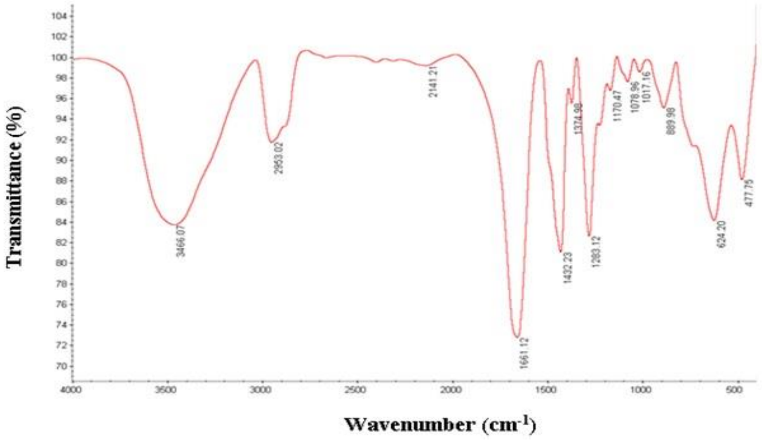


Chart 2. FT-IR spectrum of Alumina nanofiber [8].

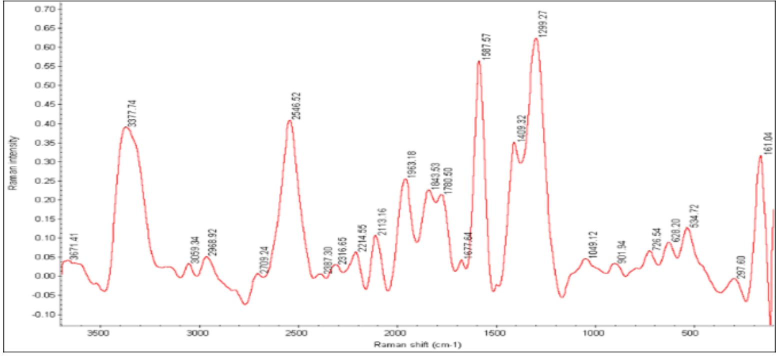


Chart 3. Raman spectrometer of Alumina nanofiber

The molecular structure and compositions of alumina nanofiber are examined using FT-IR analysis as shown in Chart 2. As shown, there is an extensive absorption group at 3100-3400 cm^{-1} regarding the bond between OH and =C-H as asymmetric stretching. Another group is observed at 2939 and 2437 cm^{-1} regarding the vibration of CH stretch group. $C \equiv C$ Stretch (2190-2260 cm^{-1}) and $C = O$ (1735) cm^{-1} interferes with weak adsorption of $C \equiv C$ group. There is a strong peak at 1357 cm^{-1} relating to C-N in dimethylformamide (DMF). 11176 to 1044 cm^{-1} show C-N in PAN compositions. The peak between 960 to 829 cm^{-1} show =C-H and normal adsorption is at 629 cm^{-1} regarding Al-O in AP [8].

Based on the importance of identifying existing molecules in compositions and presence of some elements, this study attempts to verify Fourier Transform Infrared – spectroscopy (FT-IR), Raman spectrometer and the results are shown in Chart 3. Three long spectra at 3377, 2546 and 1409 cm^{-1} indicate N-H in DMF, C-H and methyl group. The longest spectrum at 1299 cm^{-1} indicates the presence of PAN and then at 1587 cm^{-1} with regard to G group. At 1963, 178 cm^{-1} of middle spectra, C-O and carbonyl are observed. At 726 cm^{-1}, a small spectrum verifies the presence of AL of AL-O.

RESULTS

Effect of pH

The pH of the solution has a significant impact on the uptake process. pH of solution is effective on aquatic solution chemistry and the bonds of absorbent surface. In order to establish the effect of pH on the adsorption of arsenic (V) by alumina nanofiber, at values of 2, 7, 11, stirring took 2 h. In this experiment, the initial concentration of arsenic was 5 mg L^{-1}, solution volume of 50 ml and absorbent dose of 0.1 g.

Chart 4 shows batch studies. For arsenic (V) removal, optimum pH was 2 and this metal was not affected by pH 7 and 11. Arsenic (V) adsorption at this optimal pH is about 64% and is reduced by increase in pH and at pH=11, adsorption reach 34%. Arsenic removal is increased at pH=2 due to the dominance of electrostatic force between arsenic (V) molecules with positive charge and alumina nanofiber surface with negative charge. At pH higher than 2, arsenic surface is positive as alumina surface chart is also positive and electrostatic repulsion occurred and adsorption is reduced.

Effect of contact time

Contact time is an important parameter in arsenic (V) removal process. The effect of contact time on adsorption process of alumina nanofiber in arsenic (V) adsorption is examined and the results are illustrated in Chart (5). The initial concentration is 5 mg.L^{-1}, solution volume of 50 ml and adsorbent of 0.1 g. As shown in Chart 5, after 60 min, arsenic adsorption is reduced by 64%. The experiment was carried out at batch condition and optimal contact time was 1 h. At times less than 60 min, due to the lack of completion of adsorption capacity and filling out all pores, adsorption was slow and at times above 1 h, due to the contact between adsorbent and solution, resorption occurred and by releasing chrome into the environment, adsorption was reduced.

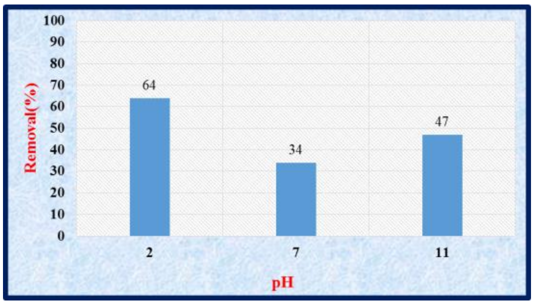


Chart 4. Arsenic (V) removal percentage at different pH, conditions:0.1 g of alumina nanofiber, 50 ml of 5 mg.L^{-1} arsenic (V), contact time: 2 h

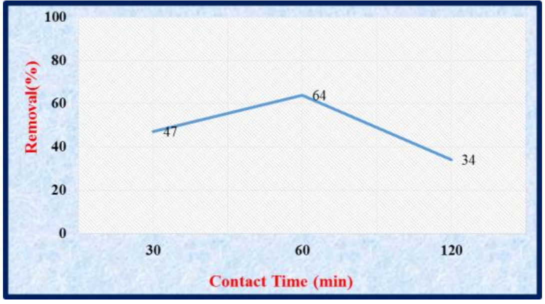


Chart 5. Adsorptive behavior of arsenic (V) with time on alumina nanofiber, conditions: 50 ml, 5 mg.L^{-1} arsenic (V), pH=2, adsorbent dose: 0.1 g

Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of arsenic (V) was studied at batch condition, pH=2 and adsorbent doses ranging from 0.05-0.12 g was added into 50 ml arsenic (V) solution. Chart 6 indicates that by adding 0.05 g electrospun, uncalcined alumina nanofiber adsorption, each 50 ml of arsenic (V) solution of 5 mg.L^{-1}, the highest removal of 90% was achieved. The solution was studied by atomic adsorption after stirring for 1 h and 5 min of centrifuge. As shown in Chart (6), at dose of 0.05 g, adsorption is low due to few pores. By increasing adsorbent dose from 0.07 to 0.12 g, adsorption percentage was reduced with increase in adsorption capacity and surface to volume ratio of the adsorbent.

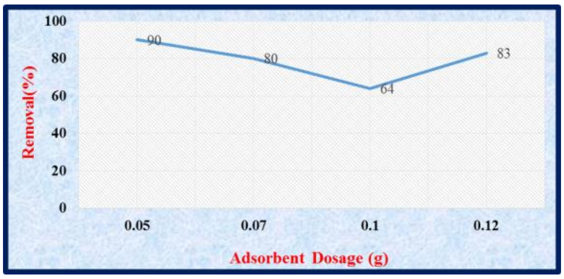


Chart 6. Arsenic (V) removal percentage at different dosage of adsorbent, conditions: 50 ml, 5 mg.L^{-1} arsenic (V), pH=2, contact time: 60 min

Effect of solution volume

Solution volume is another important factor that changes the arsenic (V) adsorption by alumina nanofiber. The volumes of 25, 50, 100 ml with arsenic (V) concentration of 5 mg.L^{-1} and optimal adsorbent of 0.07 g, pH=2 and contact time of 1 h are studied at batch condition. Chart 7 illustrates the results of these experiments. The best arsenic (V) removal at volume of 50 ml is 90%. At volumes lower or higher than 50 ml, adsorption is reduced. In other words, at volume less than 50 ml, due to increase of chrome molecules and increase of contacts with adsorbent, adsorption is performed rapidly but the pores in nanofiber surface are saturated and adsorption capacity is not adequate. At volume higher than 50 ml, arsenic molecules to solution are lower and contact between nanofiber molecules and arsenic is less and adsorption is lower.

The effect of Arsenic (V) concentration

The change in concentration of heavy metal is another parameter effective on adsorption. Regarding arsenic (V), there is no limitation in this section about using atomic adsorption (lack of possibility of assessment of the metal with concentration greater than 5 mg.L^{-1}), given that the applied atomic adsorption in arsenic (V) assessment is different. Thus, the concentrations are 3, 5 and 7 mg.L^{-1} and their effects are shown in Chart 8.

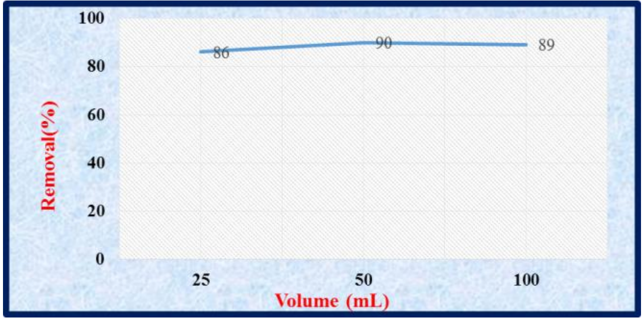


Chart 7. Arsenic (V) removal percentage at different volumes of solution, conditions:
5 mg.L^{-1} Arsenic (V), absorbent dosage: 0.07 g, pH=2, contact time: 60 min

As shown, the highest adsorption at concentration of 5 mg.L^{-1} is about 90%. The existing trend states that with increase in the concentration to 7 mg.L^{-1}, adsorption is reduced and this is due to the shortage of adsorbent to metal molecules inside the solution. In this case, the metal cannot be placed in the pores of nanofiber surface and removal is reduced. At 3 mg.L^{-1}, the metal molecules are few and they don't enter the pores of adsorbent.

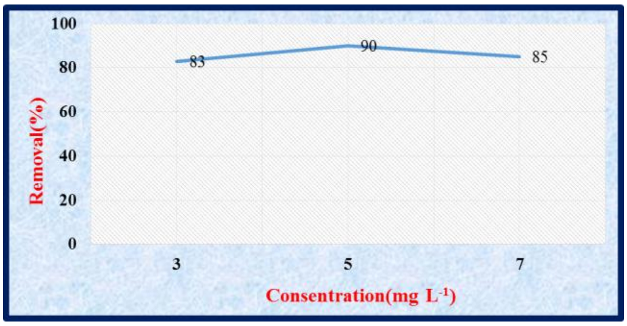


Chart 8. The effect of arsenic (V) concentration on its removal by alumina nanofiber, conditions: 50 ml solution, pH=2, absorbent dosage, 0.07 g and contact time: 60 min

Arsenic (V) desorption from alumina nanofiber

Desorption of metal ions and recovery of adsorbent is an important issue in terms of reusing the adsorbent. To evaluate resorption of electrospun, uncalcined alumina nanofiber after adsorption of arsenic (V), first it is washed using double distilled water to remove the metals attached to the sample and adsorbent. Resorption experiments were performed using 1 M nitric acid at volumes of 50 and 100 mg.L^{-1} and 0.5 g of adsorbent. After resorption of ions, the solid metals were dried at temperature of 40°C for 4 h and they were at room temperature. Then, the adsorbent was tested again. Resorbed ions were collected after 30, 120 min contact with solutions. To evaluate the metal removal of solutions, atomic adsorption spectrophotometry of As (V) was applied. The applied solutions are made under optimal conditions. The results show that 1 M nitric acid is a good solution and is used to recover alumina nanofiber. The experiments show that alumina nanofiber can adsorb about 90% As (V) at optimal conditions (pH=2, 0.05 g adsorbent and solution of 50 mg.L^{-1} with concentration of 5 mg L^{-1}). Regarding nitric acid volume of 50 and 100 mg.L^{-1} in recovery of alumina nanofiber, the results show no considerable change of metal resorption and both volumes are suitable.

Adsorption isotherms

In this study, Langmuir and Freundlich isotherm models are used regarding arsenic (V) adsorption and evaluation of adsorptive behavior of alumina nanofiber (Charts 9c-d).

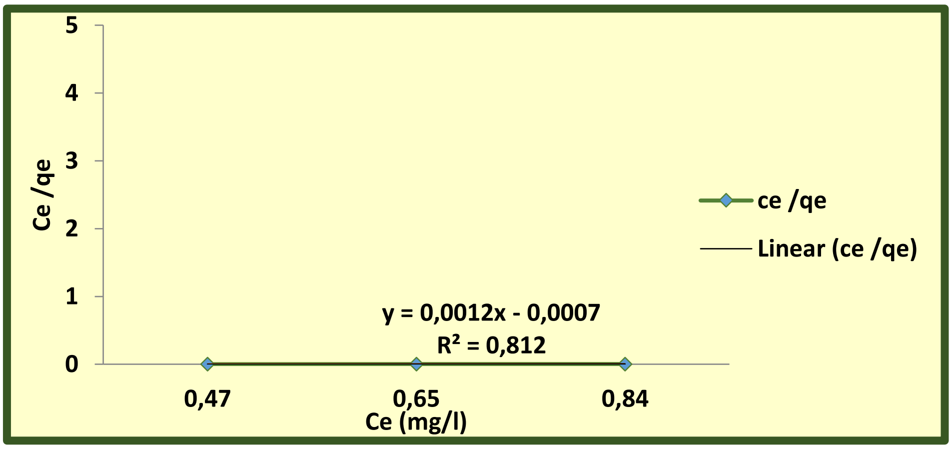


Chart (9-c). Curve of Langmuir isotherm for arsenic (V) adsorption (50 ml solution with concentrations of 3, 5, 7 mg.L^{-1}, time: 60 min, pH=2, adsorbent dosage: 0.05 g)

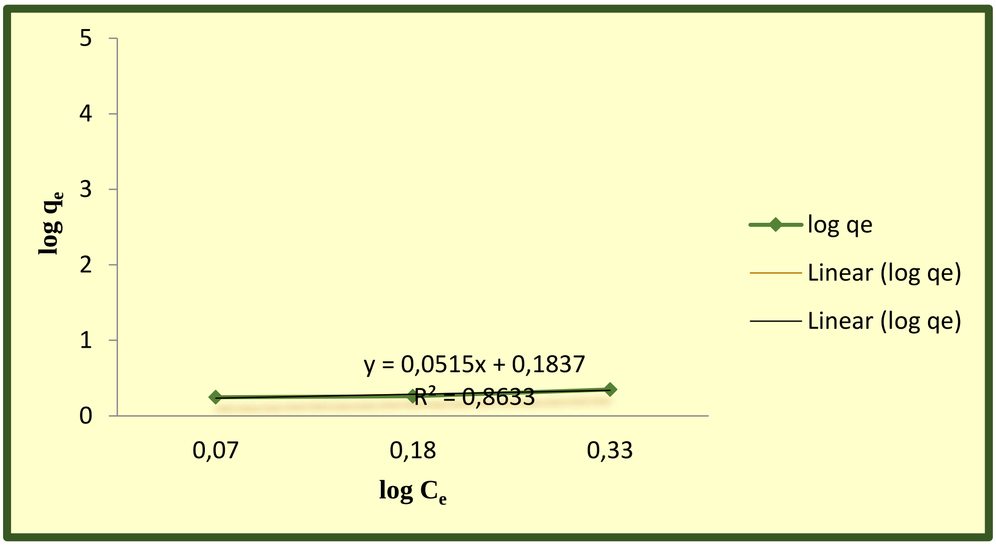


Chart (9-d). Curve of Freundlich isotherm for arsenic (V) adsorption (50 ml solution with concentrations of 3, 5, 7 mg.L^{-1}, time: 60 min, pH=2, adsorbent dosage: 0.05 g)

The results of the figures above show that these results are consistent with the results of empirical data of arsenic (V) removal by alumina nanofiber. The analysis of the data of these results is shown in Table 1.

Based on the significance of correlation coefficient in isotherm determination which is consistent with empirical data, we can use the existing coefficients in Table 1. Langmuir and Freundlich isotherm models are consistent with the empirical data and Langmuir consistency is higher

Table 1. The results and constant of different isotherms on arsenic (V) adsorption data (50 ml solution with concentration of 3, 5, 7 mg.L^{-1}, time: 60 min, pH=2, adsorbent dosage: 0.05 g)

Parameter		Isotherm
0.0001	Q_0	Langmuir
1E-05	k_L	
0.0357	R^2	
3.8	n	Freundlich
0.1	K_f	
0.25	R^2	

Kinetic studies

The results of adsorption kinetics by arsenic (V) are shown in Table 2.

Table 2. Calculation of kinetic data using different models in arsenic (V) (adsorbent dosage: 0.1 g.L^{-1}, pH=2, 50 ml solution with concentrations of 3, 5, 7 mg.L^{-1}, time: 60 min).

Parameter		Kinetic model
0.25	K^1	pseudo-first order kinetic
1600	q_e	
1	R^2	
0.059	K_2	pseudo-second order kinetic
1600	q_e	
0.0497	h	
0.8254	R^2	
167.5	Kp	Interparticle diffusion
1536.7	C	
0.1908	R2	

Chart (10-e, f, g) show the curves of arsenic (V) adsorption kinetic models.

Based on the results above, pseudo-first order and pseudo-second order kinetic models in arsenic adsorption are consistent with the empirical data.

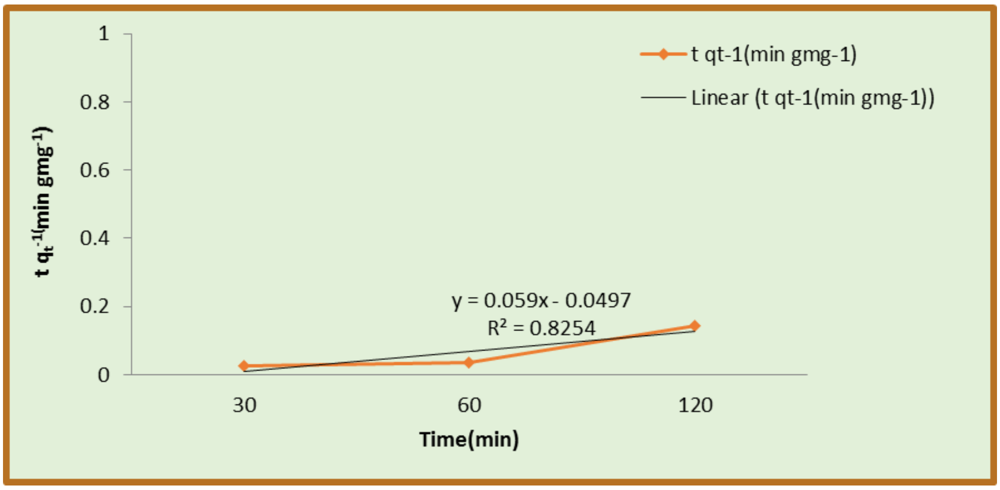


Chart (10-e). The curve of pseudo-first order kinetic model in arsenic (V) adsorption (adsorbent dosage: 0.1 g.L^{-1}, pH=2, 50 ml solution with concentrations of 3, 5, 7 mg L^{-1}, time: 60 min).

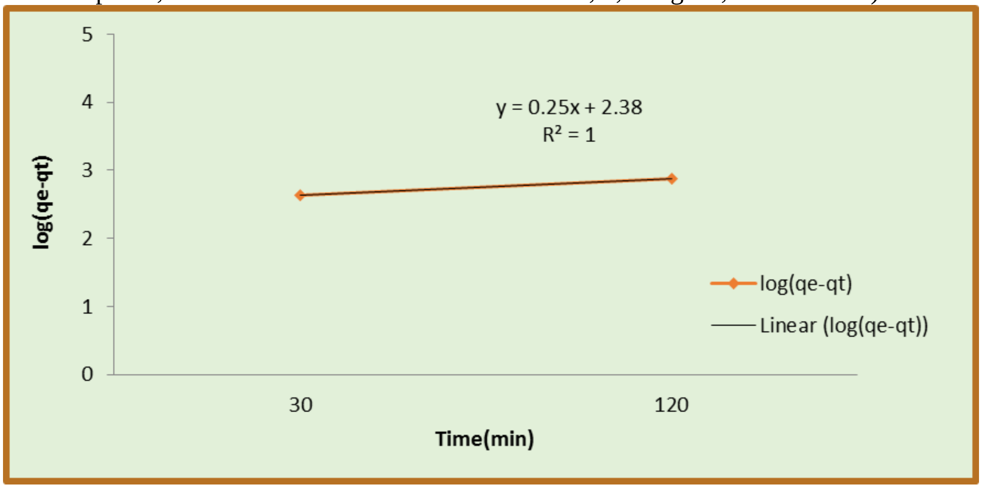


Chart (10-f). The curve of pseudo-second order kinetic model in arsenic (V) adsorption (adsorbent dosage: 0.1 g.L^{-1}, pH=8, 50 ml solution with concentrations of 3, 5, 7 mg.L^{-1}, time: 60 min).

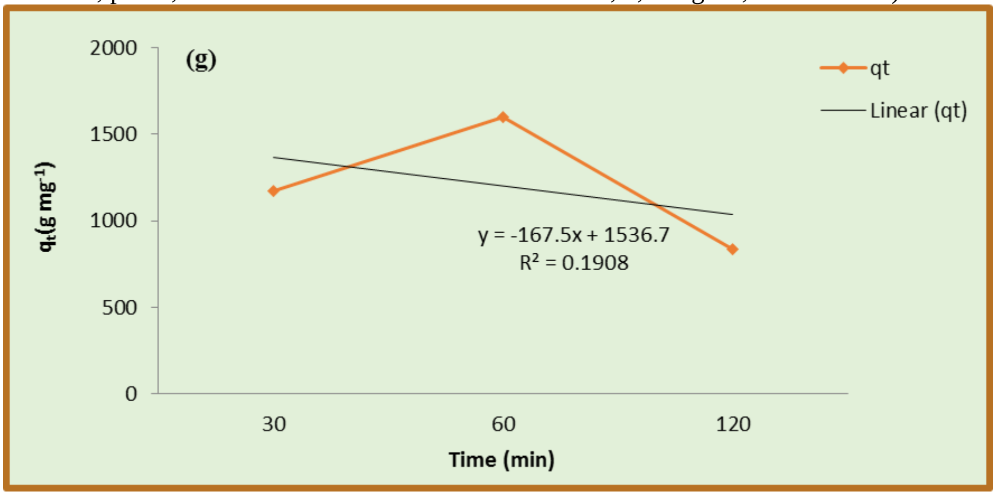


Chart (10-g). The curve of interparticle diffusion kinetic model in arsenic (V) adsorption (adsorbent dosage: 0.1 g.L^{-1}, pH=8, 50 ml solution with concentrations of 3, 5, 7 mg.L^{-1}, time: 60 min).

DISCUSSION AND CONCLUSION

This study attempts to review previous studies regarding alumina nanofiber and apply it as an adsorbent for rapid and easy removal of arsenic in water. Electrospun and uncalcined alumina nanofiber could be effective as an adsorbent to remove heavy metal ions from water despite the fact that previous studies removed heavy metals after calcination at phases $\wp$, α and boehmite. This filter is more effective in comparison to other ionic exchange methods as it is used frequently and is environment-friendly [9]. In a study entitled “Adsorption of Arsenic (V) and Arsenic (III) onto different uncalcined and calcined Aluminum hydroxide powder”, it was found that their filter was different in terms of method and materials. In 2003, a report was published by natural resources Institute of Wisconsin University in which “photocatalytic adsorption media and arsenic removal process from underground water” was investigated and they applied three types of sol-gel method and all believed that crystal phase or calcinated filter was efficient.

Arsenic (V) removal was studied under the effect of empirical parameters including pH, contact time, initial metal concentration, solution volume and adsorbent dosage. The results show that among the above parameters, pH and adsorbent dose were more effective on metal adsorption. Indeed, 90% adsorption of arsenic with less Nano at 1 h is valuable.

The majority of adsorption capacity for arsenic (V) is 3.8 $mg.g^{-1}$ according to Langmuir and Freundlich isotherm models. The results of adsorption and resorption show good potential of using alumina nanofiber in heavy metals removal from water. Regarding adsorption kinetics, the results show that arsenic (V) is consistent with pseudo-first order and pseudo-second order kinetic models. The studies at batch condition showed that this adsorbent was a good choice for the removal of arsenic (V) ions at pH=2.

The analyses verified the morphology of adsorbent and evaluated it as suitable in terms of type and application.

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