International Journal of Agricultural and Environmental Research
FREE AND OPEN ACCESS
Available online at www.ijaaer.com
ISSN 2414-8245 (Online)
ISSN 2518-6116 (Print)

ARSENIC REMOVAL FROM GROUNDWATER BY PRODUCING ACTIVATED CARBON FROM COTTON GIN TRASH (AC-CGT) - A CASE STUDY OF SAKRAND, DISTRICT SHAHEED BENAZIRABAD, SINDH, PAKISTAN

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Abstract

Pakistan has limited freshwater resources which are depleting and deteriorating as well. Quality of drinking water is also getting poorer day by day specially due to contamination of toxic heavy metals and metalloid such as arsenic. Prolong and continuous consumption of arsenic even in minute quantity can chain up with serious diseases. Safe limit of arsenic recommended by the World Health Organization (WHO) is 0.01mg/L whereas arsenic contamination in study area ranges between 0.05 to 0.1 mg/L. Elimination of heavy metals like arsenic is very complicated to achieve. Adsorption is the method which is not only efficient in removing heavy metals from water but economical also. Adsorbent production from natural material or any trash material is attracting scientific community attention because it is cost effective than the commercially available adsorbents. Cotton gin trash is a trash material, which is produced while processing cotton. There is a crucial need to develop a method by which this trash can be disposed-off systematically. This study has dealt with the disposal issue of cotton gin trash and arsenic elimination by producing cotton gin trash activated carbon (AC-CGT). Through this research, it was concluded that activated carbon can be produced from cotton gin trash by pyrolysis process and it has a significant removable capacity of arsenic from groundwater. After adsorption arsenic contamination became 0 mg/L. In this research, it was also observed that adsorption by AC-CGT has little impact on other parameters such as Turbidity, TDS, EC and pH.

Keywords: *cotton ginning trash, adsorbent, activated carbon, arsenic removal*

INTRODUCTION

Freshwater resources are limited and depleting also, less than 1% water is readily available for consumption. Nowadays, contamination of freshwater resources is an alarming issue globally. Country Pakistan has total 177 MAF freshwater resources which includes about 152 MAF of surface water and remaining 25 MAF of the groundwater. Pakistan mainly relies on snowmelt and rainfall for the recharge of freshwater resources. According to Asian Development Bank study, Pakistan will have to face approximately 32% of freshwater scarcity by 2025, (Qureshi, 2011). As stated water resources are depleting on the other hand quality of drinking water is deteriorating in rural and urban areas of Pakistan (Aziz, 2005). Presence of toxic heavy metals and metalloid in groundwater is an alarming issue nowadays (Imamoglu and Tekir, 2008). The presence of arsenic in groundwater is considered as a serious inorganic pollutant globally due to its adverse results, (Smedley et al., 2002). Arsenic Concentration in Sindh and Punjab exceeded the WHO recommended level of intake which is 0.01 ppm (Qureshi et al., 2014). Bhatti et al., (2017) observed highest arsenic concentration, 0.2 ppm at Sakrand among the rest of the area of Sindh. Removal of heavy metals is expensive and challenging, especially for large volumes of water (Demirbas, 2008). Adsorption is the method which is not only efficient, but economical also. It is favored because it does not produce sludge (Fu and Wang, 2011). The adsorbent is considered cost-effective if it requires no or small treatments or it may be byproduct or any waste material. This is the reason that adsorbent production from natural material are being used for the removal of heavy metals (Tangjuank et al., 2009).

Cotton crop is considered as cash crop for Pakistan and cultivated broadly along with Indus River. Pakistan is the fourth in world in cotton production (Malik and Ahsan, 2016). While extracting desired product from raw-cotton 16 to 42 percent a trash material is produced commonly known as Cotton Gin Trash (CGT). It contains the broken-seed, burs, leaf-fragments, and dust. There is a crucial need to develop a systematic way of disposal for cotton gin trash (Myer, 2007). Earlier, it was incinerated or dumped in open air for disposal, but after the implementation of 1970 Federal Clean Air Act both the practices were stopped (Kennedy, 2006). Then cotton gin trash was used for feeding the cattle. It contains gossypol, which can cause weight reduction, affect the reproduction and ultimately death can also be occuring if consumed in huge amount (Rossi and Stewart, 2006). According to a survey conducted in present study, it was observed that Cotton Ginning Factories of Sakrand sell out CGT to owners of Brick Kilns or Blacksmiths. They utilize it for burning purpose.

In the present study, CGT was collected from local cotton ginning factories of Sakrand, District Shaheed Benazirabad to convert into activated carbon. After characterizing the activated carbon prepared form cotton ginning trash (AC-CGT) it was used to treat the groundwater taken from the same area for removal of arsenic content.

MATERIALS AND METHODS

Preparation and activation of activated carbon: Cotton gin trash was collected from locally available cotton ginning factories. The CGT was dried under sunlight for 8 hours and then sieved (Sieve sizes No.4 to No. 20) (Sahira, et al., 2013). After that it was washed to eliminate dust impurities and kept in the oven at 105 °C for 8 hours (Ramakrishnan and Namasivayam, 2009). The freshly prepared sample was carbonized in an inert atmosphere. Inert atmosphere was achieved by filling sample in a ceramic container till it is full and covered with a lid. Then in order to eliminate the air, the ceramic container was put into another steel container and vacuum between the containers was filled with sand. Muffle furnace was used for heating this system. The sample was carbonized at 550ºC for one hour (Ramakrishnan and Namasivayam, 2009). For activation of carbonized CGT, it was impregnated with 1:1 ratio by Ferric chloride ($FeCl_3$) solution and then demoisturized in oven at 105ºC for eight hours. The carbonized material was activated by heating the sample at 650ºC for one hour and following the procedure stated above.

Characterization of activated carbon:

Characterization of AC-CGT was carried out by performing Fourier Transform Infrared (FTIR) spectroscopy, X-Ray Powder Diffraction (XRD), Methylene Blue adsorption (MBN), Iodine number (IN) and ash content. The FTIR spectroscopy was conducted by using a Nicolet iS10 FT IR Spectrometer. The recorded spectra were within the range of 400 to 4000 cm^{-1}. The XRD was carried out by using "Rigaku X-ray powdered diffraction using "Cu K-alpha" medium of X-Rays with 40 Kv. Moreover, the emissions were emitted in the duct carrying current of 25 mA. The results were recorded graphically at 2-theta with angular range 2 to 37º. The MBN was measured by following JIS K 1470 (1991) standard method. The IN was observed by following ASTM D 4607 (1999) standard method. Finally the ash content was analyzed by ASTM D2866-11 (1994).

Collection and Characterization of Groundwater Sample: Groundwater samples were collected from seven operational tube-well at Sakrand, District Shaheed Benazirabad, Sindh, Pakistan, which were not only used for domestic water supply but for irrigation also. The collection containers were washed thrice with tube well water and then the sample was collected with five replications and stored. Same procedure of collection was followed by (Van Geen et al., 2005). Characterization of Groundwater Sample was carried out by performing the arsenic test, pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS) and turbidity. The Arsenic test was carried out by QUANTOFIX Arsen 50 kit manufactured by Macherey Nagel. The pH of the water samples were analyzed by portable pH meter (Model PH 8414). The EC and TDS were measured by HACH 8163 meter. The turbidity of the samples was measured with the portable instrument manufactured by Lovibond (Model TB 210 IR).

Lab Setup for Arsenic Removal: For the removal of the arsenic in the laboratory, a PVC pipe having 9 cm diameter and 30.48 cm length was used as a column. The column was first filled with gravel layer of 7.62 cm followed by a 7.62 cm layer of pre-washed river sand. On the top of the river sand, the activated carbon makes the final layer of 7.62 cm. The remaining space in the column was empty for water sample. Moreover, for collecting the influent and effluent, both the sides of PVC pipe were plumbed by PVC nipples (Mise and Divyarani, 2013).

RESULTS AND DISCUSSIONS

Fourier Transform Infrared (FTIR) Spectroscopy: The FTIR spectra for AC-CGT is shown in Figure 1. The FTIR spectra show a peak at 2164 cm^{-1}, which represents the existence of miscellaneous class with structure R-C-N. The peak observed at 1980 cm^{-1} explains that the grouping of C=C with aromatics. The peak observed at 945 cm^{-1} confirms free and intermolecular bonded carboxylic groups with RCO-OH structure, as also observed by Moreno-Castilla, (2004). The peaks observed from 1300 to 900 cm^{-1} considered as Acids, Alcohols, Phenols, esters or ethers, respectively. Furthermore, 761 cm^{-1} and 693 cm^{-1} peaks indicates the prepared activated carbon was related to the aromatics groups. The same peaks were explained by Chunlan et al., (2005) that the bands ranging between 900 cm^{-1} to 600 cm^{-1} recognized as out of plane C–H bending mode in aromatic rings.

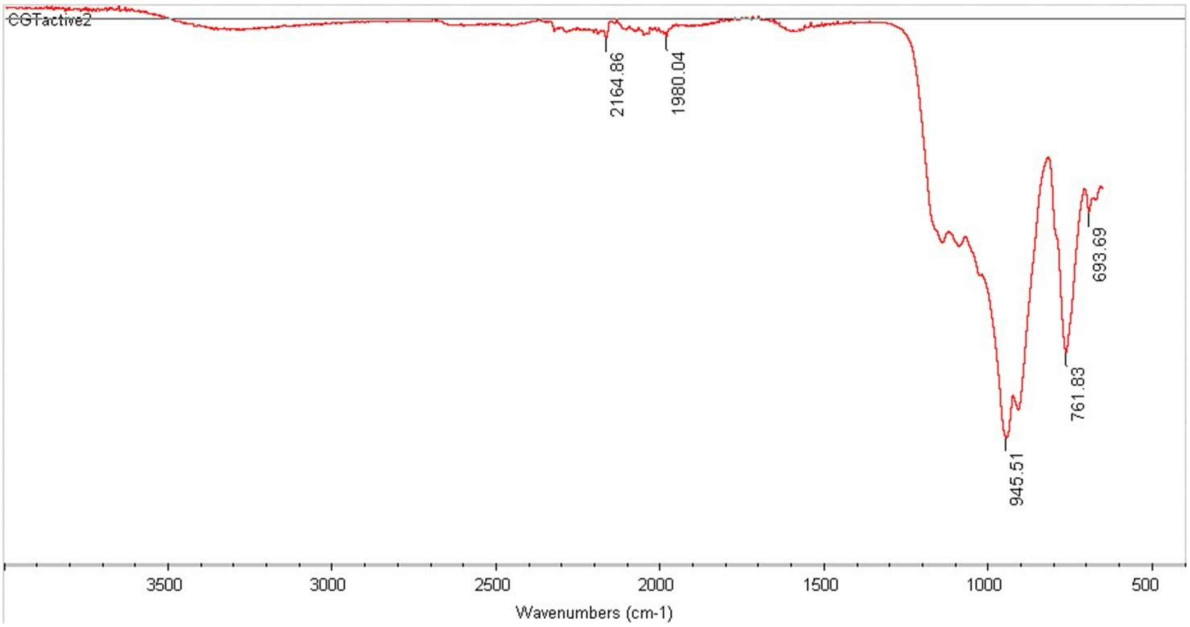

Figure 1: FTIR spectra for AC-CGT

X-Ray powder diffraction (XRD): The XRD result of AC-CGT is shown in Figure 2. The peak 27^0 at 2 theta known as graphite peak (Baghel et al., 2006). Same time it performed noise of the powdered X-Ray Diffraction which revealed that structure of carbon is amorphous. Furthermore, it indicated that chemical bonds of organic-compounds were broken down by the pyrolysis process with temperature and converted into active compounds. Standard graphite layers and stacks of planes were produced during carbonization by these compounds. Similar results at 27^o 2 theta were explained by Lua and Yang, (2004). The peak at 29^o at 2 theta confirms that produced AC-CGT is amorphous in nature as explained by Lu et al., (2002). Both the peaks at 21^o and 29^o authenticate that the prepared AC-CGT was crystallized and layered structure without the formation of any spinel structure of activated carbon.

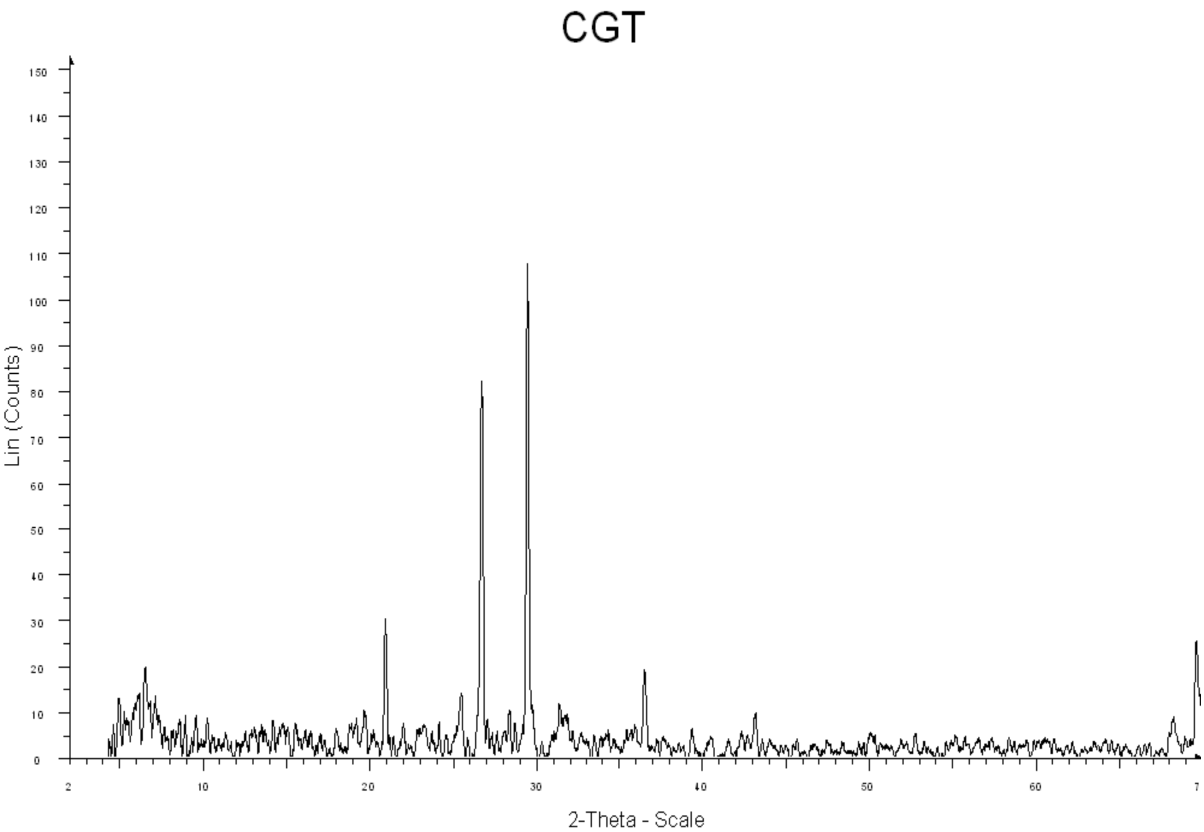

Figure 2: The XRD result of AC-CGT

Iodine number (IN): Iodine number results confirm the high availability of micropores. 643.5 mg/g iodine number was observed by performing ASTM D 4607, (1999) for cotton ginning trash activated carbon. It has revealed broad reaction between $FeCl_3$ and surface of carbon which has increased the release of CO_2 and CO gases and created micropores inside of the mesopores (Chen et al., 2011; Saka, 2012).

Methylene blue number: Cotton gin trash activated carbon has high methylene blue adsorption capacity with value of 330.25 mg/gm. This has revealed that the cotton gin trash activated carbon is mesoporous in nature with negatively charged surface, (Tseng et al., 2008; Wu et al., 2005).

Ash content: Ash content has zero capacity of adsorption and it also reduces the mechanical strength of activated carbon. ASTM method D 2866- for ash content of activated carbon was followed and it was observed that cotton gin trash activated carbon has 6% ash content. Approximately the same result was observed by Hernandez, (2007).

Arsenic Analyzation: The arsenic concentration of the samples is shown in Figure 3. All the seven samples were analyzed for arsenic contamination. Arsenic contamination ranges between 0.05 to 0.1 mg/L before treatment, approximately same results were observed by, (Kandhro et al., 2016; Baig et al, 2016). Bhatti et al. (2017) observed highest arsenic concentration in Sakrand, District Shaheed Benazirabad. Whereas, adsorption by cotton gin trash activated carbon resulted 0 mg/L residue of arsenic contamination

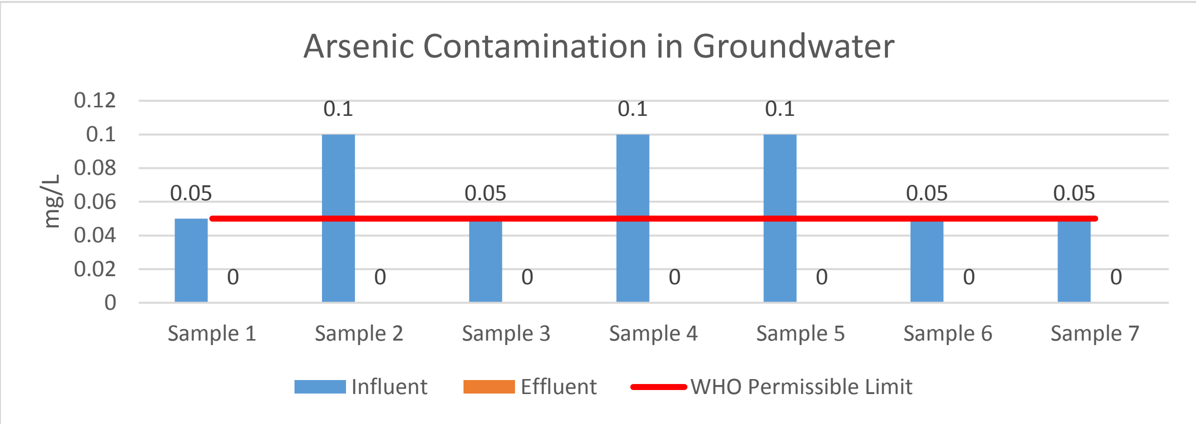

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Figure 3: Arsenic contamination before and after adsorption

The pH: The pH of samples from seven operational tube-wells was analyzed and the results are shown in Figure 4. The pH value varied between 7 and 8.2. A similar results were obtained by (Majidano et al., 2008; Kandhro et al., 2015). On the contrary, after passing through the cotton gin trash activated carbon, pH slightly decreases

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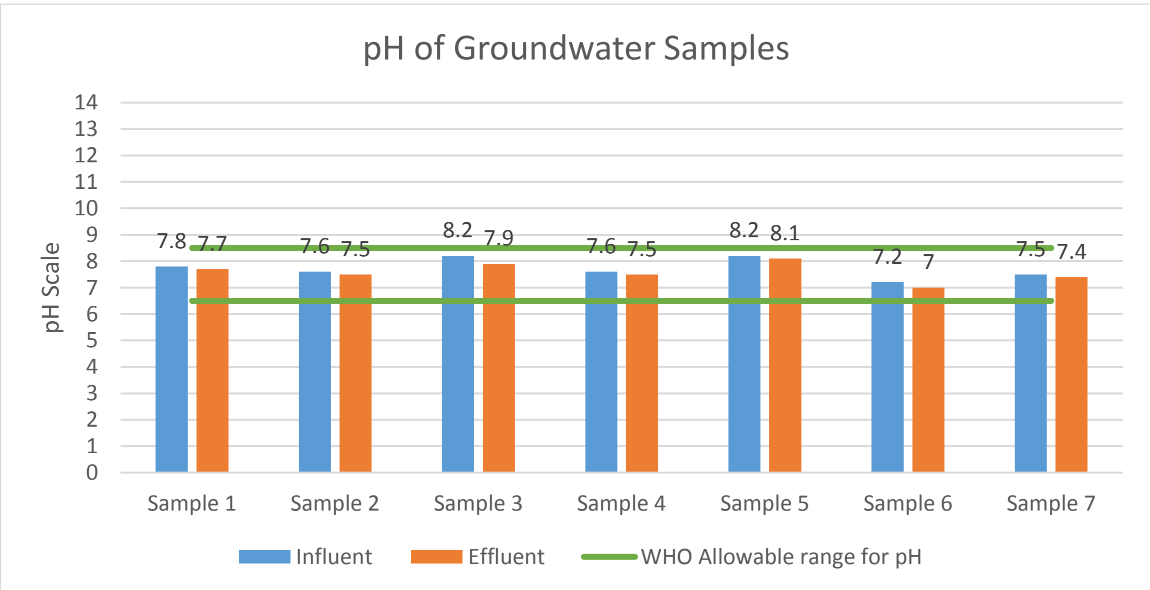

Figure 4: pH Value of Groundwater Sample Before and After Adsorption

Electrical Conductivity of groundwater samples: The EC Value of Groundwater Sample before and after passing through the adsorbent is shown in Figure 5. The EC of Groundwater Samples was analyzed with five repetition for initial and after adsorption. Minimum value of samples was observed 1.5 mS/cm and maximum value was 1.92 mS/cm before adsorption. As per the results, adsorption of arsenic decrease the EC by 1 to 2%.

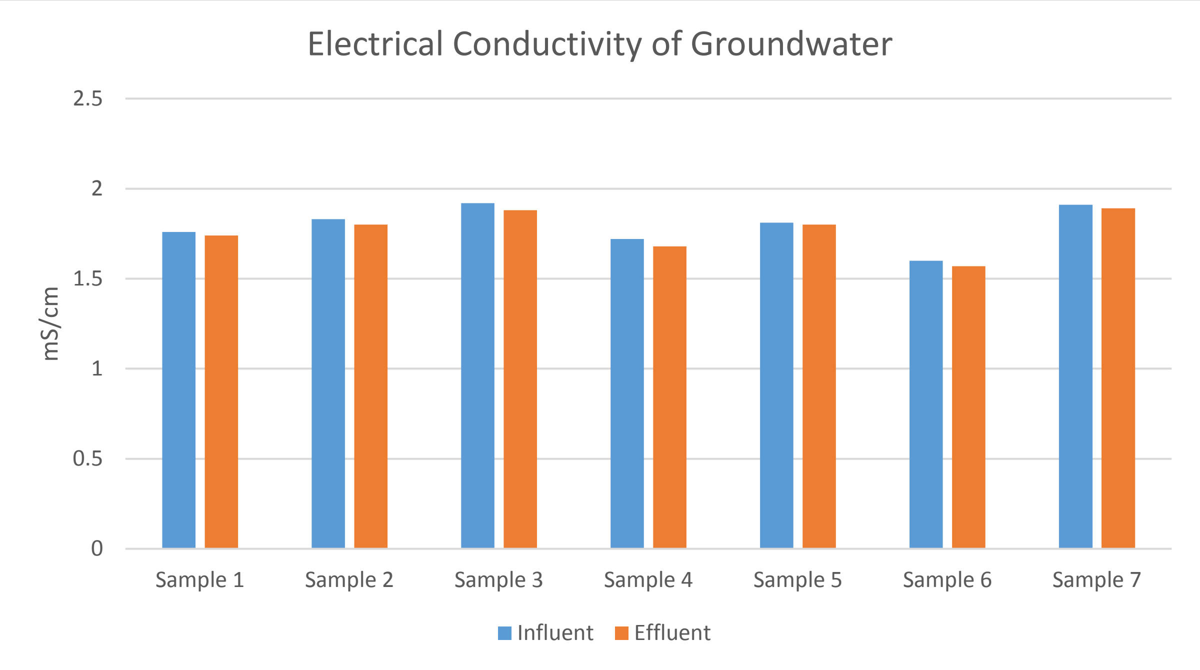

Figure 5: The EC Value of Groundwater Sample before and after passing through the adsorbent

Total Dissolved Solids (TDS) of Groundwater Sample: The TDS analysis before and after adsorption is shown in Figure 6. The TDS for all the seven samples were analyzed with five replications and minimum value was 650mg/L and maximum value was 990mg/L nearly same values were obtained by (Majidano et al., 2010)

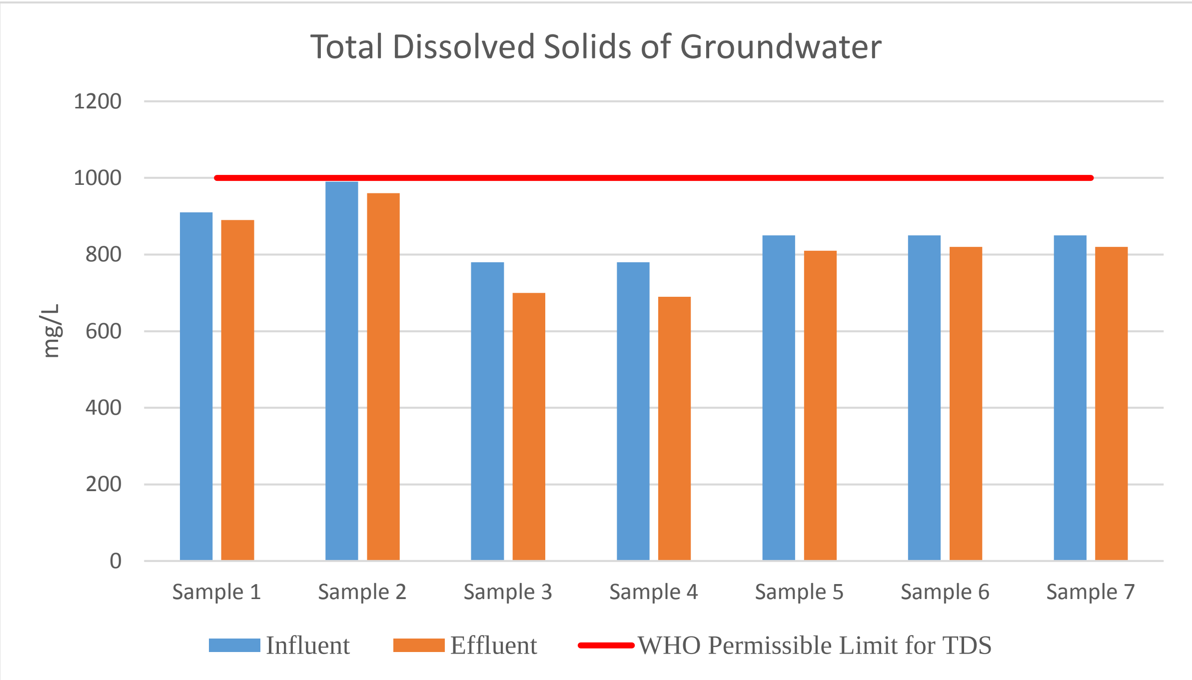

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Figure 6: TDS analysis before and after adsorption

Turbidity analysis of groundwater: The turbidity of a groundwater sample before and after analysis is shown in Figure 7. Turbidity analysis was repeated five times for all the seven samples individually. The minimum value was 1.3 NTU and maximum value 3.2 NTU was observed. Whereas 5 NTU is safe limit is recommended by WHO. After adsorption by cotton gin trash adsorbent 1 to 2% decrease was observed.

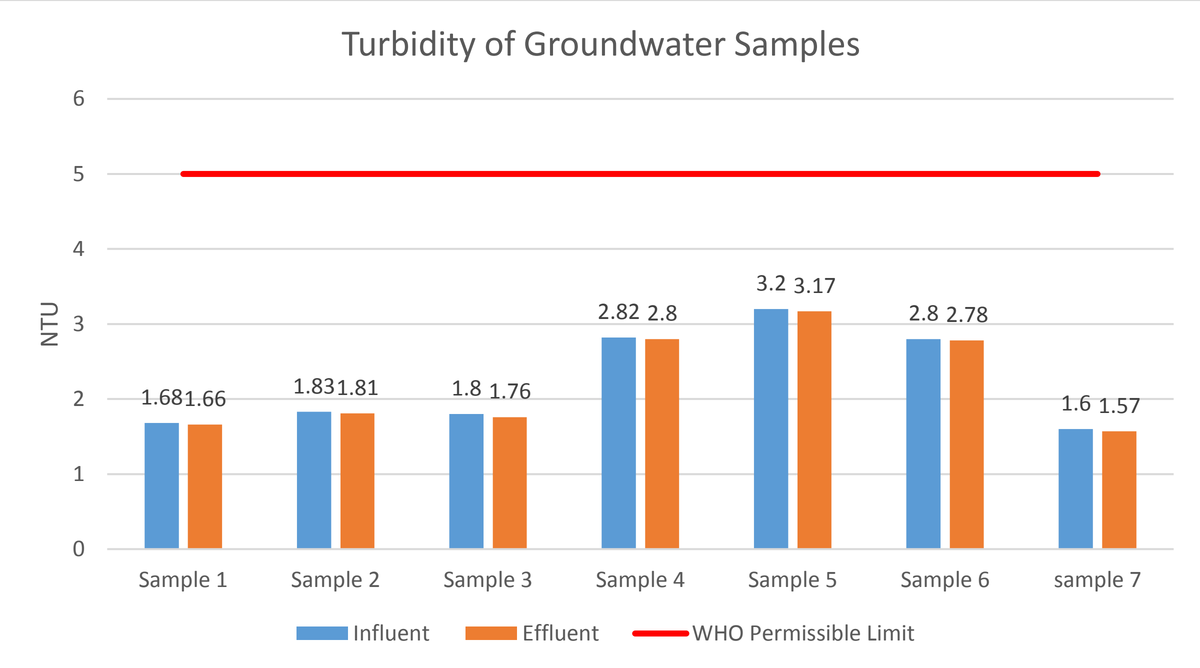

Figure 7: Turbidity of a groundwater sample before and after analysis

CONCLUSIONS

This study has provided a possible solution for the disposal issue of cotton gin trash by converting it into activated carbon for the removal of arsenic from groundwater. FTIR spectra of cotton gin trash activated carbon has witnessed the attachment of numerous functional groups. Broad peak at 2 theta 27^{o} shown by XRD which has confirmed the complex crystalline structure of cotton gin trash activated carbon. Iodine number and methylene blue adsorption have revealed efficient adsorption capability of cotton gin trash activated carbon. It was concluded that arsenic contamination up to 0.1 mg/L can be fairly removed by produced cotton gin trash activated carbon. Furthermore, it was observed that produced cotton gin trash activated carbon can decrease other physical and chemical properties like TDS, turbidity, pH and electrical conductivity.

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