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Removal of Inorganic Arsenic from Arsenic Spiked Local Tap Water using Titanium Oxide and Ferric (hydr) Oxide Based Adsorbents

Rafiqul Islam[1,2], Md. Ashraful Islam Molla[1,2]*, Tuerker Yigitoglu[1], Jan Hoinkis[1]

[1]Centre of Applied Research (CAR), Karlsruhe University of Applied Sciences, Germany
[2]Department of Applied Chemistry & Chemical Engineering, University of Dhaka, Bangladesh

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***Corresponding author:** Md. Ashraful Islam Molla

Abstract

Original Research Article

Arsenic (As) is an ubiquitous element found in the soils, rocks, natural waters and organisms. It is one of the most toxic elements and has been classified as a group I carcinogen for human. The removal of arsenic from groundwater is an important issue for environmental safety and human health. In this study, the performance of three commercial Titanium oxide and Ferric (hydr) oxide based media regarding removal of arsenite As(III) and arsenate As(V) from drinking water have been investigated. The study is carried out by column experiments on laboratory scale using arsenic spiked local tap water. The experimental work has studied the maximum bed volume and the maximum capacity which is in compliance with the recommended WHO standard (MCL) of 10 µg/L in the effluent. The achieved bed volume of granulated Titanium oxide based adsorbent (approximately 5700) is superior to that of Ferric oxide and Ferric hydroxide based adsorbents at EBCT of 3.5 minutes. At EBCT 1 min Ferric hydroxide based adsorbent exhibits highest bed volume (2300).

Keywords: Arsenic removal, Granulated Titanium oxide, Granulated Ferric hydroxide, Granulated Ferric oxide.

INTRODUCTION

Arsenic poisoning has become one of the major environmental concerns in more than 70 countries, including Bangladesh, India, West Bengal, Myanmar, Pakistan, Vietnam, Nepal, Cambodia, United States and China. About 200 millions of people have been exposed to excessive arsenic through contaminated drinking water [1]. The World Health Organization (WHO) has set the maximum level for Arsenic in drinking water at 10 µg/L [2]. Arsenic is found in the environment both in organic and inorganic forms. The inorganic forms are much more toxic and are found in groundwater, surface water and many foods. Arsenic is the main cause of physiological and metabolic disorder in animals and human such as arsenicosis, malignancies, cancers (bladder, lung, liver, kidney), diabetes, hypertension etc [3, 4].

Hence, appropriate arsenic removal technologies are of prime importance for all arsenic affected areas. To date, many technologies have been developed for arsenic mitigation. The basic principles of arsenic removal from water are based on conventional techniques of oxidation, coprecipitation and adsorption onto coagulated flocks, lime treatment, adsorption onto sorptive media, ion exchange and membrane techniques [5-7]. Arsenic removal through adsorption is emerging as most feasible option because in most cases the system is simple to operate and cost-effective [8]. Effectiveness of adsorption-based methods depends primarily on the properties of the adsorbent used. A wide array of materials have been developed and evaluated for sorption of arsenic from different categories namely activated alumina, activated carbon, iron and manganese coated sand, kaolinite clay, hydrated ferric oxide, activated bauxite, titanium oxide, silicium oxide, biological materials, polymer resins, agricultural/industrial wastes etc [9, 10]. Moreover, Bang *et al.*, [11] have showed that the granular TiO_2 adsorbent has a high adsorption capacity for arsenic removal from groundwater in a neutral pH range. Maji *et al.*, [12] have reported an iron-oxide-coated natural rock adsorbent for the removal of arsenic from arsenic-bearing groundwater. Furthermore, Tabelin *et al.*, [13] have studied that the arsenic is adsorbed onto natural geologic materials. However, many problems are encountered when these materials are evaluated in actual field conditions. The major problems identified are low adsorption capacities, slow kinetics, low selectivity, disposal of spent adsorbent and high cost.

The objective of this study is to investigate removal of inorganic arsenic from arsenic-bearing groundwater by using As-spiked tap water and typical commercial adsorbents consisting of granulated Titanium oxide (ADSORBSIA^{TM} As600), Ferric oxide (BAYOXIDE^{TM} E33) and Ferric hydroxide (GFH^{TM}).

MATERIALS AND METHODS

The performances of three different commercially available potential adsorbing media with regard to arsenic removal have been investigated:

- Adsorbent consisting of granulated Titanium oxide (ADSORBSIA^{TM} As600) [14]
- Adsorbing media consisting of Ferric oxide (BAYOXIDE^{TM} E33) [15]
- Ferric hydroxide based adsorption media (GFH^{TM}) [16]

Typical physical and chemical properties of the applied adsorption media are listed in Table-1.

Table-1: Physical and chemical properties of the applied adsorption media

Adsorbing media	**Particle size (Micron)**	**Bulk Density (g/L)**	**Specific surface area (m^2/g)**	**Moisture content (%)**
Granulated Titanium oxide (ADSORBSIA)	250–1180	640	250	<10
Ferric oxide (BAYOXIDE)	–	460–570	120–200	20
Ferric hydroxide (GFH)	315 x 2000	465–577	–	–

Arsenic Analysing Method

In this work, an analytical method according DIN 38405 D12 (German Standard) has been applied. With this method dissolved As(V) and As(III) is transformed into arsine AsH_3 by chemical reduction with KI and $SnCl_2$. Arsine gas is stripped into a silverdiethyldithio-carbamate (SDDC) pyridine solution forming a coloured complex of arsine which can be analyzed by spectrophotometry at a wavelength of 525 nm. A Merck Spectroquant Nova 60 spectrophotometer has been used. The standard deviation of this method has been observed in our experiments as ±1 µg/L. A liquid As(V) standard (1000 mg/L) has been purchased from company Merck which served as parent solution to spike tap water and for preparation of the calibration curves. Arsenic trioxide As_2O_3 in powder form, also delivered by Merck has been used for the preparation of the As(III) parent solution (350 mg/L) according to DIN 38405 D12. The arsenic trioxide is dried for 24 hours before preparing the standard solution. Arsenic trioxide (As_2O_3) of 0.462 g has been dissolved with 12 ml of NaOH (2 mol/L) and subsequently the solution has been neutralised with sulfuric acid. Finally the solution is filled up to 1000 mL with DI water.

Water Quality

All the experiments are conducted with local tap water. The quality of the local tap water used for the experiments is summarized in Table-2. This water is spiked with the parent solutions of As(V) and As(III) to prepare the required arsenic feed water concentration.

Table-2: Physico-chemical characteristics of local tap water in the city of Karlsruhe, Germany [17]

Parameter	**Unit**	**Value**
Aluminium	mg/L	<0.02
Calcium	mg/L	112
Chloride	mg/L	22.6
Electrical conductivity	µS/cm	661
Hydrogencarbonate	mg/L	322
Iron	mg/L	<0.01
Magnesium	mg/L	9.7
Manganese	mg/L	<0.005
Sodium	mg/L	11
Sulfate	mg/L	549.5
pH	–	7.23

Experimental

Figure 1 & 2 represent the experimental set-up. The water is fed to the column by a peristaltic pump bottom-up (version 1) and top-down (version 2) depending on the respective contact time. The adsorbing media are placed in plastic columns of 2 cm inner diameter filled with media of 10 cm height resulting in a packed media volume of 0.0314 L. All experiments are conducted at two empty bed contact times (EBCT) of 1 minute and 3.5 minutes with an arsenic influent concentration of 500 µg/L at 20°C until the effluent arsenic concentration exceed the MCL of 10 µg/L. The purified water (effluent) has been collected in an effluent collection tank. Prior to the experiments the fine particles of the media are removed by water back flush. The experiments are run at two contact times (EBCT) of 3.5 minutes (version 1) and 1 minute (version 2). Due to the fact that at short contact time (1 min) bottom-up flow resulted in a significant media bed expansion these experiments are conducted by version 2 and those at 3.5 min are carried out by version 1. The mass and the volume of the applied adsorbing media are listed in Table-3.

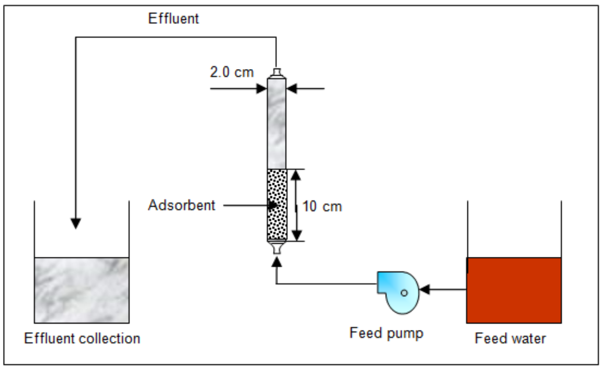

Fig-1: Experimental set-up version 1: bottom-up

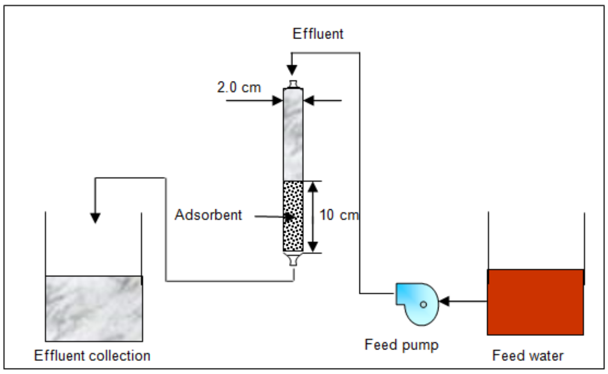

Fig-2: Experimental set-up version 2: top-down

Table-3: Masses and volume of the applied adsorbing media

Adsorbing media	Mass (g)	Volume (L)
Granulated Titanium oxide (ADSORBSIA)	20	0.0314
Ferric oxide (BAYOXIDE)	13	0.0314
Ferric hydroxide (GFH)	30	0.0314

RESULTS AND DISCUSSIONS

Experiments with As(V)

Figure 3 & 4 show the arsenic concentration in effluent over the treated bed volumes. The achieved bed volume of granulated Titanium oxide based adsorbent (approximately 5700) is superior to that of Ferric oxide and Ferric hydroxide based adsorbents at EBCT of 3.5 minutes. At shorter contact time of 1 minute all bed volumes are generally less than half of those at 3.5 minutes whereas the bed volumes of granulated Titanium oxide based and Ferric hydroxide based are comparable exceeding the MCL at around 2200 bed volumes. For both contact times Ferric oxide based lags considerably behind the results of granulated Titanium oxide based and Ferric hydroxide based adsorbents. Since the experiments at short contact time cannot be run overnight the flow has to be stopped and restarted next day. Therefore a recovery resulting in lower arsenic effluent values can be noticed for all media (e.g. at bed volume around 1200) when left overnight. This may be due to diffusion of adsorbed arsenic into inner pores in the idle period.

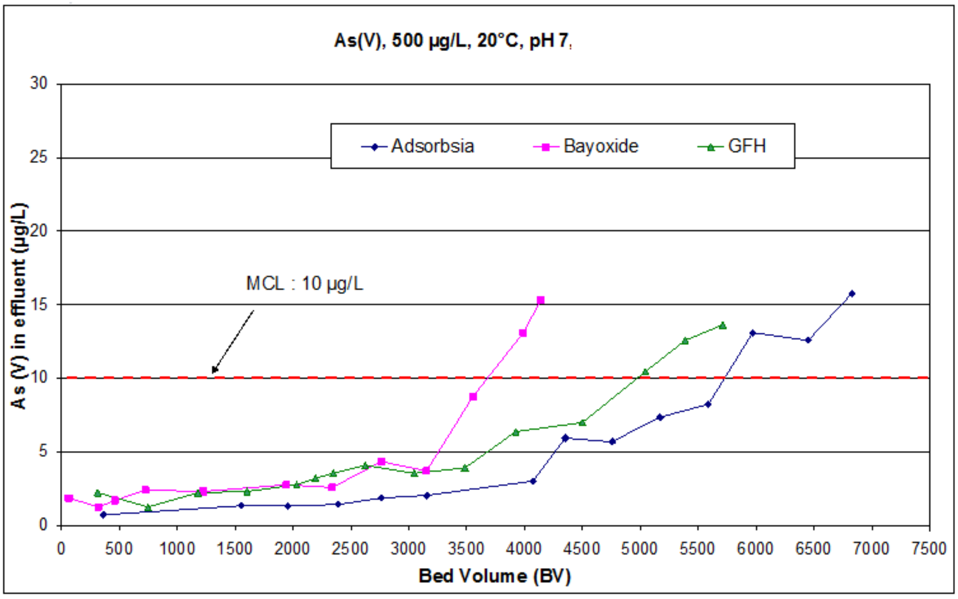

Fig-3: As (V) in effluent vs. bed volume at EBCT 3.5 min

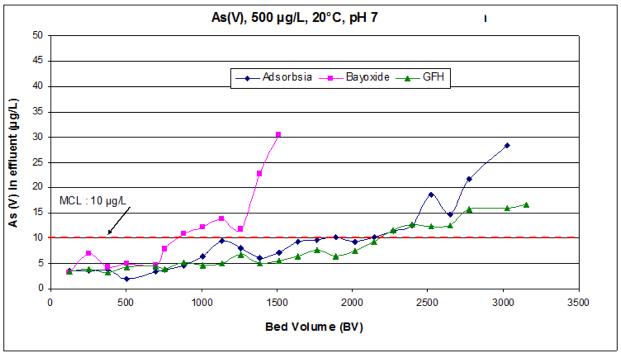

Fig-4: As (V) in effluent vs. bed volume at EBCT 1 min

Comparison of bed volumes treated and adsorbing capacities

Figure-5 compares the experimental data of the bed volumes treated complying with the MCL 10 µg/L. At EBCT 3.5 min ADSORBSIA has highest adsorption capacity with almost 6000 bed volumes treated complying with the MCL [18]. At EBCT 1 min the capacities of ADSORBSIA and GFH is comparable around 2000 bed volumes. BAYOXIDE has generally the lowest capacity. In a further step arsenic adsorbing capacity (g/kg) has been calculated using the experimental bed volumes (Figure-6). When comparing the capacities of the adsorbents type ADSORBSIA with the other two types of adsorbents based on Ferric oxide and Ferric hydroxide, it should be noted that they have different densities (Table-3). The capacity of Ferric oxide based adsorbent at 3.5 min is comparable to ADSORBSIA, however but the value at short contact time (1 min EBCT) is distinctly lower than that for ADSORBSIA. For Ferric hydroxide based adsorbent the results are the other way round, the capacity at 3.5 min EBCT is significantly lower than for ADSORBSIA and the value at 1 min EBCT is comparable to ADSORBSIA. The differences in capacities (g/kg) between the tested media can partly be attributed to the different media densities (Table-3).

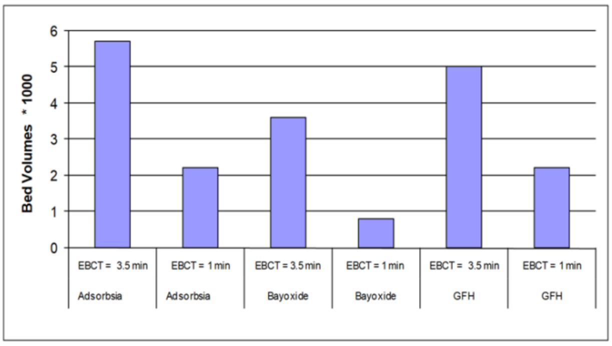

Fig-5: Bed volumes of the tested media (feed As (V) 500 µg/L)

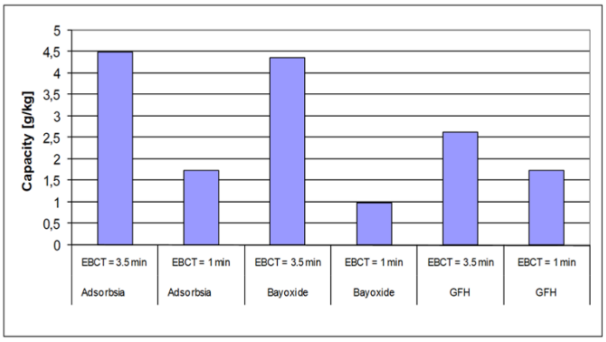

Fig-6: Capacities of the tested media (feed As (V) 500µg/L)

Experiments with As (III)

Figure 7 & 8 give the As(III) concentration in effluent over the bed volume. For all media the maximum bed volumes are significantly lower than for As(V). At EBCT 3.5 min ADSORBSIA granulated Titanium oxide performs best with a maximum bed volume of around 1600. The maximum bed volume of Ferric oxide based adsorbent is only about half of that for ADSORBSIA. At EBCT 1 min Ferric hydroxide based adsorbent exhibits highest bed volume (2300). However, the experiment at EBCT 1 min has to be stopped each day and has been restarted next day. Therefore a slight decrease of arsenic in effluent can be noticed which may be attributed to recovery due to inner pore diffusion of adsorbed arsenic.

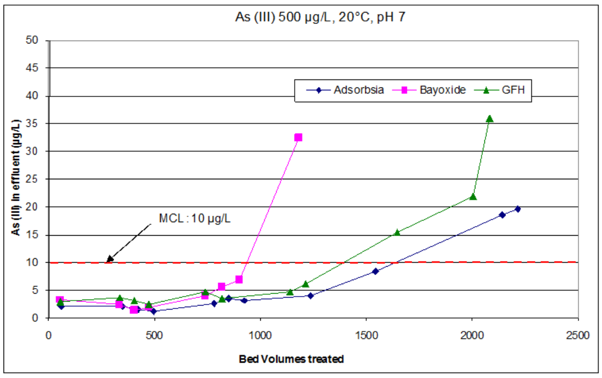

Fig-7: As (III) in effluent vs. bed volume at EBCT 3.5 min

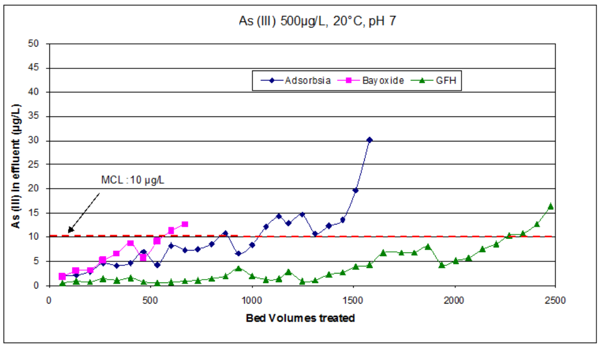

Fig-8: As (III) in effluent vs. bed volume at EBCT 1 min

Comparison of the bed volumes treated and the arsenic capacities

Figure-9 compares the experimental data of the bed volumes treated complying with the MCL 10 µg/L and Figure-10 compares the capacities of the tested media (calculated from the treated bed volumes). At EBCT 3.5 min ADSORBSIA show best performance of all tested media. In the experiments at EBCT 1 min GFH showed distinctly higher capacity over its value at 3.5 min. The GFH capacity at 1 min is as high as the ADSORBSIA capacity at EBCT 3.5 min This is in disagreement with all previous results of As(III) and As(V) for which the capacity at shorter EBCT is always lower than for the longer one and therefore needs to be further studied.

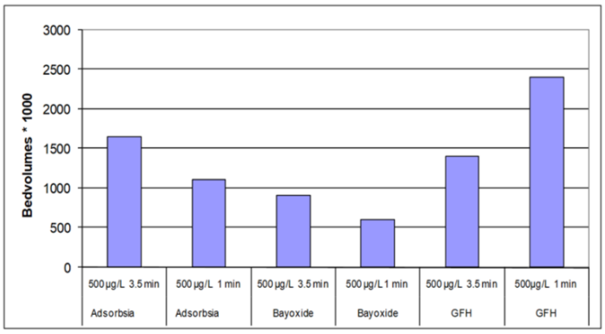

Fig-9: Bed volumes of the tested media (feed As(III) 500 µg/L)

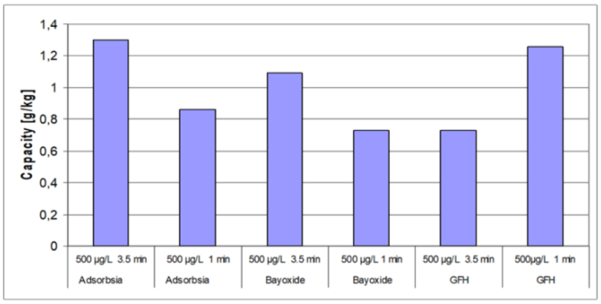

Fig-10: Arsenic adsorbing capacities of the tested media (Feed As(III) 500 µg/L)

CONCLUSION

The performance of three commercial adsorbents consisting of granulated Titanium oxide (ADSORBSIA), Ferric oxide (BAYOXIDE) and Ferric hydroxide based media (GFH) regarding removal of As(III) and As(V) from drinking water have been investigated. The column experiments on laboratory scale at EBCT 3.5 and 1 min verify the high performance of granulated Titanium oxide based adsorbent in removing arsenic from drinking water in the valence state +3 and +5 compared with commercially available ferric oxide/ hydroxide media.

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REFERENCES

1. Asere TG, Stevens CV, Du Laing G. Use of (modified) natural adsorbents for arsenic remediation: A review. Science of the Total Environment. 2019; 676:706–720.
2. `Guidelines for drinking-water quality (4th ed). WHO Press, World Health Organization, 20 Avenue Appia, 1211 Geneva 27, Switzerland. 2011; 315–318.
3. Samal AC, Kar S, Maity JP, Santra SC. Arsenicosis and its relationship with nutritional status in two arsenic affected areas of West Bengal, India. Journal of Asian Earth Sciences. 2013; 77:303–310.
4. Maity JP, Nath B, Kar S, Chen CY, Banerjee S, Jean JS, Liu MY, Centeno JA, Bhattacharya P, Chang CL, Santra SC. Arsenic induced health crisis in peri-urban Moyna and Ardebok villages, West Bengal, India: An exposure assessment study. Environmental Geochemistry and Health. 2012; 34(5):563–574.
5. Deng M, Wu X, Zhu A, Zhang Q, Liu Q. Well-dispersed TiO2 nanoparticles anchored on Fe3O4 magnetic nanosheets for efficient arsenic removal. Journal of Environmental Management. 2019; 237:63–74.
6. Hernández-Flores H, Pariona N, Herrera-Trejo M, Hdz-García HM, Mtz-Enriquez AI. Concrete/maghemite nanocomposites as novel adsorbents for arsenic removal. Journal of Molecular Structure. 2018; 1171:9–16.
7. Pariona N, Camacho-Aguilar KI, Ramos-González R, Martinez AI, Herrera-Trejo M. Structural characterization of ferrihydrite/hematite nanocomposites and their arsenic adsorption properties. Adsorption Science & Technology. 2015; 33:871–880.
8. Yazdani M, Tuudjarvi T, Bhatnagar A, Vahala R. Adsorptive removal of arsenic(V) from aqueous phase by feldspars: kinetics, mechanism, and thermodynamic aspects of adsorption. Journal of Molecular Liquids. 2016; 214:149–156.
9. Tuutijarvi T, Lu J, Sillanpaa M, Chen G. As(V) adsorption on maghemite nanoparticles. Journal of Hazardous Materials. 2009; 166(2–3):1415–1420.
10. Turk T. Removal of Dissolved Arsenic by Pyrite Ash Waste. Mine Water and the Environment. 2017; 36(2):255–263.
11. Bang S, Patel M, Lippincott L, Meng XG Removal of arsenic from groundwater by granular titanium dioxide adsorbent. Chemosphere. 2005; 60(3):389–397.
12. Maji SK, Kao YH, Liao PY, Lin YJ, YJ, Liu CW. Implementation of the adsorbent iron-oxide-coated natural rock (IOCNR) on synthetic As(III) and on real arsenic-bearing sample with filter. Applied Surface Science. 2013; 284:40–48.
13. Tabelin CB, Igarashi T, Arima T, Sato D, Tatsuhara T, Tamoto S. Characterization and evaluation of arsenic and boron adsorption onto

natural geologic materials, and their application in the disposal of excavated altered rock. Geoderma. 2014; 213:163–172.

14. ADSORBSIA™ As600. Available online: https://www.dupont.com/products/ADSORBSIAAs600.html.
15. BAYOXIDE® E 33, Available online: http://lpt.lanxess.com/en/products-lpt/product-groups/iron-oxide-adsorber/bayoxide-product-detail/bayoxider-e-33/.
16. GFH® GRANULAR FERRIC HYDROXIDE MEDIA. Available online: https://www.evoqua.com/en/brands/IPS/Pages/GFH-Media.aspx.
17. Stadtwerke-karlsruhe, Jahresmittelwerte 2018. Available online: https://docs.google.com/viewer?url=https%3A%2F%2Fwww.stadtwerke-karlsruhe.de%2Fswk-media%2Fdocs%2Fservice%2Finfomaterial%2Fprodukte%2FTrinkwasser-Jahresmittelwerte-KA.pdf.
18. Guan X, Du J, Meng X, Sun Y, Sun B, Hu Q. Application of titanium dioxide in arsenic removal from water: A review. Journal of Hazardous Materials. 2012; 215–216:1–16.