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RESEARCH PAPER

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Assessment of the arsenic content in groundwater specimens

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Abstract

Water is essential for every living thing known, although it does not supply any organic nutrients or calories. About one third of the global population consumes groundwater. It is a very good solvent for many different substances, including organics and minerals; therefore, it is extensively utilized in industrial processing. Contamination by arsenic (As) in drinking water has become a major health issue globally. Approximately 60 million persons in Asia are endangered by arsenic-contaminated water resources and over 7,00,000 arsenic-related diseases have been reported. Therefore the analysis and monitoring of arsenic is very necessary. In our present research work we have utilized As kit method for the analysis of arsenic from samples of groundwater. Total (100) groundwater samples were randomly obtained from an area of sampling in the different villages and towns of Nawab Shah taluka, Shaheed Benazir Abad district, Sindh, Pakistan. The physico-chemical parameters like electrical conductivity, pH and total dissolved salts were measured and compared with the WHO limits. The pH values of 03 specimens were (8.6-8.9) above and 07 specimens were (6-6.4 pH) below the permitted limit value. The electrical conductivity (EC) was found in the range 241-7126 μ S/cm and the EC of 75 specimens were found higher than the permitted limit. The total dissolved salts (TDS) were found in the range 155-6319mg/L and the TDS in 66 specimens were found higher than the permitted limit. The assence was found present in 70/100 samples but 40/70 (57.1%) arsenic containing water sampling was found above the WHO permitted limit.

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Introduction

Water is essential for every living thing known (Boyd, 2019), although it does not supply any organic nutrients or calories. It covers about 71% of the surface of the earth, mainly in the oceans and seas (Kaur and Kaur, 2017). Minor quantities of water are found as groundwater (1.7%) (Sahu, 2019). About one third of the global population consumes groundwater (Bouderbala, 2017; Jain and Vaid, 2018; Li *et al.*, 2019). Water has a significant contribution to the economy of the world (Distefano and Kelly, 2017). Nearly 70% of freshwater consumed by people flows into agricultural use (Jiang *et al.*, 2017).

It is a very good solvent for many different substances, including organics and minerals; therefore, it is extensively utilized in industrial processing and for the cooking and washing. Contamination of the metals in drinking water and their associated health impacts have had an impact on humans for centuries (Jamshaid *et al.*, 2018). A global study of polluted potable water sources has demonstrated that certain contaminants originating directly from the surrounding environmental area, like manganese and arsenic from rock substrate, are wide-spread and represent a persistent issue (Harvey *et al.*, 2016). Contamination by arsenic (As) in drinking water has become a major health issue globally (Rahman *et al.*, 2018; Tabassum *et al.*, 2019).

Arsenic concentrations in several naturally occurring water entities vary from marine water to groundwater. Arsenic concentration in seawater is less than that of lakes and rivers, while in groundwater it is higher (Abbas and Cheema, 2015). Depending on size of the body, the water content of the human body is between 55% and 78%. Most people consume water untreated or unfiltered, thus giving rise to numerous water-related illnesses (Singh and Railoa, 2020). In natural water, the appearance of as is mainly related to the geo-chemical characteristics of the aquifer, the hydrology and geology of the areas (Ali et al., 2019). The main sources of as contamination include geology, extraction, pesticide use, and fossils (Tewari et al.,

2017). The high concentrations of arsenic in water is because of human activities such as the discharge of household, industrial and municipal wastes in Pakistan (Rasool *et al.*, 2017).

The bad impact of arsenic (As) contaminated groundwater on people has been reported all over the world, mainly in countries in Asia (Rahman, 2017). The contamination of drinking water by arsenic poses a threat to over 150 million people worldwide (Podgorski et al., 2017). About 110 million of these persons reside in ten countries in South and southeast Asia including India, Bangladesh, Vietnam, China, Nepal, Laos, Taiwan, Pakistan, Myanmar and Cambodia (Bibi et al., 2017). Arsenic is found almost everywhere in the environment and extremely hazardous to the whole living things (Cullen et al., 2017). Approximately 60 million persons in Asia are endangered by arsenic-contaminated water resources and over 700,000 arsenic-related diseases have been reported (Bibi et al., 2017).

The arsenic (As) is considered toxic and classified as carcinogenic to humans affecting the lungs and skin (Holcomb *et al.*, 2017; Kuo *et al.*, 2017). The presence of As(V) and As(III) in groundwater is a significant issue (Fan *et al.*, 2017). Ingestion through either water or food is the primary route of this metalloid in the body where its absorption occurs in the stomach and intestines, followed by its release into the bloodstream. Then arsenic is turned by the liver into a slightly toxic form, most of which is ultimately discharged into the urine (Ponomarenko *et al.*, 2017). The commonest reason for prolonged exposure is drinking water that is contaminated (Siddiqui and Chaudhry, 2017). As exposure is responsible for many disorders in humans, animals and plants (Ali *et al.*, 2020).

The characteristic disease of long-term exposure of arsenic occurs as disease of the black foot (Spilchuk and Thompson, 2019), cancer of the skin (Al-Eryani *et al.*, 2018), obesity (Hsueh *et al.*, 2018), cancer of the bladder (Saint-Jacques *et al.*, 2018) and deactivation of an enzyme activity (Peksen and Sanal, 2018). Arsenic contact may also lead to various other health implications like high blood pressure, irritation of the gastrointestinal tract, vascular rupture, irregular heartbeats, diabetes and reduced red and white cells count (Hall *et al.*, 2017; Shakoor *et al.*, 2017).

There are various instrumental procedure that are utilized for the examination of arsenic like graphite furnace atomic absorption spectrometry (Schneider et al., 2018), electrothermal atomic absorption spectrometry (Valdivia et al., 2018), cathodic stripping voltammetry employing a mercury droplet hanging electrode (Khamkaew et al., 2019), inductively coupled plasma, mass spectrometry (Firat et al., 2017), hydride generation atomic absorption spectrometry (dos Santos et al., 2018), anodic stripping voltammetry (Garlaschelli et al., 2017), atomic fluorescence spectrometry (Luo et al., 2017), hydride generation atomic fluorescence spectrometry (Shishov et al., 2018), etc. These aforesaid techniques of analysis though have capability of very minute detection limit but are very costly, needed trained technicians for their maintenance and operation, unavailability of on-site performance. While the as kit is an easy to use and portable method for detecting as in groundwater. This method is economical, convenient to perform and maintenance free. That is why in recent study we have utilized the as kit for as detection from collected groundwater samples.

Materials and methods

Sampling Area

Groundwater samples were randomly obtained from an area of sampling in the different villages and towns of Nawab Shah taluka, Shaheed Benazirabad district, Sindh, Pakistan. In total (100) groundwater specimens were obtained from various sources at sampling sites in Nawab Shah taluka from approximately 55 to 140 feet depth utilizing plastics vessels (capacities 1.0L), of which 6 to 8 specimens were obtained at each site from May to August 2017.

Preservation and preparation of samples

The polyethylene plastic bottles were used to store the samples, which were previously soaked in 10% nitric acid for 24 hours and rinsed accurately with pure H_2O . The Whatman No. 42 filter paper was used to remove suspended solids and then the samples were kept at 4°C in the darkness. The sample list of groundwater was coded with NS 1 to NS 100 of taluka Nawab Shah, Shaheed Benazir Abad district. The 500mL of specimens picked up in a beaker mixed with nitric acid concentrated a few droplets heated at about 75°C by putting them on a hot plate in order to reduce the volume near to dry. After that, the residuals were digested with HNO₃ 2N by stirring with 33% addition of H_2O_2 further heated at 70°C to reduce to 20mL volume.

Sample Analysis

The pH was identified by means of a pH meter, by immersing electrodes into samples of water. The conductivity meter was used to test the conductivity in the unit of μ S/cm. The electrodes of the conductivity meter were immersed in water samples, showing the TDS in unit of mgL⁻¹.

Arsenic Kit method

The content of arsenic was determined with the Merck Arsenic Kit (0.01-0.5mg/L) (Merck K Ga A, 64271 Darmstadt, Germany), by using the colorimetric method by test strips at the laboratory in 48 hrs after collection of samples. Arsenic kit test container was filled to sixty milliliters of sample water to be determined and analyzed according to the recommendations of the kit manufacturer.

Results and discussion

The physico-chemical parameters of 100 samples were studied measuring electrical conductivity, pH and total dissolved salts for the evaluation of the quality of drinkable H₂O and the findings were checked by comparing them with the limits allowed by the WHO. The total dissolved salts (TDS) in ground water specimens was obtained in the range 155-6319mgL⁻¹. From these 100 samples, 34 samples were within permissible limit, while other 66 specimens were higher than the permitted limit suggested by WHO. The highest and lowest total dissolved salts values were found as 6319mg/L in NS 78 and 155 mg/L in NS 46 samples respectively as shown in Table 1. The pH of the samples was obtained from 6.0-8.9 pH value. From these 100 samples, the 22 samples were acidic with the values of pHs from 6.0-6.9 pHs, the 50 samples were observed neutral with the value of pH 7 and the 28 samples were basic with the values of pHs from 7.1-8.9 pHs. The pH values of the 90 specimens were within permissible limit, the 03 samples like NS

53, NS 58 and NS 77 were above permitted limit (8.6-8.9) value and 07 specimens such as NS 13, NS 21, NS 25, NS 39, NS 67, NS 84 and NS 91 were (6.0-6.4pH) below permitted limit as suggested by WHO. The highest and lowest values of pHs were found as pH 8.9 in NS 77 and pH 6 in NS 67 samples respectively as shown in Table 1.

Table 1. Arsenic contents in various groundwater samples.

WHO limit	6.5-8.5	2500	1000 mg/L	10 μg/L	WHO limit	6.5-	2500	1000	10 µg/L
	0 0	μS/cm	0,	1.01		8.5	μS/cm	mg/L	10,
Sample Codes	рН	EC uS/cm	TDS	As	Sample Codes	υH	EC uS/cm	TDS	As
NS 1	7	560	395	05	NS 51	8.3	1186	382	50
NS 2	7	890	270	50	NS 52	8.5	2225	900	00
NS 3	7	2570	813	100	NS 53	8.7	6972	3390	25
NS 4	7.1	2835	1353	10	NS 54	7.9	7039	6028	10
NS 5	7	3071	1128	100	NS 55	8.1	6850	6095	05
NS 6	7.3	3310	1093	250	NS 56	8.4	7121	5985	50
NS 7	7	1372	031	10	NS 57	7.9	7118	5803	05
NS 8	7	3124	1105	00	NS 58	8.6	7126	6068	10
NS 9	7.3	2780	2397	00	NS 59	7.3	7060	5001	50
NS 10	7	2616	3381	00	NS 60	7.7	6730	081	00
NS 11	7	3451	4525	25	NS 61	7	6883	5745	00
NS 12	66	2001	4278	-0 50	NS 62	73	7/3	62/	00
NS 12	6.4	2517	2265	05	NS 62	7.5	2701	5520	50
NS 14	6.8	2450	828	100	NS 64	7	2805	1080	100
NS 15	7	2430	560	25	NS 65	7	2261	050	50
NS 16	74	2182	2802	-0	NS 66	61	2265	402	00
NS 17	7.4	2001	2092	05	NS 67	6	3303	494	25
NS 18	70	2901	4180	05	NS 68	7	3/91	4/31 5986	250
NS 10	7.3	1070	045	20 10	NS 60	7	4030	5042	200
NS20	66	4160	2810	00	NS 70	7	2017	5945 5024	00
NS 01	6.0	4160	2019	50	NS 70	7	391/	0924 4865	00
NS 21	67	4103	530/	50 10	NS 71	71	3133	4005	25 250
NS 22	0./	4/20	5103	10	NS /2 NS 70	/.1	1965	491 875	250
NS 23	/	2195	901	20 50	NS 73	/	2301	0/5	50
NS 24	6 1	2753	3539	50	NS 74	7	4539	52/3	100
NS 25	0.1	3901	4032	00	NS 75	/.9	4602	6105	00
NS 20	6 -	44/0	5094	00	NS 70	0.2	4040	50195	100
NS 27	0.5	1040	540	00	NO 77	0.9	5620	5990	100
NS 20	66	3610	2810	50	NS 70	0.5	4930	0319	100
NS 29	6.6	4/33	930	50	NS /9	7.4	600	5/52	25
NS 30	0.0	4910	5994	100	NG 01	/	002	5/0	00
NS 31	7	2052	3094	25	NO OI	60	2490	485	05
NS 32	60	2995	4305	50	NG 02	0.8	23/2	405	00
NS 33	0.9	391	/20	50	NS 03	6 1	2008	33/	05
NS 34	- 9	32/5	519	100	NS 04	0.4	2569	3134	05
NS 35	7.0	4000	5149	10	NO 05 NO 06	7	3007	5/3	00
NS 30	7	4930	5904	50	NS OU	7	2137	9/2	05
NS 3/	-	5305	0090	00	NG 00	6-	10/0	/93	05
NS 38	7.9	2039	458	25	NS 88	0.5	3189	4258	05
NS 39	0.3	2991	3643	100	NS 89	7	3397	4180	00
NS 40	.,	21/5	/02	10	NS 90		2952	5301	00
NS 41	6.9	410	610	00	NS 91	6.2	3128	5350	00
NS 42	~	913	938	05	NS 92	0.7	3010	5134	00
NS 43	0.7	3371	4118	00	NS 93		3364	4968	05
NS 44	7	3803	5798	05	NS 94	7.4	2389	478	05
NS 45	7	4629	6007	50	NS 95	7	4067	837	10
INS 40	7	6103	155	05	NS 96	7.2	4976	5184	50
INO 47	8.3 6 -	6385	5998	05	NS 97	7	3855	4968	05
INS 48	0.5	2981	4446	00	NS 98	7.1	4071	5083	05
NS 49	7	241	732	10	NS 99	7	4680	5102	50
NS 50	7	2679	2973	50	NS 100	7	4396	4995	10

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The electrical conductivity (EC) of ground water specimens was obtained in the range $241-7126\mu$ S/cm. From these 100 samples, 25 specimens were within permissible while other 75 specimens were higher than the permitted limit as suggested by WHO. The highest and lowest values of electrical conductivity were found as 7126μ S/cm in NS 58 and 241μ S/cm in NS 49 sample respectively as shown in Table 1.

In our present research work the arsenic was detected by utilizing As kit method from 100 samples of groundwater taken from the different villages and towns of taluka Nawab Shah district Shaheed Benazir Abad, Sindh, Pakistan. This method is economical, convenient to perform, maintenance free and portable method for detecting of As in groundwater. The acceptable/safe limits of arsenic indicated by World Health Organization is 0.01 mg/L or 10µg/L. From the 100 samples, the arsenic was not detected in 30 samples, while arsenic was found present in 70 groundwater collected samples as shown in Table 1 and Fig 1-5. Out of these 70 groundwater arsenic containing samples, the 40 (57.1%) water sampling were beyond permitted limit while the 30 (42.9%) water sampling were in the range of the permitted limit as indicated by World Health Organization.

The 03 samples (NS 06, NS 68 and NS 72) were found with the highest value 250 μ g/L of arsenic and the 19 samples were found with the lowest value 5 μ g/L of arsenic from 70 arsenic containing groundwater samples as shown in Table 1 and Fig. 1-5.

The results 25 samples obtained by As kit for the As were validated against the results these samples analyzed by inductive couple plasma (ICP) and the results were found good in comparison to both methods, with a confidence limit of 95%.



Fig. 1. Arsenic content in samples.



Fig. 2. Arsenic content in samples.



Fig. 3. Arsenic content in samples.

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Fig. 4. Arsenic content in samples.



Fig. 5. Arsenic content in samples.

Conclusion

Our current research work concluded that the 40/70 (57.1%) samples of arsenic containing groundwater of Nawab Shah taluka were found to contain arsenic above the limit suggested by World Health Organization and are dangerous for drinking purposes without removing the arsenic.

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