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Treatment experiments for removal of hydrogen sulfide from saline groundwater in Kuwait

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ABSTRACT

Laboratory and field experiments have been carried out to find an optimum method for the treatment of hydrogen sulfide-rich groundwater that often occurs at comparatively shallow depths (15–40 m from the surface) in the urban areas of Kuwait City and is pumped to the surface during dewatering of the construction sites. The treatment would be necessary to remove the gas from the pumped groundwater before its disposal, either on the surface or to the stormwater network, to avoid health and environmental hazards created by the release of the hydrogen sulfide gas, which is toxic, to the atmosphere or to the sea. Based on these experiments, it has been recommended that an economic and reliable hydrogen sulfide treatment facility for groundwater pumped at the study area should consist of sand filters, followed by aeration units for the removal of major part (60–70%) of hydrogen sulfide. Chlorination or activated carbon adsorption can be utilized as a polishing process to remove the residual hydrogen sulfide, depending on its concentration in the water after the aeration treatment and the rate of groundwater pumping.

Keywords: Groundwater treatment; Remediation; Water quality; Kuwait group aquifer; Batch experiments; Column experiments; Field experiments

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1. Introduction

Hydrogen sulfide, for which a non-anthropogenic origin has been suggested [1], occurs in groundwater in high concentration (10–200 mg/L) in different parts of Kuwait City and its suburbs (Fig. 1) at relatively shallow depths (15–40 m from the surface). The upward movement of sulfide-rich water from depth and its differential flushing by surface recharge through outcrops of the aquifers appear to have given rise to the present sub-surface distribution of hydrogen sulfide in Kuwait City and its adjacent areas. In the recent years, groundwater rich in hydrogen sulfide is increasingly being encountered in and around Kuwait City during dewatering at construction sites with deep foundations, creating significant pollution problems for the public and the authorities. It may be noted that concentrations of hydrogen sulfide above 80 mg/L in air is toxic to humans and can result in death. Furthermore, in low-lying areas, the gas can accumulate,

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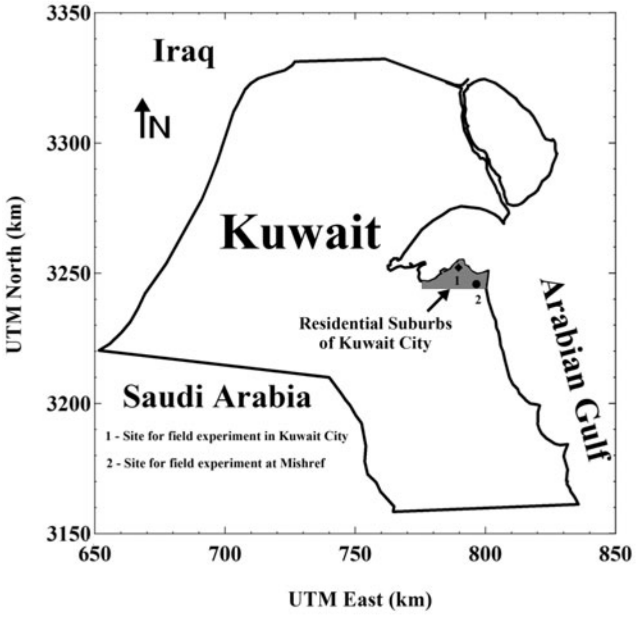


Fig. 1. Kuwait City and its suburbs.

resulting in total concentration above this lethal concentration. To combat the problem, concerned authorities are considering the possibility of the treatment and removal of hydrogen sulfide from the pumped water. The Kuwait Institute for Scientific Research (KISR) conducted a study to identify and focus on the most feasible technique for the removal of hydrogen sulfide from groundwater, out of a vast number of available techniques. The results are presented here.

2. Experimental methods

Most of the available hydrogen sulfide removal technologies were tested in contaminated water with low salt content (total dissolved solids, TDS, less than 500 mg/L). The objective of the current research was to apply and test the effectiveness of the available technologies in saline groundwater with TDS greater than 10,000 mg/L. At such high salinity, the chemistry of the solution will be drastically altered as the increase in the "ionic strength" will reduce the "ion activity" [2]. The experiments were conducted in three different scales as follows:

- Batch laboratory experiments
- Column and tanks experiments
- Field experiments

2.1. Batch laboratory experiments

The objective of the batch laboratory experiments was to assess the relative removal capabilities of some of the available treatment techniques. All the batch experiments were conducted in beakers, small burettes (columns), or conical flasks (Fig. 2). A subset of these techniques was selected for further tests in larger scale column and tank experiments, which were designed based on the laboratory experiment results.

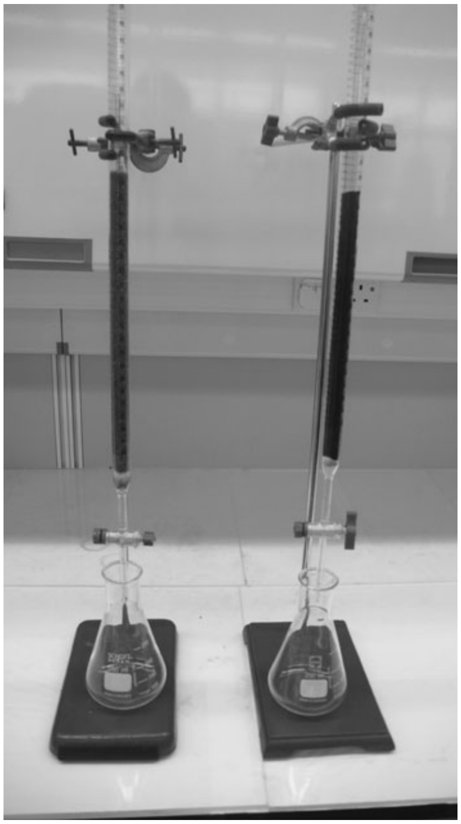


Fig. 2. Typical setup for laboratory experiments.

The batch laboratory experiments covered following techniques:

(1) Activated carbon column
(2) Ion-exchange resin column
(3) Oxidation by chlorination
(4) Aeration and air stripping
(5) Multimedia filter column
(6) H_2S Scavenger (Sulfamin 3001)
(7) Aerobic biological treatment
(8) Electrolysis

2.1.1. General experimental procedure for the batch laboratory experiments

Small columns (burettes) of the material to be tested were prepared by packing 25 g of the media (activated carbon, ion exchange resin, gatch, and multimedia) in granule form in 15 mm diameter burettes. A piece of fluff cotton was placed at the bottom of the burette to prevent the media from escaping the column. Spiked groundwater with sodium sulfide concentrations in the range of 100–600 mg/L (106–635 mg/L hydrogen sulfide) was passed through the media at flow rates between 6 and 20 mL/min. The spiked groundwater was contained in a 10 L polyethylene bottle, elevated above the burette inlet and connected to it through rubber tubing. Flow was manually regulated by simultaneously adjusting a clamp on the inlet rubber tubing and the burette's bottom tap. The effluent was collected in 100 mL aliquots and tested for sulfide concentration. The standard iodine titration method was used for the sulfide concentration determination [3].

2.2. Column experiments at Mishref site

2.2.1. General setup

The column and tank experiments conducted at Mishref site included those techniques that were proved to be applicable for the saline groundwater of Kuwait in the laboratory setup. These were as follows:

1. Activated carbon column
2. Ion-exchange resin column
3. Oxidation by chlorination
4. Aeration and air stripping
5. Gatch (local name of calcretized sand) column
6. Multimedia filters

Additionally, adsorption by ceramic column (provided by GranSpec) was tested at the site, at the request of the supplier.

The new sewage pumping station construction site in the Mishref neighborhood (MNSPS) was selected for these experiments (Fig. 1). Dewatering was ongoing in the site, and high concentration of hydrogen sulfide was observed in the pumped groundwater. The overall area of the station was 40 × 60 m, and the excavation was 34 m deep. The Ministry of Public Works (MPW) provided a large open space for the testing setup. The site was also supplied with all the necessary facilities, such as electricity, to conduct the treatment study.

The static water level at the site was found to be approximately 3 m below ground surface. A total of 24 production wells were designed to lower the water table below the pumping station depth that was to reach a final excavation depth of 36.5 m. The pumped groundwater from all of the wells was discharged through a manifold pipe that carried it to the water disposal manhole. The groundwater from this manhole was pumped via polyvinyl chloride (PVC) pipes to the experimental station of KISR, where several hydrogen sulfide treatment units were installed and evaluated.

The treatment technologies tested had previously been used in several countries, including the USA ([4–6]). In general, low concentration of hydrogen sulfide associated with fresh groundwater was reported in the previous studies in USA, while high concentration of hydrogen sulfide has been found in brackish, saline, and brine groundwater in Kuwait. Two treatment techniques, namely aeration and activated carbon treatment, were selected for further performance evaluation under conditions as close as possible to those prevailing in the field. Since the hydrogen sulfide content of the aggregate effluent from the excavation site was very low, at the time of the experiments, the groundwater tested was spiked with sodium sulfide to adjust the sulfide concentration to levels (160 ppm, approximately 170 mg/L hydrogen sulfide) experienced at the start of the dewatering activity at Mishref site.

2.2.2. Setup of hydrogen sulfide treatment units

The layout of the hydrogen sulfide treatment units installed at the KISR experimental station is shown in Figs. 3 and 4. For the purpose of monitoring the different water parameters, several flow cells were used. All the columns were fed with the same spiked groundwater (Fig. 5). The units included activated carbon, multimedia filters, resin, ceramic, gatch (collected locally and crushed) columns, and oxidation units that used aeration and chlorination. Sand filters were installed to remove the suspended solids from the water before the groundwater was passed through each treatment unit. Two small air injection pumps were installed for removing hydrogen sulfide from groundwater using aeration. Treatment columns were prepared using acrylic pipes (3m in diameter and 1 m in height) and filling them with 1.25, 2.5, and 4.75 kg of activated carbon, resin, and gatch, respectively.

Groundwater was pumped from the water disposal manhole at the MNSPS into two 500-gal storage tanks using two booster pumps. The groundwater was then pumped from the 500-gal tanks and filtered through a sand filter to remove the suspended solids before storing in 500 L PVC tanks. The concentration of hydrogen sulfide of the pumped groundwater reduced to low levels (1–15 mg/L) during September–November 2003, though it was still high and unacceptable for discharge to the marine environment in

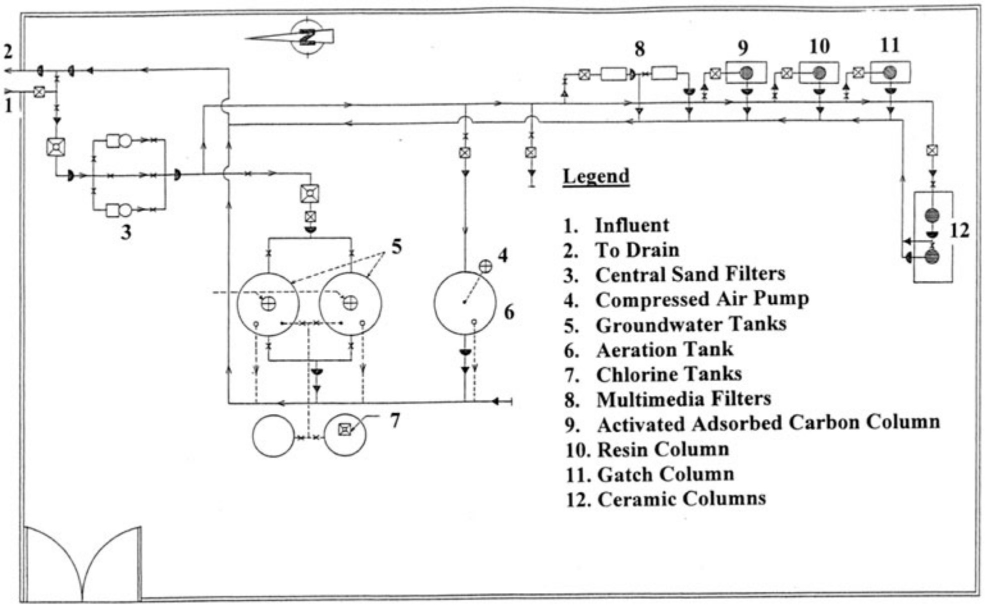


Fig. 3. Layout of the hydrogen sulfide treatment units for pumped groundwater at the Mishref excavation site.

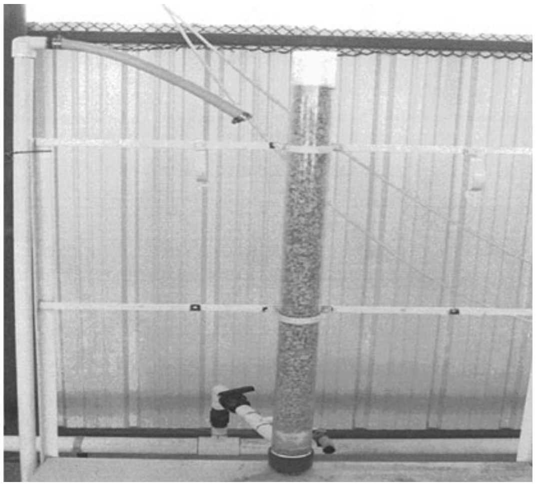


Fig. 4. Typical setup for column experiment at the Mishref site.

many countries. Sodium sulfide ($Na_2S.xH_2O$) was used to boost the hydrogen sulfide concentration to the required level.

2.2.3. Experimental procedure

Two bottles of sodium sulfide were dissolved completely in a 5 L graduated glass beaker and then transferred into the 500 L PVC tank using a 1-m-long electrical stirrer, maintaining a hydrogen sulfide concentration of 141 mg/L (133 mg/L sulfide). The groundwater from the 500 L tank was pumped to the hydrogen sulfide treatment units using pulse injection pump with a capacity of 11 L/h (Fig. 5). Fresh spiked groundwater was prepared each week, and the concentration of the hydrogen sulfide and the other field parameters of the stored spiked groundwater were measured daily. Groundwater samples were collected and analyzed for hydrogen sulfide before and after each treatment unit to evaluate the removal efficiency of the units. Twelve points along the pipe network, connecting the treatment units, were selected for sampling and monitoring of the concentration of hydrogen sulfide and other relevant physical, chemical, and biological parameters (e.g. biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and total petroleum

Fig. 5. Pumping of hydrogen sulfide-spiked groundwater to the treatment units at Mishref site.

hydrocarbon (TPH)) for this purpose. The treatment capacity of each treatment unit was estimated based on measured time and removal efficiency.

Field parameters such as temperature (T), pH, dissolved oxygen (DO), redox potential (Eh), and electrical conductivity (EC) were measured at all points of water sampling. Sampling was conducted according to the standard methods for the examination of water and wastewater [7]. All the sampling bottles were rinsed twice with groundwater before sampling. All the samples were collected in glass bottles, except those collected for the analysis of inorganic non-metallic (e.g. Na, K, Ca, Mg, SO_4, Cl, etc.) samples which were collected in 1 L plastic bottles. Samples to be used for measurement of parameters such as sulfide, TOC and COD were collected in 500 mL glass bottles.

At the beginning, the sulfide concentration in the groundwater was measured in the field using an ion-selective meter, supplied with a sulfide electrode. However, the concentrations were later measured using iodometric titration to avoid interference from high salinity of the groundwater. Titration based on this reaction is an accurate method for determining sulfide at concentrations above 1 mg/L. The concentrations of hydrogen sulfide in the air were also measured in the field using a hydrogen sulfide gas detector near the manhole for the groundwater disposal.

2.2.4. Groundwater quality

A total of 500 groundwater samples were collected from the inlet point (i.e. water disposal manhole of MNSPS) during the early stages of study to determine the fluctuation in the quality of groundwater to be treated. The results revealed that hydrogen sulfide was associated with saline groundwater (i.e. EC and TDS ranged between 30.2 and 85.0 ms/cm and between 17,000 and 45,000 mg/L, respectively) in acidic and reduced environments (i.e. where pH and Eh ranged between 6.1 and 6.9 and between −192 and −356 mv, respectively). Also, the analytical results indicated that nutrients such as ammonia and phosphate and organics such as COD, BOD, TOC, and petroleum hydrocarbons were present in the groundwater.

2.3. Field experiments for removal of hydrogen sulfide at Kuwait City

The treatment techniques used in the field were:

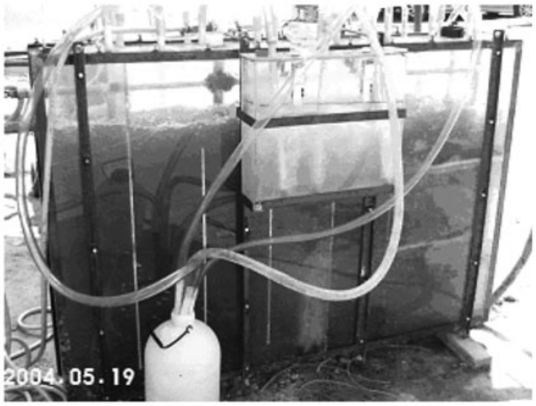
(1) Oxidation by aeration and
(2) Activated carbon

A hydrogen sulfide gas-stripping unit (Figs. 6(a) and (b)) was used at two monitoring well sites in Kuwait City, where groundwater was high in the pollutant. The unit employed the techniques of oxidation and gas-stripping, followed by adsorption on activated carbon to remove ionized and dissolved hydrogen sulfide from saline groundwater that could be defined as "sour water" due to its content of sulfur compound.

2.3.1. The design and construction of the unit

The hydrogen sulfide removal system was composed of five separate units, each with its respective inlet and outlet for fluid. The units were as follows:

(1) The main compartmentalized gas stripping/ adsorption tank of 210 L total volume.
(2) The influent groundwater flow cell where selective membrane probes were mounted and connected to their respective display meters.



(a)

(b)

Fig. 6. Hydrogen sulfide treatment unit used at the well site.

(3) The hydrogen sulfide dissolving tank which was mounted to the side of the main gas-stripping unit of capacity 12 L.
(4) The air compressor.
(5) The effluent orifice meter.

The design parameters for the main gas-stripping unit that might affect the removal efficiency were the volume of the unit, the sour water flow rate, the geometry of the unit, the airflow rate, and the configuration of the air diffusers. Because of cost considerations, the size of the unit was minimized to a practical inexpensive size while maintaining the possibility of extrapolating the results to larger flow and reactor volumes. The residence time, which could be defined as the length of time that each drop of water could take to travel through the treatment unit from the inlet to the outlet, is given by the relation:

$$T = V/Q$$

where T = the theoretical residence time [min]; V = the total volume of water in the treatment unit [L]; and Q = the flow rate of the sour water [L/min]. The residence time was an important factor in determining the removal efficiency.

It should be noted that the above relationship assumes that there is no short-circuiting of the treated water within the treatment unit. The laboratory batch tests indicated that a residence time of 10–15 min was sufficient to attain removal rates higher than 95% in the 0.5 L sour water samples with sulfide concentration in the range between 100 and 200 mg/L (106 and 213 mg/L hydrogen sulfide). Consequently, an initial estimate for the residence time for the field treatment unit was set to 15 min. The available sampling pump (Grundfos MP1) could deliver flow rates in the range of 10–20 L/min. From these data, and the above equation, the volume of the treated water for a 10 L/min discharge rate was computed as follows:

$$V = T.Q = 15 \times 10 = 150L$$

However, the actual volume of water in the treatment unit should be larger than 150 L, or the flow rate should be less than 10 L/min, as the above calculation was based on the theoretical residence time. To minimize short circuiting, the unit was subdivided into five 20 × 20 × 74 cm compartments for air stripping, followed by one 40 × 20 × 74 cm compartment for activated carbon treatment as a polishing step in the last stage. It would be important to mention that the system could be constructed to maintain a minimum volume; but as constructed, the volume of water within the unit could be increased to the maximum capacity of the unit (210 L) during run time by raising the outlet pipe. Increasing the volume or reducing the flow rate of the sour water would increase the residence time within the treatment unit that would allow the testing of different residence times.

The outer shell of the unit was constructed with Plexiglas of 10 mm thickness. The partitions within the unit were of 6-mm-thick Plexiglas sheet. Fig. 7 shows the elevation and the plan views of the constructed unit. The whole unit was braced using 2 inch iron angles. Although the outer Plexiglas shell could withstand the normal operating pressures, the bracing was necessary to protect the unit from accidental increase in the air supply pressure beyond the normal operating design pressure or stresses during transportation. As seen in the figure, the air could be supplied from the compressor through an air hose connected to the piping within the unit with a "quick-release" connection. The air delivery pipe network within the unit was made of 20 mm PVC pipes terminating with diffusers which were normally used for water sprinklers in lawn irrigation system or water fountains. A single sprinkler head was provided for each 20 × 20 cm compartment.

As shown in Fig. 7, the baffles were set to a height of 74 cm, allowing 1 cm of water head above the weirs. The volume of the first five individual cells was approximately 30 L each and that of the last one was 60 L, with a total approximate volume of the water in the unit equal to 210 L. However, initially, only the first five compartments (150 L) were involved in the gas stripping process. The original design allowed the use of the last 40 cm compartment (60 L) for the activated carbon.

The top view of Fig. 7 shows seven 20 mm holes. These holes were used for exhaust air (four holes), sampling, introduction of pH meter probe, and acid addition (if needed). The exhaust air ports were fitted with short (10 cm) pipe stems. The short stems were connected to the clear plastic hoses from the main unit leading to the hydrogen sulfide dissolving tank (dimensions at 40 cm × 30 in × 10 cm). The exhaust hoses of 25 mm diameter are connected to the dissolving tank through three 40–cm-long pipes fitted with diffusers and immersed in alkaline solution to dissolve the stripped hydrogen sulfide gas. The influent flow cell was the standard 13 L flow cell in use. However, in future field tests, a special tank that can act as a flow cell and flow rate controlling device may be built since maintaining the flow rate in the field was the biggest hurdle in the test operation.

The last unit of the removal system was the orifice meter which measured and logged the flow

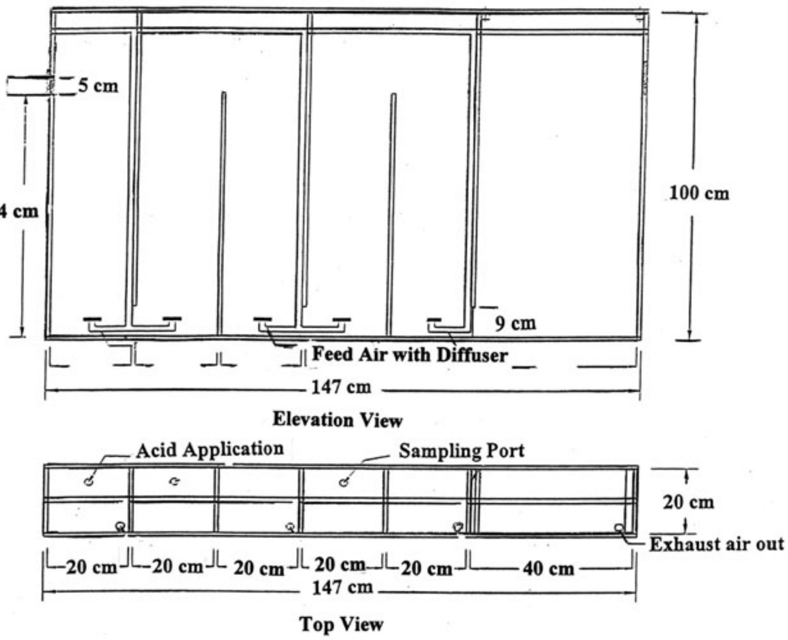


Fig. 7. Schematic diagram of the hydrogen sulfide treatment unit for field experiment.

rate through the treatment unit. The unit was made from a 160 mm diameter pipe section. The wall thickness of the pipe was 12 mm, which allowed threading and screwing on it a 200 mm aluminum cap. The cap accommodated a 100 mm orifice plate, which could be screwed into the 200 mm cap and could be replaced when a different sized orifice plate was needed. A 20 mm orifice plate was used, which was capable of measuring flow rates between 10 and 30 L/min. The unit was fitted with a 7 mm glass tube mounted on a scale for direct reading of the water level and the equivalent flow rate for the 20 mm orifice. A transducer was also attached on the opposite side to continuously read and log the reading of the water flow rate for later computation of the total volume treated.

2.4. Experimental results

The experimental results for the three scales of tests were used in evaluating the relative efficiency of hydrogen sulfide removal for each technique used. The percent removal (R%), although a meaningful parameter for a particular test, is in a way misleading to be used to compare different techniques, as the removal percentage is a function of initial concentration, pH, and salinity of sour water to be tested which were varying among all experiments. For the purpose of comparing treatment technologies, the ratio of removed sulfide ion mass per mass of treatment media was used in this study.

2.5. Activated carbon

2.5.1. Results of laboratory batch experiments

The results of the two activated carbon column experiments, presented in Tables 1 and 2, indicated that the activated carbon was highly effective in removing sulfide from saline groundwater with efficiency in the range of 9–11 mg of sulfide ion (10–12 mg/L hydrogen sulfide) removed per gram of activated carbon in the column. Table 1 presents the results of the first experiment for an application rate of 0.8 mL/min per one gram of carbon (mL/min/g), while Table 2 shows the results from an application rate of approximately 0.4 mL/min/g (the second experiment), which represented half of the application rate on the onsite activated carbon column at Mishref site. The amount of sulfide which was completely removed from the groundwater before any measurable sulfide concentration could be observed in the effluent in the first experiment (application rate of 0.8 mL/min per one gram of carbon) was 137 mg sulfide, while in the second experiment (application rate of 0.4 mL/min per one gram of carbon) it was 127 mg for the same condition. Considering the accuracy of concentration measurement, the result indicated that doubling of the application rate had no significant

Table 1
Activated carbon column performance in removing sulfide: high application rate (approx. 20 mL/min)

Sample no.	Time interval (min)	Incremental volume (mL)	Total volume treated (mL)	Effluent sulfide (mg/L)	*R* (%)	Comments
0	0	0	0	140		Initial concentration Experiment started at 10:50 am
1	20	260	100	–		Sulfide not measured
2	20	100	360	0	100	pH = 8.59
3	13	260	620	–		Sulfide not measured
4	13	100	720	0	100	
5	20	260	980	–		Sulfide not measured
6	20	100	1,080	2	99	pH = 8.58
7	20	260	1,340	–		Sulfide not measured
8	20	100	1,440	6	96	pH = 7.84
9	20	260	1,700	–		Sulfide not measured
10	20	100	1,800	12	91	pH = 7.81

Table 2
Activated carbon column performance in removing sulfide: low application rate (approx. 10 mL/min)

Sample no.	Time interval (min)	Incremental volume (mL)	Total volume treated (mL)	Effluent sulfide (mg/L)	*R* (%)	Comments
0	0	0	0	94		Initial concentration Experiment started at 10:15 am
1	10	100	100	0	100	
2	10	100	200	0	100	
3	10	100	300	0	100	
4	10	50	350	0	100	
5	10	505	855	0	100	
6	10	500	1,355	0	100	Experiment stopped at 2:00 pm. Column was left submerged in treated groundwater
7	10	100	1,455	2	98	Experiment resumed 9:30 am
9	10	100	1955	4	96	
10	10	100	2055	4	96	
11	10	100	2,155	4	96	
12	10	100	2,255	0	100	
13	10	100	2,355	2	98	
14	10	100	2,455	4	96	
15	10	100	2,555	6	94	
16	6	100	2,655	6	94	Change in flow rate
17	6	100	2,755	6	94	
18	6	100	2,855	6	94	
19	6	100	2,955	6	94	
20	6	100	3,055	6	94	
21	6	100	3,155	6	94	
22	6	100	3,255	8	91	

effect on the removal efficiency before a measurable concentration can be observed in the effluent. However, less total sulfide removal took place in the first experiment compared to that observed during the second experiment, considering that the higher application rate removed sulfide at the rate of 9 mg of sulfide/g of activated carbon (9 mg-S/g-C) compared to 12 mg-S/g-C for the lower rate. At the breakthrough, the removal rate for both experiments was 8 mg-S/g-C.

In an effort to investigate the mechanism of removal by activated carbon, the sulfide-saturated activated carbon was washed using 177 mL of distilled water, further purified from all ionic forms by passing it through an ultra-filtration media (hence the name ultra-pure water). In the second step, 100 mL of the ultra-pure water was heated to about 100˚C and used to wash the carbon column. In a third test, 100 mL of the ultra-pure water was saturated with 5% NaCl, and then was used to wash the saturated carbon column, which contained approximately 298 mg of S. The outflow, in all cases, was tested for the presence of sulfide ion.

Table 3
Carbon column experiments

Sulfide mass (mg)	*R* (%)	Sulfide mass (mg)	*R* (%)
55	100	8,268	100
275.5	100	9994.8	100
551.2	100	9921.6	100
1102.4	100	10748.4	100
1653.6	100	11850.8	92.7
2204.8	100	12622.4	91.7
2,756	100	12850.8	89.1
3307.2	100	13008.3	81.9
3858.4	100	13201.2	78.2
4409.6	100	13394.2	70.9
4960.8	100	42993.6	25.6
5,512	100		
6063.2	100		
7441.2	100		

The results from washing the spent activated carbon indicated that there was less than 1 mg S recovered from the 298 mg S removed from the treated groundwater and adsorbed to the activated carbon (approximately 0.3%). The insignificant amount of sulfide released from the carbon indicated that the sulfide was not physically removed by adsorption or absorption. A possible interpretation of the removal is that some chemical reaction has taken place between the sulfide and other ions or compounds present, or with the activated carbon itself. Possibility of conversion of some of the removed sulfur compounds to elemental sulfur in the activated carbon column that is not soluble and not amenable to removal by washing should also be considered. Further research is needed to identify the mechanism of removal, and possibly the development of a technique for regenerating the spent carbon.

Based on the above results, it was concluded that the spent activated carbon could not be regenerated, or at best it was difficult to regenerate, and the process was not economically feasible for the limited discontinuous operation of removal of sulfide ion from pumped groundwater at dewatering sites.

2.5.2. Results of carbon column experiments at the Mishref site

These results are summarized in Table 3 and Fig. 8. The column designated as mass (mg) in Table 3 is the cumulative mass removed by the treatment unit after a period of time since the start of the experiment. The mass removed in specific time interval was computed as follows:

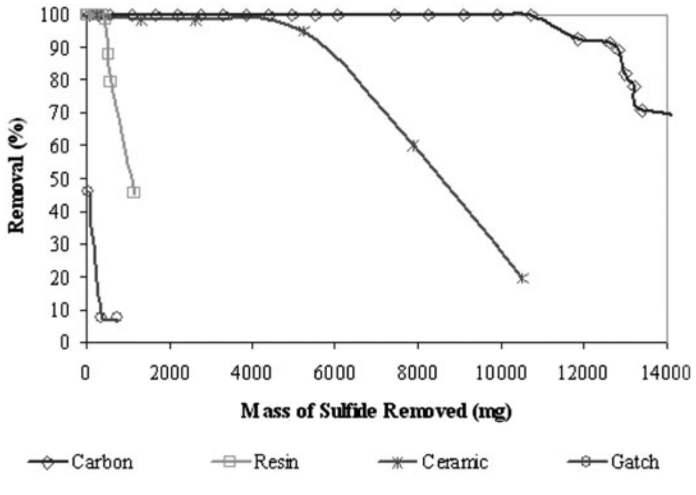


Fig. 8. Removal rate and mass of hydrogen sulfide removed using several different hydrogen sulfide column units at Mishref.

$$\text{Mass removed} = \text{Time} \times \text{Flow rate} \times (\text{Influent concentration} - \text{Effluent concentration})$$

The R% in Table 3 presents the removal percentage of sulfide mass with respect to the influent sulfide mass to the column and is expressed as follows:

$$R\% = 100 \times \text{Mass removed}/(\text{Time} \times \text{Flow rate} \times \text{Influent concentration})$$

The onsite activated carbon column used an application rate similar to the second batch experiment (0.4 mL/min/g) that resulted in similar removal efficiency (9.6 mg-S/g-C).

2.6. Ion-exchange resin

The resin column was prepared in the same way as that for activated carbon. In the laboratory, spiked deionized water was used instead of groundwater to assess the ability of the resin to remove the sulfide ion without competition from other ionic forms in the saline groundwater. The application rate was on an average 0.8 mL/min/g of resin. The amount of sulfide that was completely removed from the applied water before the breakthrough was 277 mg, giving the removal capacity of the resin column as 11 mg of S/g of resin when no competing ions were present in the treated water.

2.7. Oxidation by chlorination

Chlorine is known to be a strong oxidant and has been used extensively in the treatment of hydrogen sulfide by the MPW. In the Mishref site, hydrogen sulfide was removed by chlorine oxidation and the pH was adjusted by sodium hydroxide solution.

The objective of the experiment was to establish the appropriate chlorine dose and the contact time needed to remove the sulfide ions by oxidation. In the laboratory setup, no adjustment of the pH was necessary since the addition of sodium sulfide tended to increase the pH to the appropriate range, given that the ionization of sodium sulfide took place according to the following reaction:

$$Na_2S + H_2O \rightarrow 2Na^+ + OH^- + HS^-$$

Bleach solution (sodium hypochlorite, NaOCl) was used to provide the source of free chlorine. The manufacturer label indicated 5.25% NaOCl, which was equivalent to approximately 25 g-Cl/L; however, laboratory confirmation shows the concentration to be 18 g-Cl/L. Aliquots of sodium hypochlorite solution in the range 1–30 mL (18–540 mg Cl/L) were added to one liter bottles containing 1,000 mL of spiked groundwater of 136 mg-S/L (145 mg/L hydrogen sulfide). The test was done in two batches to determine the appropriate chlorine dose. The first used aliquots of volumes 1, 5, 10, 15, 20, 25, and 30 mL and the second batch used aliquots of volumes of 20, 21, 22, 23, and 24 mL. The contact time was set to 20 min. The results of these experiments are presented in Table 4.

Table 4
Chlorination batch tests to determine chlorine dose

Volume of NaOCl added	Residual (Cl) (mg/L)	pH	EC (ms/cm)	DO (mg/L)	Eh (mv)	Residual sulfide (mg/L)	R (%)
1 mL	0	9.7	42.2	0.22	−323	124	
5 mL	0	9.82	42.8	0.17	−325	104	24
10 mL	0	9.93	43.2	0.14	−326	80	41
15 mL	0	9.82	43.9	0.16	−315	40	71
20 mL	0	9.84	44.1	0.1	−311	10	93
20 mL (dub)	0	9.72	45.3	0.19	−202	10	93
21 mL	0	10.22	44.8	0.21	−225	6	96
22 mL	0	10.34	45.2	0.48	7	0	100
23 mL	0.75	10.23	45.3	0.46	127	0	100
24 mL	2	10.21	44.7	0.49	322	0	100
25 mL	4	10.2	44.9	0.35	584	0	100
30 mL	>10	2.6	46.6	0.41	1,112	0	100

A typical contact time in disinfection process for water supply is 20 min. Consequently, for the first round of tests to determine the chlorine dose, 20 min of contact time was used. However, the contact time needed to accomplish the complete oxidation was investigated in the second round of tests. As expected, the results confirmed that the chemical reaction between the hypochlorous ions and the monohydrogen sulfide ions was almost instantaneous and contact time of 0.5 min or less was appropriate, provided that complete mixing was achieved in the reactive vessel.

2.8. Gas stripping and oxidation by aeration

2.8.1. Laboratory batch tests

Initial tests with aeration were not conclusive with regard to the mechanism of removal, as it was not possible to determine whether volatilization or oxidation of the hydrogen sulfide gas was more dominant. To further investigate the removal mechanism, spiked deionized water with high sulfide concentration of 576 mg-S/L (612 mg/L hydrogen sulfide) was poured into a flexi-glass tank of capacity of 14 L. The tank was provided with ports for fitting ion-selective probes. These ports were used to introduce six delivery lines for air and were fitted with stone diffusers. Two probes were used to monitor DO and pH together with temperature sensor. Samples of 100 mL volume were withdrawn at fixed time intervals for the analysis of sulfide concentration.

The sulfide concentration did fluctuate throughout the experiment around the initial concentration despite the high DO concentration, which indicated that the aeration had no significant impact on the high concentration of sulfide when the pH was kept around 9. The experiment results support the conclusion that both oxidation and volatilization are not effective in this range of pH [8]. To confirm that volatilization was the responsible mechanism when the pH was dropped below 7, a small volume of 6 N hydrochloric acid was added while monitoring the pH and the hydrogen sulfide gas concentration in the air. The alarm of the gas detector was set off as the measured hydrogen sulfide was greater than the threshold concentration of the gas detector. Sodium hydroxide was added immediately to raise the pH and stop the volatilization of the hydrogen sulfide gas.

2.8.2. Aeration tests at the Mishref site

Limited aeration tests were carried out at the Mishref site when the initial sulfide concentration was lower than 13 mg-S/L (14 mg/L hydrogen sulfide), which was the detection limit of the sulfide concentration measurement by the colorimetric disc. The results of these experiments indicated that the aeration was very effective in the removal of hydrogen sulfide when the pH was around 6.8. Further confirmation of the sulfide concentration revealed that these tests were conducted to groundwater with 6 mg/L of hydrogen sulfide. The results indicated that complete oxidation of the hydrogen sulfide for a volume of 165 L of sour groundwater took place in less than 2 min. Also aeration batch tests were carried out using two air pumps with spiked groundwater containing a sulfide concentration of 130 mg/L (138 mg/L hydrogen sulfide). The results of the aeration tests showed that treating 13.1 L of groundwater containing 130 mg/L sulfide required 85 min for a removal of 75% without adjustment to the pH, which was raised to about 9 due to the addition of sodium sulfide. It was concluded that the aeration technique would be more effective if it was tested in the original environment of the groundwater, i.e. high hydrogen sulfide and low pH.

2.8.3. Field tests of aeration technique

Because of time and budget limitations, only two field tests were carried out at two well sites. Both tests were made on groundwater with high hydrogen sulfide concentration of around 230 mg/L.

The first well was a 100-m-deep well completed in the Dammam Formation and hydrogen sulfide concentration in the groundwater was found to be in the range of 200–230 mg/L. This was significantly higher than the preset design concentration of 160 mg/L. Nevertheless, the test was carried out after adding an auxiliary 100 L compressor, which was rented from the local market for the day of the test.

The unit shown in Fig. 6(a) was first allowed to fill up with the filtered sour groundwater at pH 6.28. Keeping the activated carbon from floating and overspilling in the presence of air bubbling presented a major challenge in the first test. Another drawback was the inability to throttle and control the groundwater flow rate from the pump, where the minimum attainable flow rate from the pump and the controller was between 16 and 22 L/min. Although the airflow rate to sour water flow rate ratio was very high in the laboratory (22:1), the field tests were started with a small 24 L compressor (1.5 Hp) for low hydrogen sulfide concentrations. In the later tests, a 100 L compressor was acquired. The small compressor was fitted with an air flow manometer that measured air flow rates up to 16 L/min.

Effluent was free from sulfide ion for the first 30 min of the experiment. Subsequently, the effluent concentration increased gradually to peak at 100 mg/L at which point, the auxiliary compressor was started after adding more air diffuser stones which were air supplied from the small 24 L compressor. The breakthrough of sulfide concentration indicated that the activated carbon adsorption capacity was exhausted. Due to all the surcharges on the system, the effluent sulfide concentration was about 70 mg/L (74 mg/L hydrogen sulfide), which was equivalent to a removal rate of about 70%.

It was decided to test the efficiency of the aeration system alone without the last treatment step with activated carbon or chlorination. Consequently, the last compartment of the unit was emptied from the activated carbon and more diffuser stones were added in that 60l compartment. The modified unit was moved to another nearby well and the second test was run on the same day. The influent sour groundwater had almost the same chemical characteristics as that from the previous well. As can be seen in Fig. 7(b), the unit was provided with extra three 10 L plastic bottles to dissolve the evolving hydrogen sulfide beside the small side tank. This addition of more gas-dissolving capacity with extra outlets reduced the pressure within the treatment unit and allowed more air to be supplied to the sour groundwater. However, the full capacity of the compressor to provide more air was reached far below the target ratio of air flow rate to sour groundwater flow rate of 22.

The second test confirmed the results of the first test with respect to the removal efficiency of about 70%. To test the effect of pH control, concentrated hydrochloric acid (HCl) was added to the first compartment of the unit to drop the pH. The effluent sulfide concentration decreased to about 28 mg/L, which was close to the sulfide residual concentration attained in the laboratory experiments. Hence, it was concluded that some benefits could be reaped from controlling the pH ([9–11]).

2.9. *Sand filter media column*

It was observed in many pilot studies and experiments that the multi-media sand filtration by itself is responsible for removing a significant amount of the sulfide concentration, when the total sulfide concentration is low. In an effort to investigate the extent of sulfide removal by filtration media, different sand filter columns were prepared in 10 mm diameter burette; spiked groundwater was allowed to pass through them, and the hydrogen sulfide concentration in the effluent were measured. The compositions of the different columns were as follows:

Column 1: Multi-media filter column, 50 g each from fine sand, coarse sand, and small gravels.
Column 2: Multi-media filter column, 25 g each from fine sand, coarse sand, and small gravel and 12.5 g of anthracite.
Column 3: Gravel packed to height of 30 cm.
Column 4: Fine sand packed to height of 30 cm.
Column 5: Coarse sand packed to height of 30 cm.

The results indicated that the multi-media filter removed only small quantities of the sulfide ion. It is believed that the mechanism responsible for the removal is the mechanical filtration of residual suspended sulfide compounds. This is confirmed further by noting that the finer the filter media, the better is the ability of removal. The effluent concentration also remained somewhat at steady value which represented the completely dissolved sulfide ions. The presence of anthracite enhanced the removal ability of the multi-media filter, since anthracite can absorb some dissolved matters. Nevertheless, filtration can be used as pretreatment unit for the removal of hydrogen sulfide from water.

2.10. *H_2S Scavenger (Sulfamin 3001)*

A set of batch reactors was set up to test the claimed potency of a chemical with trade name H_2S Scavenger and brand name SULFAMIN 3001 in removing the sulfide ion from saline groundwater. The groundwater was spiked with sodium sulfide up to the concentration of 140 mg/L (149 mg/L hydrogen sulfide) for the purpose of the test.

The results showed that the dose of the Scavenger had no effect on the concentration of residual sulfide ion in the water. It was observed, however, that adding the Scavenger to deionized water tended to increase the pH up to the range where all the hydrogen sulfide would be in the ionized form (HS^-). This could be the mechanism by which hydrogen sulfide was arrested in solution to purify the stream of gasses passing through it. Nevertheless, the Scavenger was not suitable for the application under consideration in this research, i.e. removing sulfide ion from saline groundwater.

2.11. *Aerobic biological treatment*

It has been suggested [12] that some facultative or aerobic bacteria in wastewater sewers are responsible for oxidizing the mono-hydrogen sulfide ions to thiosulphate and water, as demonstrated by the following reaction equation as follows:

$$2\mathrm{HS}^- + 2\mathrm{O}_2 \rightarrow S_2\mathrm{O}_3^{2-} + \mathrm{H}_2\mathrm{O}$$

It was further suggested that oxidation of aqueous hydrogen sulfide gas to sulfur and water can also be accomplished by bacteria in sewers, as demonstrated by the following reaction equation [12]:

$$\mathrm{H}_2\mathrm{S}_{(\mathrm{aq})} + 1/2\mathrm{O}_2 \ \rightarrow \ S_2\mathrm{O}_3^{2-} + \mathrm{H}_2\mathrm{O}$$

Consequently, batch experiments were set up to test the above hypothesis using spiked groundwater with different amounts of carbon source and bacterial seeding. The carbon source used was glucose ($C_6H_{12}O_6$) solution with a BOD_5 of 80 mg/L, i.e. 0.8 g BOD_5/g of glucose (80% of the theoretical ultimate biological oxygen demand, BOD_u). The bacteria seedings were extracted from mixed liquor suspended solids (MLSS) from one of the wastewater treatment plants. Five sets of bottles were tested for contact times of 10, 20, 40, and 60 min. The pH of the liquid content of all the bottles was adjusted to 7.5, except the first set of bottles that had a pH of 9.5. The initial DO concentration was 7.5 mg/L. The bottles in all sets were left open and were agitated at 300 rpm on the shaker for the length of the stated contact time. In each set, except for the first, two control bottles were included to monitor the reduction of hydrogen sulfide due to volatilization or other mechanisms. The control bottles included neither seeding (MLSS) nor glucose. The initial set included extra two bottles to test whether the addition of glucose by itself has any effect on the results. The seeding (MLSS) was acclimated to the spiked groundwater (170 mg S/L, approximately 181 mg/L hydrogen sulfide) environment by adding the MLSS in 13 L of continuously aerated groundwater for over 48 h with 20 g of glucose. To test the viability of the microorganisms, bottle number 4 from the second set was tested for residual BOD_5. The measured residual BOD_5 was 77 mg/L, which confirmed the viability of the microorganisms.

The results showed that the tested microorganisms from the MLSS did not contribute to the significant reduction of the sulfide ion in the groundwater. It is possible that the type of the micro-organisms, which are typically present in MLSS of activated sludge, are not suitable for removing (oxidizing) the sulfide ions. More investigations are called for the culture and growth of the type of facultative bacteria that will be effective in oxidizing the hydrogen sulfide. Colonies of these bacteria can be collected from wastewater sewers.

2.12. Electrolysis

Over 50% of hydrogen sulfide will be present in ionized form in pH ranges above 7, and significant ionization is present below a pH value of 7 [12]. It is, therefore, prudent to consider electrolysis as an effective technique in removing hydrogen sulfide ([13,14]). Although electrolysis has recently been suggested for desalination by ion-selective membrane, there is hardly any reported work in the removal of hydrogen sulfide by electrolysis. The technique is based on the principle that sulfide ions can be combined with most metals and precipitated, since metal sulfides are insoluble or their solubility is low. Some of the many parameters that affect the electrolysis are as follows:

(1) Current intensity and voltage across the probes.
(2) Salinity of the groundwater and the ionic strength of the solution.
(3) Constituents of the groundwater.
(4) Length of the probes immersed in solution.
(5) Type of metal or alloy used for the anode and the cathode.
(6) Duration of current application.
(7) Initial concentration of sulfide ions.

It was the purpose of this research to identify the most effective parameters that would influence the removal of hydrogen sulfide. Several laboratory experiment runs were made for this purpose. Fig. 9 presents the sulfide removal efficiency of the experiments vs. applied power measured in ampere-volts. The removal efficiency varied in the range of 50–96%. The results were very encouraging. More research is, however, needed to minimize the prob-

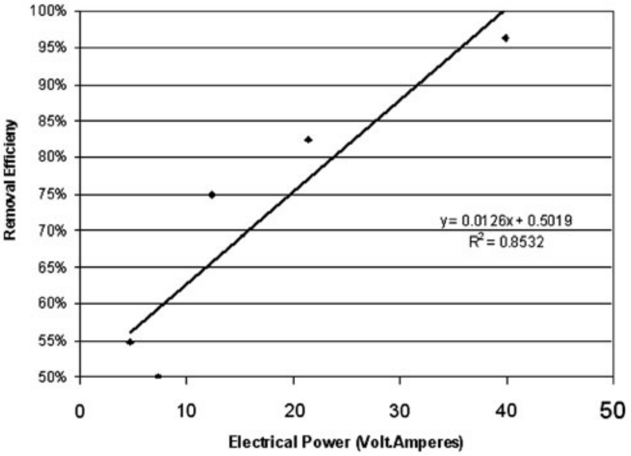


Fig. 9. Removal efficiency vs. electrical energy consumption for electrolysis method.

lem of the black residue that were formed during the experiment, and that could be copper/iron sulfate.

2.13. Ceramic

The GranSpec Company designed and installed two acrylic pipe columns (5.25 inch/57.2 mm in diameter and 0.9 m high) filled with 1 kg of acid-washed carbon-impregnated ceramic material manufactured by the company at the Mishref site for the treatment test. The results of the sulfide mass removal are shown in Fig. 8.

2.14. Gatch

The gatch columns were prepared from the crushed greenish-grey calcareous silty sand layers encountered during excavation of the pit at MNSPS. The breakthrough time of hydrogen sulfide in the groundwater at the outlet point of the gatch column was short (i.e. less than 10 min) compared to that of activated carbon column (i.e. more than l80 min.). The results of sulfide mass removed are shown in Fig. 8.

2.15. Comparison of the tested technologies

The analysis of the column results revealed that the hydrogen sulfide removal efficiency by activated carbon was better than other treatment technologies (Fig. 9). The breakthrough time of hydrogen sulfide in the treated groundwater at the outlet point of the gatch, resin, and ceramic columns was short (i.e. less than 10 min), compared to that of activated carbon column (i.e. more than l80 min) for a groundwater flow rate of 30 L/h and sulfide concentration of 110 mg/L (117 mg/L hydrogen sulfide).

2.15.1. Practical and economic feasibility of treatment techniques

Table 5 shows comparison among the removal techniques tested in the study. Electrolysis technique was excluded for this comparison since it was not possible to investigate the removal of the black residue byproduct. The removal efficiency which has units of milligram (mg) of sulfides removed per gram of the chemical, or the media used to extract the sulfide ion, was calculated by dividing an average mass in mg of hydrogen sulfide removed (= sulfide concentration difference between influent and effluent × flowrate × time) by the used weight of the material to treat it. Clearly, the higher the removal efficiency, the more effective and more feasible would be the use of the particular substance to treat sour groundwater. Chlorination mass of 0.414 g was based on the batch experiments, where 23 mL of nominal 5.25% (actually 18 g-Cl/L) sodium hypochlorite was required to treat 1 L of groundwater with hydrogen sulfide concentration of 136 mg/L (128 mg/L sulfide). Although the material used was liquid bleach, the table shows weight in grams for chlorine. It would be easy to convert it back to volume of liquid bleach if weight is divided by the appropriate concentration. The weight of air used in the aeration was calculated using an approximate warm air density of 1 g/L.

Based on the removal efficiency, chlorination seems to be the best treatment technology, followed by activated carbon and aeration. The practical feasibility of the implementation of the technique was evaluated further by considering a hypothetical case of dewatering, where sour groundwater with sulfide concentration of 160 mg/L (170 mg/L hydrogen sulfide) was being pumped at the rate of 10,000 m^3/d. It was not practical to use chlorination alone, although it was the most efficient technique for the removal of hydrogen sulfide. Chlorine of 4.9 tons required for the treatment (Table 5) was equivalent to 272 m^3 of liquid bleach at concentration of 18 g/L. This is equal to approximately 12 truck loads (with a capacity of 5,000 gal each) of chlorine each day. Similar conclusion was reached about the activated carbon because of the large quantity involved (Table 5). Further consideration of cost of treatment materials, based on running cost only (i.e. no capital cost), revealed that aeration is the best technology for the removal of hydrogen sulfide from the pumped groundwater. The field results suggested that with the present setup about 75% removal of hydrogen sulfide can be achieved with aeration. The augmentation of the system with chlorination or activated carbon units to polish the effluent from the aeration unit will be required to improve the removal efficiency.

In some parts of the world, as in Qatar, hydrogen sulfide-rich groundwater produced during dewatering is reinjected back in the aquifer through a closed loop. In some cases, removal of sediments from the water produced is necessary to avoid clogging during reinjection. Though the concept is simple and apparently less costly than the elaborate treatment for the removal of hydrogen sulfide, at least in case of Kuwait, such reinjection in the urban areas may not be possible due to the problem of rising groundwater table due to recharge from water distribution and sewage networks and irrigation in private gardens and public parks [15]. The transport of the discharged water at a suitable location for injection away from the urban areas will involve the construction of a

Table 5
Comparison of hydrogen sulfide removal techniques

Description	Unit	Activated carbon	Ceramic	Resin	Gatch	Chlorination	Aeration
Weight of material used	g	1,250	2000	2,500	4,750	0.414	11
Mass of sulfide removed at 99% removal efficiency	mg	10,900	920	442	30	136	68
Removal efficiency	mg/g	8.72	0.46	0.177	0.006	328.5	6.2
Required treatment materials to treat 10,000 m^3 of groundwater @160 mgS/L	tons	183	3,478	9,040	266,667	4.9	259
Cost of material per g[a]	USD/g	0.008	0.010	0.011	6E-6	0.021	1E-6
Removal cost of 10,000 m^3@160mgS/L	USD	1,520,733	37,965,219	100,338,983	1,480,000	100,118	407

Note: [a]The cost per gram of material was computed as follows: (1) Activated carbon: USD $104 per bag of 12.5 kg. (2) Resins: USD $555 per bag of 50 kg. (3) Ceramics: USD $11 per kg. (4) Gatch: USD $44 per truck load of 8 tons. (5) Chlorination: Although liquid bleach can be bought from local market at about USD $0.45/l, it was assumed that for bulk quantities, it could be purchased for USD $0.37/l at a concentration of 18 g-Cl/l. (6) Aeration: is based on electrical energy consumption of 1 HP (0.7457 Kilowatt) air blower that can provide 35 m^3/h at electrical energy cost of USD $0.07/kWh.

pipeline and an injection system that is to be protected from corrosion by hydrogen sulfide and from the cost point of view, counterproductive.

3. Conclusions

Experiments were carried out to test different hydrogen sulfide treatment technologies in the laboratory at the construction site for a new sewage pumping station and at dewatering wells drilled in Kuwait City. The treatment techniques tested included treatment using gatch (calcretized sand), resin, ceramic, activated carbon adsorption, chlorination, bacterial oxidation (i.e. biological treatment), sand filter, electrodialysis, and aeration. The treatment experiments indicated that chlorination had achieved the best removal rate among all treatment technologies tested, followed by aeration and activated carbon treatment.

The overall conclusions may be summarized as follows:

- The experiments with the aeration techniques indicated that significant (60–70%) reduction of hydrogen sulfide concentrations from sour groundwater can be attained with this technique with low running cost and capital expenses.
- The cost for running such a system for a typical dewatering site which pumps around 10,000 m^3/d will be less than USD 0.75 per day.
- To reduce energy consumption by the compressors and capital cost for air supply equipment, two alternatives can be tested and used in the future. These are as follows:

  (a) Air injectors which can provide about 45 m^3 of air per kilowatt-hour.
  (b) Air jets for which a self-contained system can be designed with only re-circulating pumps and no extra air compressors or air injectors.

- Chlorination should be used as an alternative polishing treatment technique for complete removal of the remaining sulfide ion from the effluent of the aeration system (about 25 mg/L, approximately 27 mg/L hydrogen sulfide). Also, the pH adjustment of the groundwater enhanced the removal of hydrogen sulfide while conducting aeration experiments.
- A series of sand filters should be used to remove the suspended solids and to reduce the concentration level of hydrogen sulfide from the pumped groundwater before using any treatment technology for removal of the gas.
- The recommended hydrogen sulfide treatment facility for the study area should consist of the following units: sand filters, chlorination, and aeration as the main processes for the removal of hydrogen sulfide, followed by activated carbon adsorption as a polishing process, depending on the concentration of the gas and the rate of groundwater pumping.
- All the four parts of the removal units should be truck mounted, and the system in this compact form can be transportable between dewatering sites.

- Well chlorination as a treatment technology for low hydrogen sulfide concentration should be introduced in Kuwait for treating hydrogen sulfide-contaminated fresh or brackish groundwater.

It may be emphasized here that no significant discharge of hydrogen sulfide, either to the atmosphere or to the stormwater network, should be allowed to maintain the integrity of the environment. In case the treatment system fails, the discharge of sulfide-rich groundwater should be stopped immediately.

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