Journal of Water Process Engineering 55 (2023) 104217

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

In situ stannous reagent generator (SRG): An alternative hexavalent chromium treatment technology in drinking water industry

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A R T I C L E I N F O

Keywords:
Drinking water
Ferrous ion
Hexavalent Chromium (Cr (VI))
Stannous ion

A B S T R A C T

Access to safe drinking water is a basic necessity for human health. Rock and soil are rich sources of chromium, a metal that is present naturally. Chromium commonly exists in two oxidation states: trivalent chromium (chromium-3, Cr (III), Cr^{3+}) and hexavalent chromium (chromium-6, Cr (VI), Cr^{6+}), in the natural environment, as well as in the water treatment and distribution systems. While Cr (III) is an essential nutrient for humans, Cr (VI) is a dangerous pollutant that can build up in both the environment and the tissues of living things. The Cr (VI) treatment traditionally uses techniques such as electrodialysis reversal, ion exchange, electrochemical, reduction, coagulation, oxidation and filtration systems. Chemical costs, secondary waste production, and unintentional regeneration of Cr (VI) after treatment are difficulties with standard Cr (VI) treatment. In order to remediate Cr (VI) in raw water, this study looks into the in-situ stannous reagent generator (SRG) package as a potential disruptive green technology. SRG was able to reduce roughly 40 parts per billion (ppb) of Cr (VI) to below 1.0 ppb after being installed on a raw water source site for a 10-day trial period. The In Situ SRG technology provides an efficient and safe method for treating Cr (VI) in drinking water, reduces the health risks associated with Cr (VI) exposure by converting it to a less toxic form and reduces chemical handling risks. Reductive Cr (VI) treatment technologies based on the use of stannous tin hold tremendous promise in the future to overcome green-house gas (GHG) emissions and other anthropogenic environmental change, in addition to effectively reducing Cr (VI) in drinking water to the permissible limits and high energy cost challenges. In Situ Stannous Reagent Generator (SRG) technology is designed to convert Cr (VI) to its less toxic trivalent form, Cr (III), which is less harmful and easier to remove from water.

1. Introduction

Local populations and biodiversity are seriously threatened by river pollution. Agricultural practices, land clearing, and industrial emissions, in addition to sewage disposal are additional sources of pollution [1]. One of the trace elements frequently detected in surface and groundwater is Cr (VI). It has caused public health concerns over the past 20 years, and the World Health Organization (WHO) has identified it as a human carcinogen that is spread through inhalation [2–4]. The operations of electroplating, textiles, mining, fertilizers and cement frequently produce Cr (VI) [5]. An analysis of a recent US Environmental Protection Agency (EPA) database on chromium – Unregulated Contaminant Monitoring Rule Round 3 (UCMR3) showed that Cr (VI) is prevalent in drinking water sources across the US. The Ministry of Health of Malaysia and the U.S. Federal Government appear to be in agreement that the concentration of Cr (VI) in treated drinking water should not exceed 100 μg/L. Therefore, given the risks that Cr (VI) poses to public health, establishing efficient treatment methods to lessen these hazards are essential.

The cost of traditional trace metal remediation systems is expensive, as are their startup and ongoing running expanses. An innovative remedial strategy is necessary to lower treatment costs, support stricter

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https://doi.org/10.1016/j.jwpe.2023.104217
Received 14 February 2023; Received in revised form 17 August 2023; Accepted 24 August 2023
Available online 1 September 2023

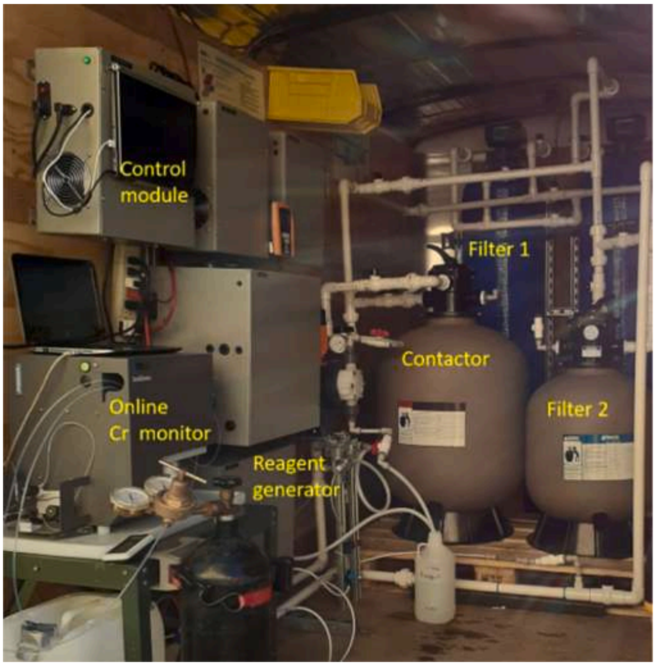

Fig. 1. Pilot SRG package assembly unit for removal of Cr (VI).

regulatory standards, and provide access to clean drinking water for everyone. The ferrous ion, Fe (III), based reduction coagulation method is one of the conventional therapy modalities that is frequently used to treat Cr (VI). This traditional approach puts the operators at risk because it necessitates having a significant amount of bulk chemicals on-site, which leads to numerous handling and safety predicaments such as corrosive, severe skin burn, eye damage and toxic to aquatic life. This results in the formation significant amounts of iron sludge waste that is difficult to manage operationally [6]. The SRG package may potentially be more effective in treating Cr (VI) in raw water, compared to the conventional chemicals and other best available technologies (BATs), such as filtration, ion exchange, and reverse osmosis [7]. Another type of chemical that can be added into raw water to convert Cr (VI) to Cr (III) is stannous chloride ($SnCl_2$) [8]. However, the solution must be preserved chemically, such as with acids, which pose operational safety risks and potential harm. Additionally, the solutions shelf life is limited by easy oxidation, necessitating frequent replacement, which drives up handling and shipping expenses.

SRG uses and electrolytic technique to produce an in-situ stannous ion reagent to address the trace metal contamination of Cr (VI) in an efficient and cost-effective manner. The integrated system includes a feature that is exclusive to this intelligent technology: an online trace metal water quality analyzer for real-time monitoring of pollutant levels to help manage and optimize the treatment process. The fully integrated, online SRG package treatment strategy helps create a cost-effective and reliable remediation process by eliminating the drawbacks of conventional systems. There are no other technologies that combine a low lifetime cost contaminant treatment system with real- time performance controls like the SRG package does. This technology's capacity to scale across big and small water systems and point-of-use systems, will provide safe drinking water free of hazardous contaminants to homes and small communities.

A full scale of SRG demonstration unit with a treatment capacity of 10 gal per minute (gpm), was installed at site for a 10-day evaluation period. The objective of the demonstration unit is to evaluate the performance of the integrated SRG package system in treating Cr (VI) to undetectable levels (under 1 parts per billion (ppb)) in unchlorinated well water. This assessment will confirm the efficacy of the technology and provide a third-party validation of the system as a practical substitute for conventional Cr (VI) treatment systems.

Fig. 2. Stannous ion generator.

2. Materials and method

2.1. Raw water source

The characteristics of the source water were found to be extremely arduous; in addition to having elevated Cr (VI) levels of 38–39 ppb, there were also the presence of uranium (U), conductivity, sulfate, and hardness, all of which can pose problems with conventional Cr (VI) remedial systems by potentially interfering with the removal of Cr (VI). A general set-up for the SRG package is shown in Fig. 1, including the galvanostat, control module, Cr (VI) online analyzer and stannous reagent generator.

2.2. Stannous ion

Stannous ions are powerful reducing agents that have been employed to eliminate numerous toxic pollutants from water, including hexavalent chromium, dissolved mercury, selenite and hydrogen sulfide [9]. The proprietary stannous ion generator is shown in Fig. 2.

Carcinogenic heavy metals are transformed by the stannous ions to less harmful and or to forms that can be easily removed. For example, stannous ion converts the insoluble and highly toxic Cr (VI) to low solubility Cr (III), which is about one-hundred times less toxic to humans. The reagent generator is a proprietary electrolytic cell that is capable of releasing stannous ions into solution on demand in response to an applied current. The controlled dissolution of the tin anode within the reagent generator results in the generation of the stannous reagent into the reagent generator electrolytes. The following reaction take place:

$$Sn^0 \rightarrow Sn^{2+} + 2e \quad (1)$$

The electrolytic stannous ions that are produced is then introduced into the main flow, where they react with Cr (VI) to reduce it to Cr (III), as demonstrated in reaction (2).

$$2CrO_4^{2-} + 3Sn^{2+} + 4H_2O \rightarrow 2Cr(OH)_3(s) + 2SnO_2(s) + 2H^+ \quad (2)$$

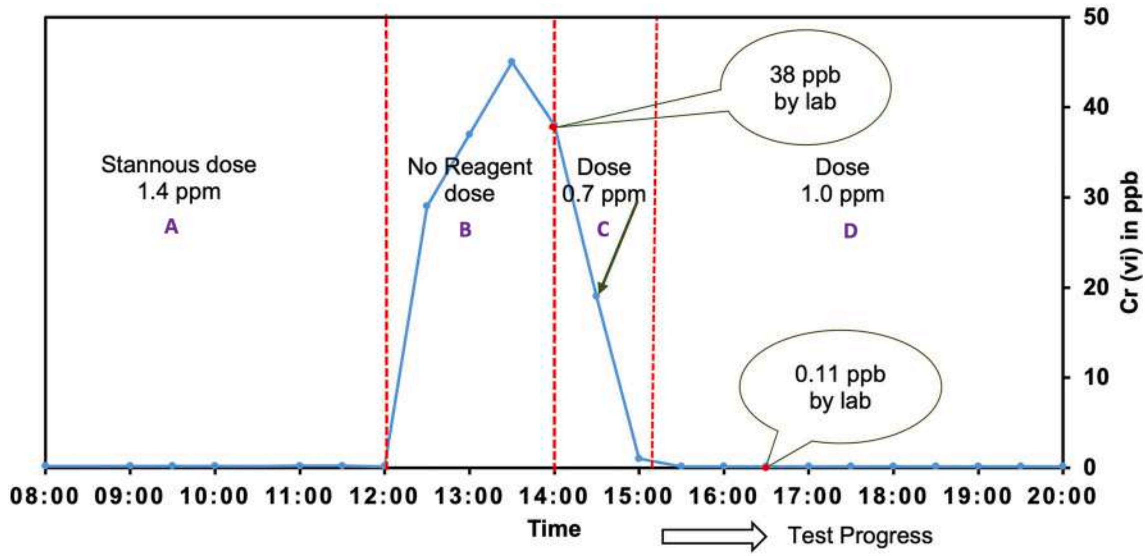

Fig. 3. Determination of the optimal stannous reagent dose.

2.3. Galvanostat

The galvanostat, which keeps the current constant no matter the load, controls and monitors the reagent generator. The system is built with an automated online Cr (VI) analyzer to monitor and offer feedback on the rate of removal of Cr (VI) and to enhance stannous ion formation. Faraday's Second Law is used to calculate the concentration of stannous ion reagent concentration;

$$C = 29 \times I/Q \tag{3}$$

Where:

C = stannous dose concentration, mg/l.
Coefficient = 29.
I = generation of current, Ampere.
Q = treated water flow rate, liter/min.

The treated water will have to pass through two sand filters after passing through a contactor vessel (5 min nominal contact time), where reduction of Cr (VI) into the Cr (III) takes place. To produce a retention time of only approximately 3 min, the contactor vessel volume may be decreased. Tin and Cr (III) particulates are further filtered from the treated water using a filter that contains sand with an effective size of 0.45–0.55 mm.

3. Results

3.1. Determination of the optimal stannous reagent dose

Fig. 3 demonstrates the online Cr (VI) values obtained from the 10 gpm SRG treatment system effluent as a function of the stannous reagent dose. Area A shows that a stannous dose of 1.4 parts per million (ppm) led to undetectable residual levels of Cr (VI) in the effluent. Cr (VI) levels

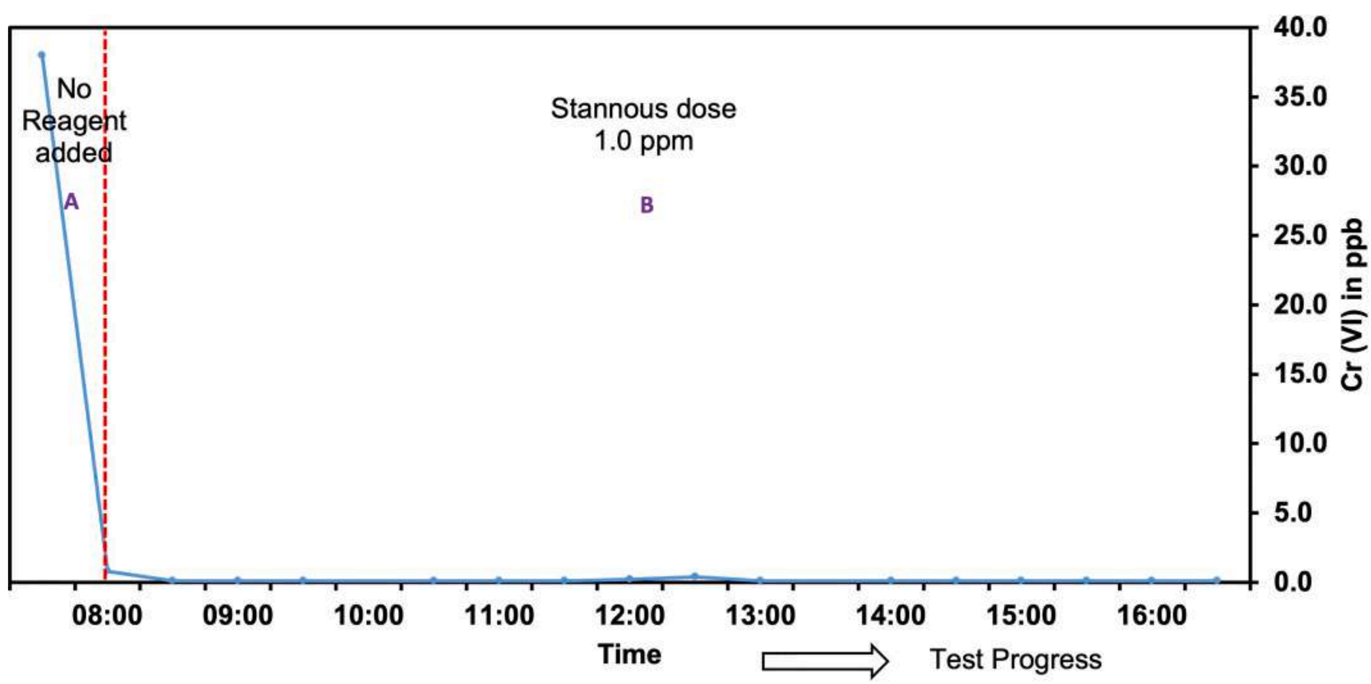

Fig. 4. Steady state treatment of Cr (VI) using stannous ions.

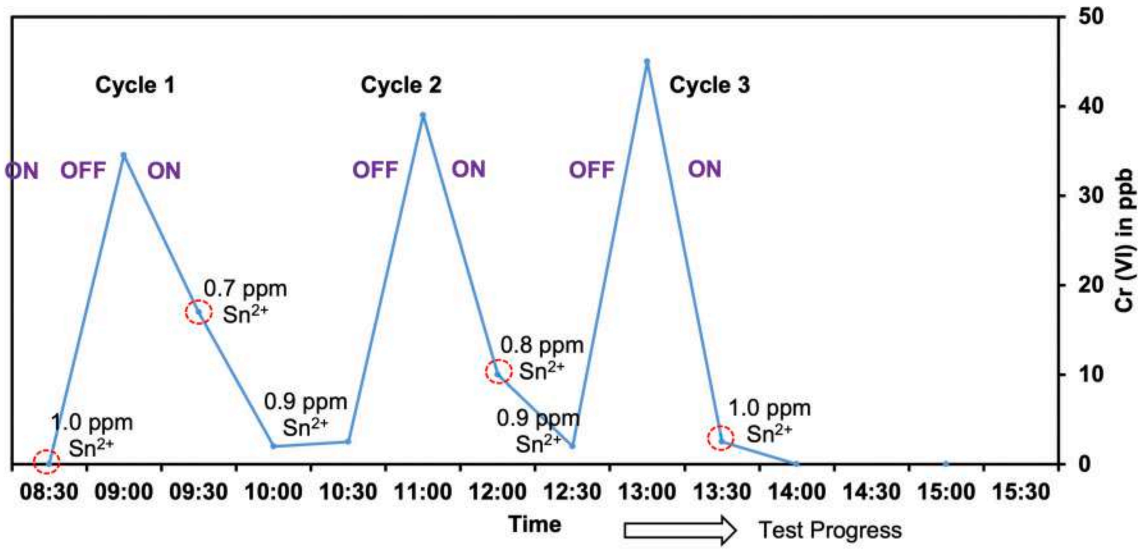

Fig. 5. SRG treatment system response under alternating reagent generation.

in the treatment system effluent showed a significant increase after reagent production into the treated water was deliberately halted, and stabilized around an influent level of 38–39 ppb at area B. The effluent Cr (VI) level in area C decreased to 18 ppb when the stannous dose was raised to 0.7 ppm. A further increase of the reagent dose to 1.0 ppm resulted in Cr (VI) levels dropping to below 1 ppb and remained stable over the following 6 h of systems operation, as shown in area D. By way of these findings, it can be seen that a stannous reagent dose of 1.4 ppm appears to be significantly higher than what is required for total elimination of Cr (VI), while a stannous reagent dose of 0.7 ppm is insufficient to achieve therapeutic objective. A stannous reagent dose of 1.0 ppm was chosen as the ideal reagent level for meeting the treatment objective of <1 ppb as it ensures nearly zero residual pollutant levels in the effluent.

3.2. Steady state Cr (VI) treatment

Fig. 4 displays the SRG treatment system's performance under constant settings. Without the addition of a stannous reagent, the Cr (VI) level in the treatment system effluent was 36 ppb, as shown in Area A of Fig. 4. The effluent Cr (VI) level rapidly dropped to below 1 ppb following the introduction of an optimal stannous reagent dose of 1.0 ppm into the water flow. As shown in Area B, the reading remained stable around undetectable readings for more than 8 h.

The demonstration was then put to the test using alternating reagent dose modes, as seen in Fig. 5. The three cycles alternating reagent modes are as follows;

Cycle 1: The treatment process began at 0800 h with stannous reagent dose of 1.0 ppm which caused the level of Cr (VI) in the effluent to be almost zero. The reagent dose was later stopped resulting in high Cr (VI) value of above 33 ppb. The reagent generator was then turned on with 0.7 ppm of stannous reagent introduced into the treated water. As a consequence, 17 ppb Cr (VI) was detected indicating insufficient treatment. The Cr (VI) reading was then decreased to 2 ppb in two consecutive readings as a result of increasing the stannous reagent to 0.9 ppm.

Cycle 2: The same procedure as Cycle 1 was carried out, with the exception this time the reagent dose was restored at 0.8 ppm, lowering the Cr (VI) reading to 10 ppb. The residual Cr (VI) value fell just below 2 ppb when the reagent dose was increased to 0.9 ppm.

Cycle 3: The addition of 1.0 ppm of the stannous ion reagent resulted in immediate stabilization of the treatment system and non-detectable effluent Cr (VI) values. This test has demonstrated low treatment system inertia, high accuracy and reliability of the in situ stannous reagent generation method, combined with fast and predictable treatment system response, improved by an accurate and timely effluent monitoring method.

Table 1
Comparative online SRG treatment results vs lab measurement under optimal conditions.

Sample	Cr (VI) ppb	
	Online SRG package	Third party lab
2/24 16:30	<1	ND
2/26 16:30	<1	0.11
2/26 14:15	<1	0.11
3/1 16:20	<1	0.12
3/2 15:10	<1	0.1
3/3 13:40	<1	ND
3/4 12:45	<1	0.07
3/4 13:00	<1	0.1

Table 2
Comparative online SRG treatment results vs lab measurement under deliberately non-optimized conditions.

Sample	Cr (VI) ppb	
	Online SRG package	Third party lab
2/25 14:30	39.4	38
3/1 11:40	35.4	32
3/1 13:05	15.9	23
3/2 11:15	2.4	3.9
3/2 12:15	10.2	10
3/2 13:05	44.1	37
3/5 11:30	8.9	8.4

3.3. Correlation between online Cr (VI) results and corresponding grab samples

Table 1 summarizes the effluent Cr (VI) findings for the SRG treatment system compared to lab tests when the system was run under optimal and steady conditions. Under steady state treatment settings, grab samples of the effluents were taken at least once a day. The samples were sent to a third-party accredited laboratory for Cr (VI) analysis. Online Cr (VI) findings in all eight comparative tests showed excellent correlation.

According to the laboratory tests, the effluent's residual Cr (VI) did

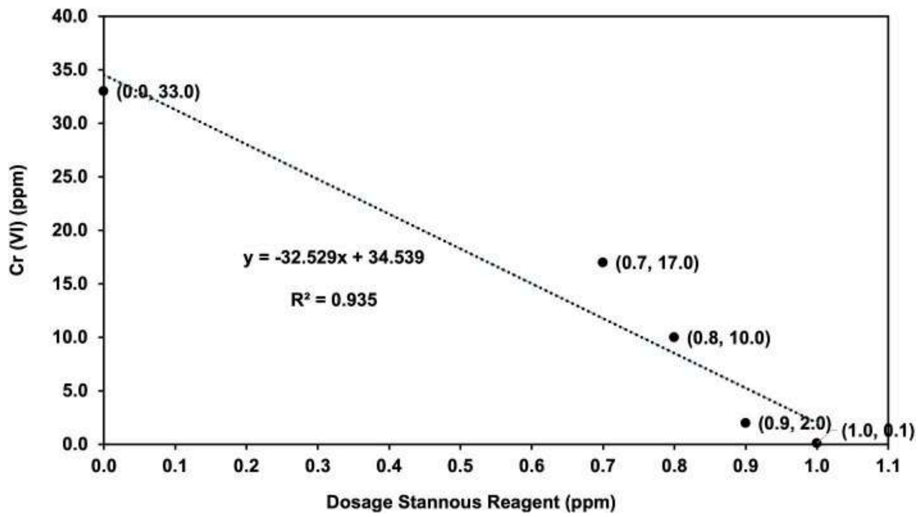

Fig. 6. A linear regression graph for Cr (VI) vs dosage of stannous ions reagent.

not exceed 1 ppb and complied with the EPA's Cr (VI) drinking water regulation [10–12].

In other instances, the stannous reagent dose was deliberately altered from its ideal value while grab samples were being acquired. Table 2 showed good correlation between online Cr (VI) and lab analysis results during the entire trial period.

4. Discussion

The SRG produces reagents on-site by the electrolytic decomposition of tin or mild steel, resulting in reagents that are non-toxic and safe to handle. By producing the necessary chemicals on-site, problems with health, safety and environment are markedly reduced, as are disruptions in the bulk chemical supply chain. The SRG treatment system has proven to operate dependably in ideal stable conditions to produce effluent with Cr (VI) levels below 1 ppb. Fig. 3 illustrates a significant decrease of 99.1 % in the concentration of Cr (VI) as the dosage of stannous ion is increased from 0.7 ppm to 1.0 ppm. As depicted in Fig. 4, the utilization of stannous reagent ions led to a prompt and consistent response in the treatment system, effectively maintaining the residual concentration of Cr (VI) below two parts per billion (ppb). Based on the previous systematic validation processes, it can be inferred that the presence of 1.0 ppm of stannous ion has the capability to eliminate roughly 99 % of Cr (VI) from the water sample. According to Fig. 5, it can be shown that the concentration of Cr (VI) increased when the administration of stannous ions was discontinued, and then decreased to a level below 2 ppb when the dosage of stannous reagent was reinstated at 0.9 ppm. The linear regression analysis depicted in Fig. 6 provides insight into the positive link between the dosage of stannous reagent and the percentage of Cr (VI) elimination.

The high accuracy and stability of the electrolytic reagent generator, the high reactivity of the in-situ fresh stannous reagents, which led to the fast conversion of Cr (VI) to Cr (III), and the high accuracy of the online Cr (VI) monitoring system all contribute to the high treatment system controllability (timely and adequate treatment system response on the reagent dose change). However, the availability of source the material i.e., tin or metal could raise some challenges.

5. Conclusion

Water systems with elevated Cr (VI) levels will benefit immediately from Sn (II)-based reductive technology, and an implementing this technology would be an affordable and simple retrofit to the existing water treatment infrastructure. This technology is anticipated to be a heavily considered candidate in the future when new Cr (VI) drinking water regulatory standards are established and used as benchmark to compare against other new technologies, even though questions regarding the stability of stannous and chromium residual products need to be better understood through more careful laboratory-scale research and pilot-scale testing. Global Warming Index (GMI) has estimated the global water and waste water consumes 6 % of all energy. The pilot trial concluded that SRG technology has potential to lower long-term operations costs, in addition to carbon footprint. Further research on pilot scale trial is needed to spur the idea of using SRG to treat other trace metal contaminants in the water such as manganese, mercury, and arsenic. Tighter regulations often stimulate the development and deployment of advanced treatment technologies designed to remove hexavalent chromium and other contaminants from water sources. This can drive technological innovation in the water treatment sector, resulting in more effective and efficient treatment methods. The In situ SRG is an innovative technology offers a more efficient and cost-effective approach compared to traditional treatment methods. The technology efficiently converts Cr (VI) to Cr (III) through a reduction reaction, effectively neutralizing its harmful effects. By generating the reducing agent on site, risks associated with transporting and storing hazardous chemicals are minimized, enhancing safety for both workers and the environment, in addition SRG technology produces only the required amount of stannous reagent, minimizing the generation of excess waste. In situ SRG technology offers a promising alternative for treating hexavalent chromium in the drinking water industry, addressing both environmental and health concerns while optimizing efficiency and cost-effectiveness.

Declaration of competing interest

The authors declare that they have no potential conflicts of interest regarding the write up or publication of this paper.

Data availability

The research data used to support the findings of this study are included within the article. The presented work is part of the pilot scale trial to treat Cr (VI) at ground water source. The authors are grateful for the data and report shared by the company (FIRAS3NERGY) and its principal.

Acknowledgement

This work was supported by the Ministry of Higher Education, Malaysia under Fundamental Research Grant Scheme FRGS/1/2021/TK0/UTM/02/86 and Universiti Teknologi Malaysia Matching Grant Scheme Q.K130000.3001.04M15.

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