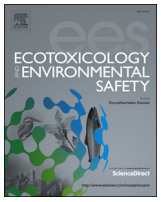
Ecotoxicology and Environmental Safety 196 (2020) 110559

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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



SPE based soil processing and aptasensor integrated detection system for rapid on site screening of arsenic contamination in soil

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ARTICLE INFO

Keywords:
SPE
Biosensor
Soil arsenic monitoring
Colorimetric detection
Smartphone

ABSTRACT

Rapid industrialization and urbanization have resulted in serious environmental deterioration, especially in terms of heavy metal contamination in soil. Arsenic is one of the primary heavy metal contaminants in the soil and possesses a severe threat to all the plants and animals including humans. The conventional methods for analyzing arsenic contamination in soil have tedious, time-consuming sample preparation steps and require laboratory equipped instruments and skilled personnel. The present work demonstrates a novel method for arsenic As(III) detection in the contaminated soil based on field applicable sample preparation and smartphone-based optical sensing. Soil sample preparation has been simplified and optimized using acid extraction and serial application of different solid phase extraction (SPE) cartridges for the removal of interfering ions with high arsenic yield in one step. The acidic extraction and SPE efficiencies were found to be 35.4% and 54.0%, respectively, for arsenic contaminated field soil samples. The quantification of As(III) was performed by aptamer-AuNPs based colorimetric assay with a smartphone coupled optical unit. This aptasensor integrated detection system (ADS) has shown a detection limit of 14.44 ppb for aqueous samples and 1.97 ppm for field soil samples. In the accuracy comparison with ICP-MS, arsenic contaminated field soils from various sources have been tested and the results depicted a highly significant correlation coefficient of 0.997 with an average difference of 1.67 ppm. By integrating all the required analytical steps into a portable format, the presented setup enables on-site tests of arsenic contamination in soil.

1. Introduction

Soil testing for heavy metal contamination is a constantly evolving process. The estimation of heavy metal ions in the soil sample is more complicated than water because of relatively higher mystical factors such as varied concentration of metal ions, organic and inorganic compounds, salinity, and pH. The entire process of heavy metal estimation can be divided into three steps, extraction (isolation of organic and inorganic compounds from the soil), purification (removal of non-specific compounds) and quantitation. Several independent protocols for the efficient extraction, purification, and quantification of the heavy metal ions in the soil sample are readily available (Jung, 2008; Wang et al., 2017). These protocols are well-optimized in the laboratory settings, but their performance suffers heavily when extrapolated on-site. Rapidity, simplicity, specificity, portability are the major targets for the on-site soil sample testing (Kaur et al., 2015b). Therefore, there is an immediate need of a wholesome device capable of quantification of specific metal ion in the field soil samples.

Only three heavy metals, i.e., lead (Pb), cadmium (Cd), and mercury (Hg) were declared toxic in the Global Monitoring Program adopted by the United Nations (UN) in 1973 (Vodyanitskii, 2016). Later, in the report delivered by the Executive Director of the UN Environmental Program (UNEP), seven other heavy metals (Cu, Sn, V, Cr, Mo, Co, and Ni) and three metalloids (Sb, As, and Se) were added to the list of the most hazardous elements (McLaughlin et al., 2000). The toxicity of arsenic spans across the tree of life, affecting microbes, plants, and animals (Jayasumana et al., 2015; Mandal and Suzuki, 2002; Molin et al., 2015; Podol'skaya et al., 2002) Arsenic contamination of soil and water in various parts of the world is an outcome of natural and/or anthropogenic sources such as mining, industrial waste deposition, and application of fertilizers and chemicals, leading to adverse effects on human health and ecosystem (Wuana and Okieimen, 2011). The current recommended World Health Organization (WHO) maximum contamination limit (MCL) for arsenic in soil and drinking water is 5 mg/L and 10 μg/L, respectively. Arsenic forms various toxic compounds through biochemical modification and causes severe toxicity by

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https://doi.org/10.1016/j.ecoenv.2020.110559
Received 15 November 2019; Received in revised form 24 March 2020; Accepted 29 March 2020
Available online 04 April 2020

inhibiting many crucial enzymes and proteins involving in deoxyribonucleic acid (DNA) synthesis and repair system (Wu et al., 2017). It is now well recognized that consumption of trace amount of arsenic can lead to carcinogenesis in humans (Paul et al., 2012).

Arsenite, As(III), and arsenate, As(V), are the two major inorganic forms that are harmful to the organism, the former being approximately 60 times more toxic (Dovick et al., 2015; Ratnaike, 2003; Walsh et al., 1977). As(III) can easily bind with specific proteins and move into the cell. For example, only the As(III) can cause allosteric inhibition of pyruvate dehydrogenase, the formation of acetyl-CoA from pyruvate stops, interrupting the citric acid cycle, thus, crippling the energy metabolism of the cell activity (Bergquist et al., 2009; Shen et al., 2013). Also, As(III) can bind with sulfhydryl(-SH) group present in many proteins, enzymes, thus inhibit their activity (Shen et al., 2013). Most forms of As(V) such as arsenobetaine are metabolized by our body and eliminated via urine (Molin et al., 2015). Accordingly, As(III) is considered as the most poisonous and mobile of all the isotopes of arsenic (Ahmann et al., 1997; Redman et al., 2002). Hence, determining the redox states of arsenic in environmental samples is crucial due to the distinct level of toxicity and mobility of the various forms (Cordos et al., 2006; Kaur et al., 2015a; Saha et al., 1999). Soil arsenic is partially mobile and can be a potential secondary contaminant in the air or water by natural and uncontrollable phenomenon such as wind, leaching, and weathering (Dousova et al., 2016; Dragović et al., 2008; Nriagu et al., 2007; Yang and Donahoe, 2007).

Numerous conventional analytical methods for accurate detection of arsenic in the environment like hydride generation atomic absorption spectroscopy (HG-AAS), inductively coupled plasma mass spectrometry (ICP-MS), flow injection hydride generation atomic fluorescence spectrometry (FI-HGAFS), flow injection hydride generation atomic absorption spectrometry (FI-HGAAS), atomic fluorescence spectroscopy (AFS), and neutron activation analysis (NAA) are available and readily utilized (Pereira et al., 2015; Shahlaei and Pourhossein, 2014). These methods offer extremely high sensitivity up to 0.5 ppb. However, the chief weaknesses of aforementioned methods are mandatory sample preparation steps, costly and bulky instruments, the requirement of skilled personnel, and maintenance of high safety standards which entails a standard laboratory. Despite swift development in on-site testing, there is still a considerable gap between the abilities of laboratory-based and on-site tests for heavy metal detection for soil samples. The foremost factor for the difference between on and off-site detection is the lack of on-site protocols or instruments for the preparation of device compatible samples. Recently, we have proposed a smartphone-based device for the assessment of arsenite in the spiked soil samples (Siddiqui et al., 2018a). While providing the portability in operation, the previous method has shown the limitation in field soil analysis in terms of accuracy due to the lack of relevant sample preparation steps. Extraction and purification of target analytes from field soil samples are generally complicated and offer challenges such as the removal of high bound organic acid content, interfering ions, plant and animal residues etc (Maiz et al., 2000). Thus, the importance of efficient sample preparation methods is more emphasized for field soil analysis, and should be aligned and optimized with a specific detection method to enhance analytical accuracy.

In this study, we propose, for the first time, a device capable of conducting streamlined analytical processes including extraction, purification, and detection of arsenite in field soil samples. Simplified extraction and purification methods based on acidic digestion and solid phase extraction (SPE) have been designed and integrated with customized smartphone-based detection. While several studies have shown the utilization of SPE to separate the arsenic species from water samples, efficient processes for field soils have never been reported, which essentially requires the in-depth analysis of the matrix interferents (Yalcin and Le, 2001b). Generally, the non-selectivity of the extractant and associated reagents, improper representation of contamination due to uneven sampling, storage of samples, and soil to extractant ratio cause disparity in quantitative estimation (Rapin et al., 1986; Tack and Verloo, 1995). In order to develop efficient purification protocols for field soil samples, we have designed different serial combinations of SPE cartridges and experimentally examined the efficiency of arsenic purification and the selective removal of other interfering ions and organic acids. Then, for the quantification of As(III) in the purified samples, an aptamer and gold nanoparticle (AuNPs) based colorimetric assay is developed, and the sensitivity of smartphone detection system is optimized. Finally, the performance of the ADS has been evaluated with field soil samples collected from contaminated area, and the results are compared with the standard instrument, ICP-MS.

2. Materials and methods

2.1. Soil samples and extraction

Reference soil (CRM 109-03-002) was purchased from the Korea Research Institute of Standards and Science (KRISS). Field soil samples were collected from several contaminated sites in South Korea, and spiked soil samples were prepared in laboratory by adding arsenite and other analytical grade solutions of different interfering ions like iron (Fe), sodium (Na), zinc (Zn), nickle (Ni), cadmium (Cd), Copper (Cu), lead (Pb) and As(V) (Daejung Chemicals, South Korea) to soils collected from uncontaminated area. Arsenic extraction from the soil samples was tested using hydrochloric acid (HCl, Samchun chemicals, South Korea) and sodium hydroxide (NaOH, Merck, Germany). The sodium arsenite (NaAsO2, Sigma-Aldrich, USA) spiked soil and extractant were mixed and rotated at 60 rpm at room temperature for 60 min. The prepared mixtures were filtered through 0.2 μm filter paper (Chmlab, Spain) and dispensed into the centrifuge tube for subsequent analysis. The filtrates were then analysed by Varian 810/820-MS ICP Mass Spectrometers (Varian, Australia), following the manufacturer's protocol. Before proceeding to purification, the extracted samples were neutralized by adding NaOH powder.

2.2. Purification

For the selective purification of arsenite and the removal of matrix interferents including arsenate As(V) and natural organic acids (NOC), five different SPE cartridges, containing sorbent, namely, strong cation exchange (SCX) and IC-Na (Alltech, Canada), silica-based anion exchange (SAX) and strong cation exchange (SCX) (Supelco, USA), and alumina (Millipore Waters, Canada) were tested (Supplementary Fig. 1). The purification through SPE involved preconditioning with 50% methanol buffer (Daejung Chemicals, South Korea), application of soil extractants, flow through collection, and elution steps of retained ions with 1 M HCl to maintain the uniformity of the solution. Both flow through and eluted samples were analysed with ICP-MS. A peristaltic pump was used to dispense the samples at a flow rate of 2 ml/min. Determination of natural organic acids was performed with FLASH 2000 Organic Elemental Analyzer (Thermo Scientific, Italy), according to the manufacturer's protocol. 1 M HCl extracted and SCX purified samples, adjusted to pH ~7, were used to compare the level of NOC in crude and purified soil extracts.

2.3. Colorimetric detection protocol and optical device development

Arsenite level of the prepared samples of 100 μl volume was quantified by aptamer-AuNPs based colorimetric detection protocol. 20 nM arsenite binding aptamer (ARS-3)-5′GGTAATACGACTCACTATAGGGAGATACCAGCTTATTCAATTTAAGAACAACCAACGTCGCTCCGGGTACTTCTTCATCAGATAGTAAGCAATCT-3'- (Bioneer, South Korea) was diluted from stock solution in 50 mM HEPES buffer-pH 7.2 (Sigma-Aldrich, USA) and incubated at 95 °C for 5 min 10 μl of ARS-3 Aptamer and 10 μl of arsenite were incubated at room temperature (RT) for 10 min. Subsequently, 70 μl of 2 nM citrate capped gold nanoparticles

(Nanopartz, USA) were then added to the mixture and incubated at room temperature for another 10 min. Finally, 7 μl of 0.3 μM NaCl (Merck, Germany) was dispensed to develop the concentration dependent color variation.

Colorimetric analysis and subsequent quantification of arsenite concentrations were performed via a smartphone (LG-F470L, LG Electronics, Korea) with a removable optical unit. The phone was furnished with android operating system (Android 4.0.3, IceCreamSandwich) and 8-megapixel complementary metal oxide semiconductor (CMOS) image sensor with light emitting diode (LED) flash. The optical unit was comprised of an adapter, cartridge holder, polarizer, and a test chip. The components of the optical unit were designed with Solidworks 2010 (Solidworks Corporation, USA) and fabricated with a 3D printer (Wiibox 3D printer, Measurement Korea Corp, Korea) by using black polylactic acid (PLA). The test chip was fabricated with polydimethylsiloxane (PDMS) having two reaction chambers for control and test samples. Reactions were performed in the wells and the flash illuminated image was captured by the smartphone camera (Supplementary Fig. 2). The mean of RGB pixel values were calculated from the captured image, the ratio of blue to red (B/R) was evaluated and correlated with the concentration of target analyte. The measurements of different concentration of standard arsenic solutions and field soil extracts were repeated five times. The weight of ADS is estimated to be ~55 g and the volume of PDMS chip wells was 100 μl.

2.4. Statistical analysis

The difference in the extraction and purification parameters was analysed by one-way ANOVA (SPSS 16.0 software; Macrovision Corporation Santa Carlo, California, USA) followed by turkey's post-hoc test to compare the differences between the time points. $P < 0.05$ was considered as statistically significant.

3. Results and discussion

3.1. Arsenic extraction from soil

Previous literature report that a series of experiments have been performed for arsenic extraction using a reference or fortified soil with different acidic and alkaline solutions such as HCl, sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), nitric acid (HNO_3), hydrofluoric acid (HF), and NaOH, etc (Alam and Tokunaga, 2006). Most of them, such as HF, H_3PO_4, and H_2SO_4 are highly efficient in extracting arsenic from the soil. However, these strong acids can change the nature of the target ions, leach ions from the soil, and be toxic to handler and the environment (Tandy et al., 2004). To reduce the environmental and handling hazards for simple on-site operations, several extractants have been tested including HCl, EDTA, HNO_3, and NaOH, and the relatively mild 1 M HCl has been finally selected as extractant in current study based on the comparison of extraction efficiencies for arsenic. The chemical nature and concentration of the extractant are dominant factors for extraction but the efficacy is also volume dependent (Tandy et al., 2004). Higher soil to acid ratio has shown better extraction efficiency in case of reference soil samples (Supplementary Fig. S3), nevertheless, the effect of extractant volume was statistically insignificant ($p \leq 0.05$) in the case of field soil samples (Fig. 1). Several reports have claimed that the spiked soil data closely resembles with the field soil, while other reports showed that there could be a significant difference between the spiked and field soil experiments mostly because the ion binding is more stable in field soils due to aging (Hamels et al., 2014; Leśniewska et al., 2017; Smit and Van Gestel, 1998). Futhermore, the high soil to acid ratio avoids dilution constrains, aids in miniaturization, and eases overall handling by reducing initial sample volume. Thus, 1 M HCl as extractant and 1:5 soil to acid ratio were selected in the finalized protocol for the field soil extraction. The average extraction efficiency with the field soil samples was found to be 35.40%.

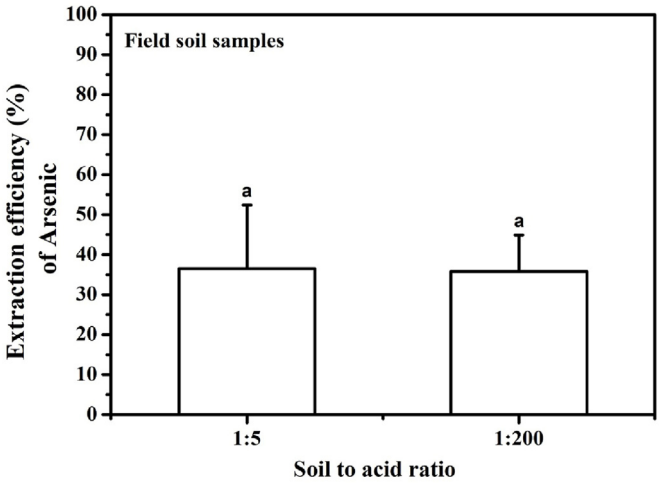

Fig. 1. Extraction efficiency of field soil samples at two different soil to acid ratio using 1 M HCl. Different letters indicate different level of significance, $P < 0.05$. Error bar indicates the standard deviation of five repeated experiments.

3.2. SPE based sample purification

The soil extract contains various metal ions, free and bound-organic substances, and other unidentified matrix components. Most of these components are potential interferents in the quantification of any heavy metal ion, especially in the bioassay-based detection. Minimizing these interferents is central to attain reliable and reproducible data. For the purification of arsenic samples, we have designed purification method by using SPE cartridges with different sorbents. The mechanism of SPE are primarily based on the principle of exchange of protons, hydroxide, and acids packed inside the cartridges (Acikara, 2013). Out of the five cartridges used in the present study, the SAX (quaternary amine, Cl^- counter-ion), SCX-alltech (styrene divinyl benzene sulfonic acid) were hypothesised to be efficient for flow through study in soil samples as it has shown low retention for As(III) in the water solution (Yalcin and Le, 2001a). SCX-supelco (aliphatic sulfonic acid, Na^+ counter-ion), IC-Na (Na^+ counter-ion) and Alumina (hydrophilic) were preconceived to selectively capture As(III) due to their strong cation exchange and high elution efficiency in water. As there is scarcity of research on the As(III) purification from the soil, we have designed and conducted comprehensive experiments for the selective collection of the target ions and the removal of matrix interferents.

To characterize purification efficiency and select the optimal combination, arsenic-spiked soils have been tested first, which provide minimum inter-contamination site variation but environmentally applicable chemistries. Fig. 2 summarizes the performance of five different SPE cartridges for the removal the interfering ions and the collection of target As(III) ions from the spiked soil samples. As we have hypothesised, the SCX (alltech) and SAX (supelco) cartridges have shown relatively low loss of As(III) with efficiencies of 25% and 11%, respectively, while other cartridges have retained most of As(III), which can only be collected with additional elution steps (Fig. 2a). For the high As(III) retaining cartridges, elution based collection was performed and an average elution efficiency of 45% was observed with IC-NA cartridge, whereas, a negligible amount of arsenite was eluted with SCX (supelco) and alumina (Fig. 2b). Due to the low efficiency of elution steps, flow through collection approaches with SCX (alltech) and SAX (supelco) have been chosen as the purification method. As SPE cartridges in this approach are assumed to provide a selective filtration of interfering components other than the target ion, the removal of common interfering heavy metal ions existing in field soils has been tested. As shown in Fig. 2c and d, the retention efficiency of SCX and SAX for other interfering ions including Fe, Na, Zn, Ni, Cd, Cu, and Pb

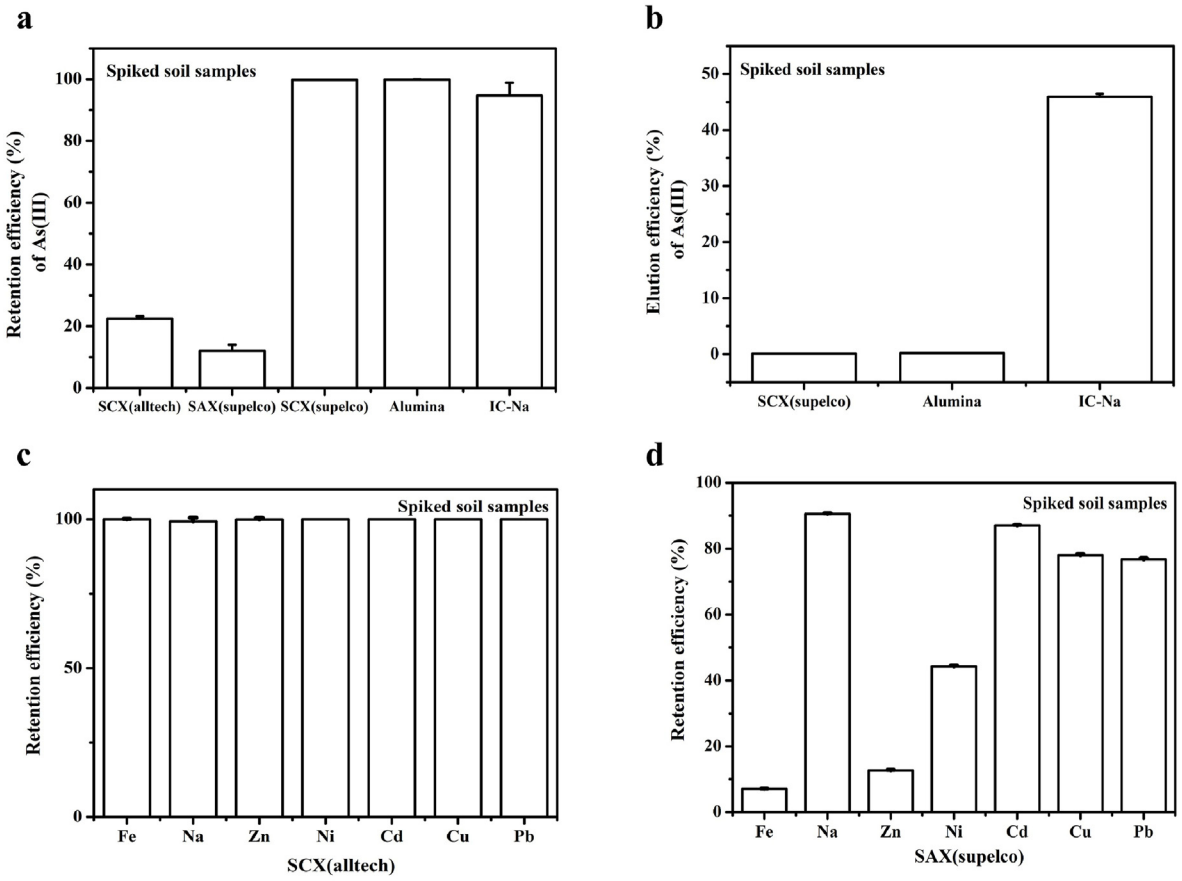

Fig. 2. Comparison of cartridge efficiencies for the target and interfering ions. a) retention efficiency of As(III), b) elution efficiency, c) retention efficiency of interfering ions for SCX (alltech), d) retention efficiency of interfering ions for SAX (supelco). Error bar indicates the standard deviation of five repeated experiments.

was 100%, 99.25%, 99.91%, 100%, 100%, 100%, 100% and, 7.09%, 90.55%, 12.68%, 44.24%, 87%, 78%, 76.72%, respectively. Thus, both cartridges have depicted excellent capabilities for the removal of interfering metal ions, ensuring a highly efficient purification of arsenic which complements the robustness and reproducibility of our colorimetric assay. In conventional laboratory-based approaches, the removal of interfering ions by SPE can simply be performed because column based standard protocols are available and the importance of purification is not emphasized as the laboratory-based instruments like ICP-MS, FI-HGAFS, and FI-HGAAS etc. can detect arsenic at extremely low concentration on non-interfered low-background isotopes (Yalcin and Le, 2001b). Thus, the study of the removal of interfering ions has largely been ignored in the literature. However, simple and efficient sample purification steps are crucial for on-site measurements since the standard laboratory instruments are not available and the efficiency of sample preparation affects the detection sensitivity as well as the performance of the system.

Besides the interfering metal ions existing in field soil samples, organic matters are also important potential interferents, especially in the highly sensitive aptamer-based detection of arsenite. Neutralized sample (pH ~7) is a prerequisite for the current colorimetric assay, however, the pH and ionic strength of the solution regulate the conformational changes in aptamer which is responsible for the development of the color (Supplementary Fig. S4) (Hianik et al., 2007). Consequently, it is mandatory to neutralize the acidic soil extracts after the extraction. The neutralization with NaOH functioned efficiently in case of spiked soil samples, however, insoluble precipitate with clear supernatant was observed with the field soil sample as the pH of the solution increases. Fig. 3a shows acidic field soil extracts without neutralization (control sample) and neutralized extracts at different pH. The ICP-MS results also show that the neutralization with NaOH decreases the level of arsenic in field soil extracts (Fig. 3b). Similar phenomenon of As precipitation was observed by Acre et al. in the study of the neutralization of acid drainage, and the precipitation development with increase in organic acid concentration has been reported (Arce et al., 2017). The same study showed that precipitation causes inaccurate evaluation As by ICP-MS at pH 3, but the effect of precipitation at higher pH was not covered. Additionally, the neutralization of the field soil samples dramatically increases the retention efficiency of SCX cartridges (Fig. 3c**).** In the literature, it has been reported that the presence of high concentration of interfering ions and total organic acid in field soil samples may cause the precipitation and sorption on the surface of organic matter at pH > 2 (Beauchemin et al., 1992; Christl et al., 2005). As experimentally observed, the aggregation of the metal ions and organic acids causes the poor yield and the removal of organic acid is required to avoid the pH induced precipitation and maintain the uniformity of the solution. However, there is absence of study which suggest tools for onsite removal of organic matter for accurate evaluation of As in neutralized samples. Recently, hypercrosslinked strong cation-exchange polymers were used to extract purine, an organic component of nucleic acid, from urine samples (Xu et al., 2016). Thus, we have passed the acidic extracts (non-neutralized solution samples) through the SCX cartridge and then neutralized it with NaOH. As a result, no precipitation was observed, moreover, the organic carbon analysis results showed a significant reduction in the level of organic acids after passing the extracts through SCX (Fig. 3d). The present study demonstrate the importance of removal of organic acids from the field soil samples ans suggest the use of SCX before neutralization for the accurate estimation of the As, even when the detection is performed through highly sophisticated instrument such as ICP-MS.

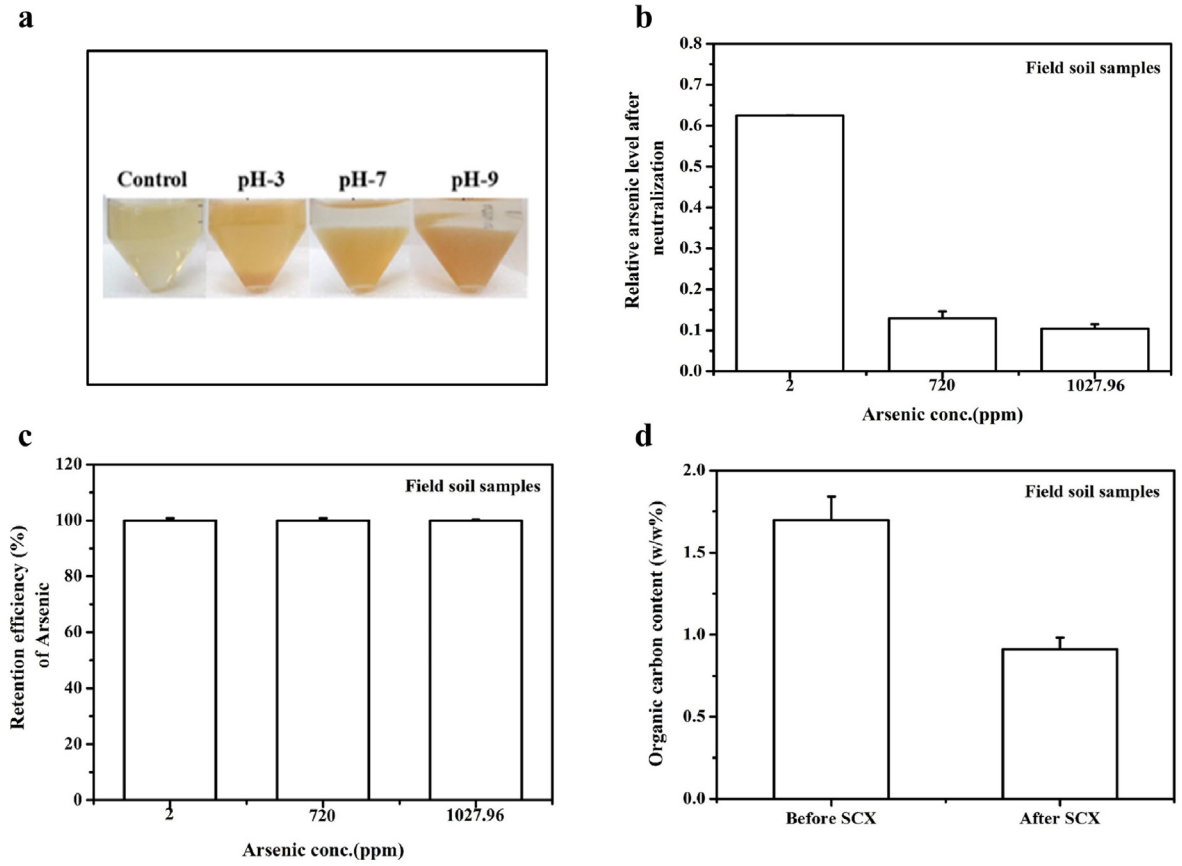

Fig. 3. Effect of pH induced precipitation a) precipitation in field soil samples at different pH, b) Relative arsenic level in field soil extracts after neutralization for different soil samples, c) retention efficiency of SCX cartridge for field soil sample after neutralization, and d) % W/W of organic carbon before and after passing through SCX cartridge. Error bar indicates the standard deviation of five repeated experiments.

After the removal of organic acids, the SPE based purification of arsenic ions was validated again with field soil samples. The average arsenic collection efficiencies after passing through SCX and SAX cartridges have been observed as 69.98% and 77.85%, respectively (Fig. 4a), thus the collective efficiency of purification for As(III) in two cartridges connected in series is found to be 54.60%. As compared with the spiked soil samples, slightly lower collection efficiency has been observed for both cartridges in case of the field soil samples. The lower collection could be dedicated to the time-dependent sorption of arsenic with the matrix interferents which might not be present in the spiked soil as prepared in lab. The retention efficiencies of SCX for other ions such as Fe, Na, Zn, Ni, Cd, Cu, and Pb were 99.47%, 100%, 94.47%, 99.94%, 100%, 74.83%, 97.352% respectively (Fig. 4b). The average retention efficiencies of SAX were 57.19%, 100%, 97.15%, 68.75%, 100%, 88.92%, and 86.85%, respectively (Fig. 4c), which confirms that the application of both cartridges in series allows the removal of most of interfering ions.

A further purification of target analyte was performed by removing As(V) with SAX which showed almost 100% removal efficiency if the concentration of the interfering ions and organic acid is regulated (Fig. 5). As the SCX cartridge efficiently retains the interfering ion and organic acid, sequential arrangement of SCX before SAX ensures the efficient purification of As(III) from the field soil extracts. The direct application of soil extracts to SAX can decrease the efficiency of the overall process (Su and Chen, 2018), so the order should be maintained as suggested in the proposed device (Supplementary Fig. S3). Cumulatively, it has been demonstrated that the combination of two SPE cartridges can selectively remove organic acids and interfering ions with low retention of arsenic, indicating the utility of current arsenic purification in various geographical settings.

3.3. Quantification of arsenite contamination

The colorimetric method can provide an attractive detection platform with high sensitivity in the range of pico-nanogram, fast readout, and portability, aided by integration with the smartphone camera. The simplicity of the current assay lies in the straight forward nature of the protocol. In contrast to our previous study, we have reduced the assay time by adding the premixed solution of aptamer and SPE purified As (III) in the AuNPs instead of sequentially incubating the aptamer with AuNPs and followed by incubation with the As(III) (Siddiqui et al., 2018b). The modification in the assay was concluded on the basis of a novel finding which shows that ARS-3 aptamer cannot bind arsenic (Zong and Liu, 2019). ARS-3 aptamers, a positively charged oligonucleotide, strongly bind on the surface of negatively charged AuNPs through coordinate bonds, providing the stability of AuNPs. However, in the presence of arsenite ions, the As(III) gets adsorbed on the surface of AuNPs through electrostatic interaction, preventing the adsorption of the aptamer on the AuNPs causing the NaCl induced aggregation. As a consequence, the color of the solution mixture changes from red to purple in a concentration dependent manner. The selected 20 nM aptamer concentration is the minimum concentration of aptamer which is sufficient to prevent aggregation in the presence of NaCl. The entire assay works at room temperature and takes less than 30 min. The total assay volume of the current aptamer-AuNPs based detection is 100 μL and requires only 10 μL of the field soil extracted solutions. The miniaturized test volume provides the reduced cost of the assay, less use of pretreated samples, and quantitative determination of As(III) level even the samples are available in limited quantity.

The sensitivity of the developed assay was first tested with standard samples prepared by a series of dilution of arsenite in neutralized

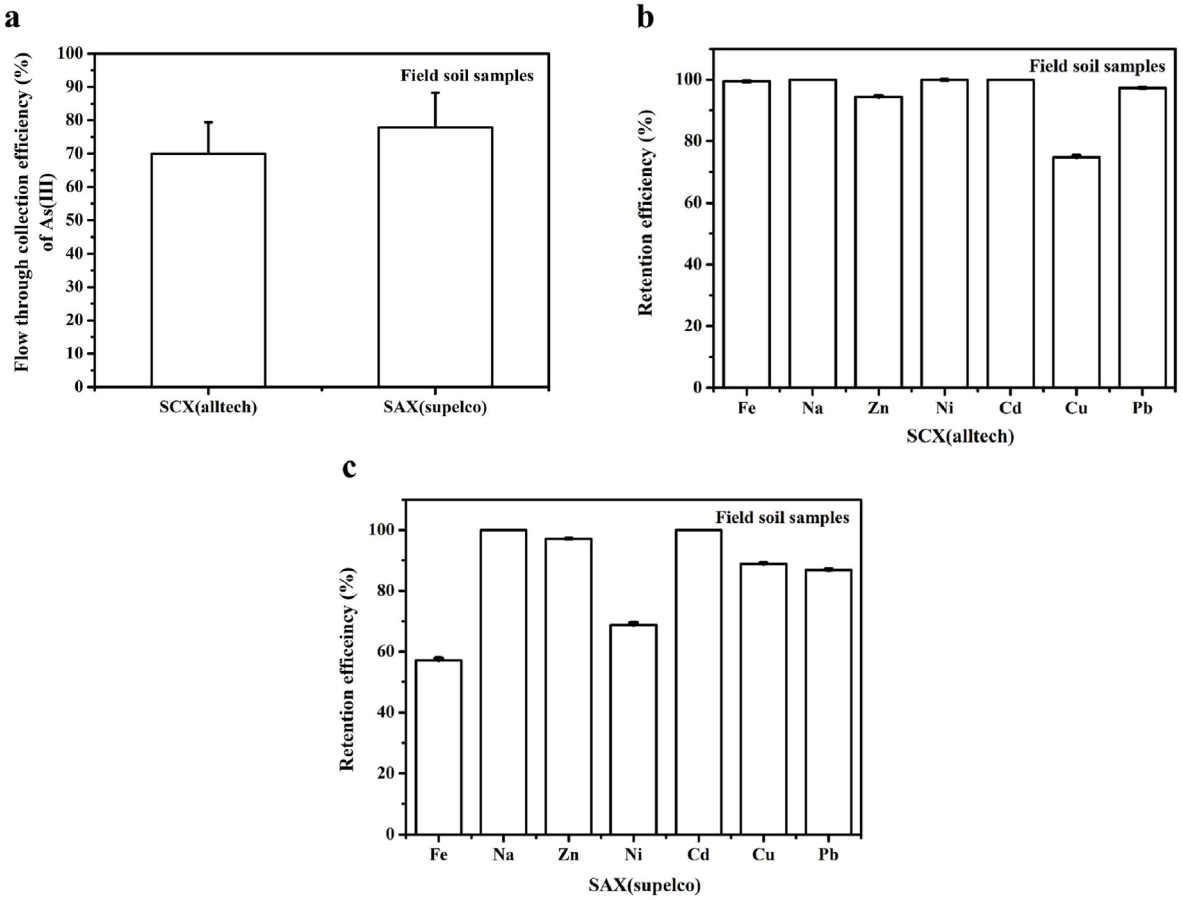

Fig. 4. Field sample purification efficiency a) collection efficiency of SCX (alltech) and SAX (supelco) b) retention efficiency of SCX (alltech) for various interfering ions c) retention efficiency of SAX (supelco) for various interfering ions. Error bar indicates the standard deviation of five repeated experiments.

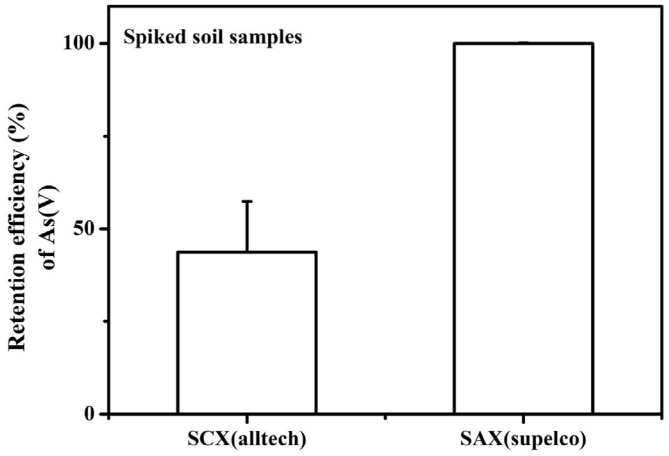

Fig. 5. Retention efficiency of the SCX (alltech) and SAX (supelco) for As(V). Error bar indicates the standard deviation of five repeated experiments.

solution (1 M HCl + 1 M NaOH, pH 7.0) to mimic the buffer conditions of extracted and purified samples. Fig. 6a shows the measured standard curve. The LOD of the detection assay was measured 14.44 ppb, which can provide highly sensitive optical detection for water samples or pretreated samples. After the validation of the colorimetric assay, the resultant analytical sensitivity of the measurement system including sample preparation and detection has been evaluated with the field soil samples as shown in Fig. 6b. In order to extrapolate the plot for calculating the limit of detection for field soil samples, the data points of standard curve must be normalized by dividing them with the dilution factor and the sample preparation efficiency. Cumulatively, the normalized LOD of 1.97 ppm for the field soil sample has been attained. This LOD for field soils is comfortably under the guidelines of WHO and U.S. Environmental Protection Agency (EPA) which has set the maximum permissible limit of arsenic in the soil below ~5 ppm (Atsdr, 2007).

For further validation of the present setup, the ADS has been evaluated with the field soil samples (2, 13.45, 24.07, & 53.85 ppm) collected from different contaminated areas. The field soils were extracted by 1 M HCl, for 60 min at a ratio of 1:5, and purified by SCX and SAX cartridges, and the level of As(III) was quantified by the smartphone-based setup. The results showed a highly significant correlation coefficient of 0.997 with an average difference of 1.67 ppm, compared with the conventional instrument (ICP-MS) measured values (Fig. 7). The high coefficient of correlation confirms the utility of ADS for on-site detection. Additionally, the developed assay works well with the field soil extracted samples and anomalous behavior such as pH dependent AuNps aggregation was not observed, which represents the suitability of the simplified sample preparation for highly sensitive bioassay.

4. Conclusion

In this study, we present ADS for the on-site sample pre-processing and quantification of As(III) in field soil samples. With the combination of single mild acid extraction and SPE cartridge based purification, the matrix interferents such as organic acids and metal ions have been removed effectively and thereby, generate a bioassay compatible samples for highly sensitive aptamer-based colorimetric detection. The presented smartphone-based measurement system has demonstrated the detection limit of 14.44 ppb in aqueous samples and 1.97 ppm in field

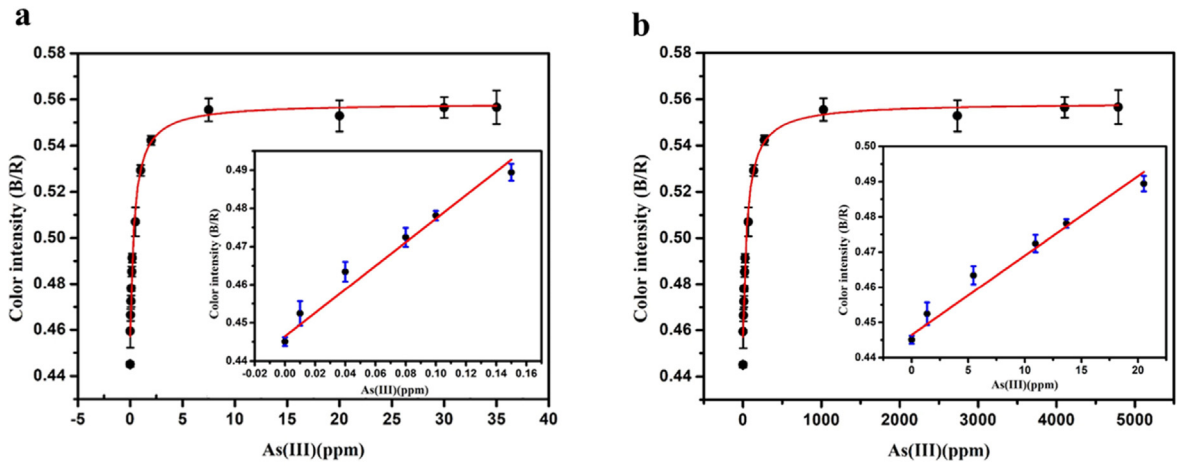

Fig. 6. Standard curve for detection of arsenic in a) aqueous samples and b) field soil samples. Detection limits are 14.44 ppb and 1.97 ppm respectively. Effects of sample preparation are included in the generation of the field soil curve. Error bar indicates the standard deviation of five repeated experiments.

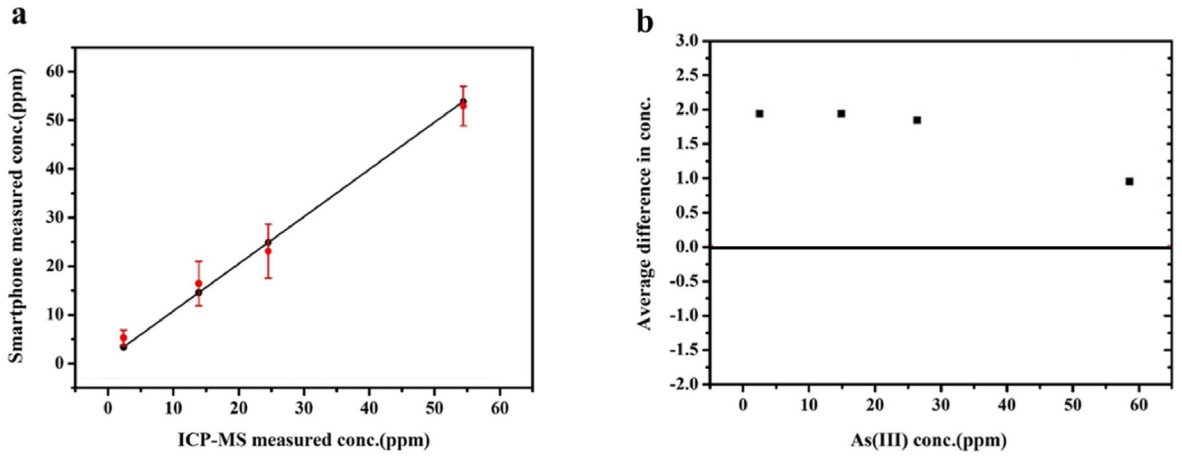

Fig. 7. Analytical performance validation for the smartphone based setup by comparing with ICP-MS results. a) correlation of arsenic quantification in field samples (R^2 = 0.997) b) Quantification difference (1.67 ppm in average). Error bar indicates the standard deviation of five repeated experiments.

soil samples. Finally, the setup has been evaluated with four different field soil samples and a highly significant coefficient of correlation of 0.997, and the average difference of 1.67 ppm was observed in comparison with the measurements by conventional instrument (ICP-MS). The ADS is time-efficient and expected to take less than 3 h for on-site detection with the proposed setup (Supplementary Fig. S5). However, further validation and optimization through field tests at multiple sites are warranted to ensure the robustness and the sensitivity.

CRediT authorship contribution statement

Mohd F. Siddiqui: Methodology, Data curation, Writing - original draft, Validation, Writing - review & editing, Investigation. **Zeeshan A. Khan:** Methodology, Data curation, Writing - original draft, Validation, Writing - review & editing, Investigation. **Hyoil Jeon:** Methodology, Data curation, Investigation, Resources. **Seungkyung Park:** Formal analysis, Writing - original draft, Writing - review & editing, Supervision, Visualization, Project administration, Resources.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgment

This subject is supported by the Korea Ministry of Environment (MOE) as a “Geo-Advanced Innovative Action Project” (2015000540008) and Korea University of Technology and Education as “Professor's Education and Research Promotion Fund”.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecoenv.2020.110559.

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