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Simultaneous Determination of Heavy Metals in Competitive Aqueous Solutions and Contaminated Soil Systems

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Abstract - Often times, errors and unreliable results arise from the analytical instruments employed. In this study, Potentiometric Stripping Analysis (PSA) was used to quantify heavy metals in a competitive aqueous solution containing Spirulina platensis—Spirulina maxima cells containing heavy metals due to the following advantages; higher sensitivity, lower detection limits, simultaneous multielement detection, accuracy, fast, suitability for on-line and in-situ measurements and cost-effectiveness. Electrochemical and chemical parameters were optimized for efficient deposition and stripping steps. Measured data were fitted onto Langmuir and Freundlich isotherms which demonstrated the best fit for the Langmuir isotherm where R_L=0.963067 and R^2= 0.99901 whereas the data less fitted the Freundlich isotherm with 1/n = 1.024391 and R^2 = 0.98735. Linear logarithm and stripping relationship were thus achieved as follows; 3.12 × 10 to 4.20 × 10^7 cfu mL^{-1}, 2.67 × 10 to 2.3 × 10^7 cfu mL^{-1}, 1.31 × 10 to 2.10 × 10^7 cfu mL^{-1} for Cu^{2+}, Zn^{2+} and Pb^{2+} respectively. Phytoavailability test on complex soil from mining areas was also performed. The physical and chemical properties are responsible for the non-phytoavailabilty of Cr and As in these soils. Potentiometric Stripping Analysis and Atomic Absorption Spectroscopy results have been compared.

Keywords: *Atomic Absorption Spectroscopy (AAS), Freundlich isotherm, Langmuir isotherm, Phytoavailable, Potentiometric stripping analysis (PSA)*

INTRODUCTION

In the environment (soil, water, and air), toxic elements are persistent and undegradable [1]. Anthropogenic sources like mining, agriculture as well as other sources [2]. There are several elements that are important for life. However, many other elements are highly toxic, especially at higher concentrations. Industrial discharges of harmful toxic chemicals into the environment are responsible for several ailments including damage to the central nervous system. Industrial processes are the cause of Lead (Pb) and Cadmium (Cd) pollution in the environment resulting in several diseases [3]. The soil is the final destination of toxic metals in the atmosphere [4]. Several toxic elements including Ni, Cr, etc. have been determined in the environment [5]– [6]. Determining these toxic metals provides an in-depth understanding of metals' occurrence and behavior anthropogenically [7]– [8] for the purposes of heavy metals concentrations in the environment [9]. Therefore, it is imperative to apply accurate, reliable, cost-effective methods. The objective of this study is to apply Potentiometric Stripping Analysis for the determination of heavy metals in complex soil systems and competitive aqueous solutions. Also, employ Atomic Absorption Spectroscopy analysis as a second analytical tool and compare the reliability of the measured results. Bio-absorption phenomena of the algae cell used in the investigations were determined. Additionally, phytoavailable As and Cr species in soils from mining areas in Konongo in Ghana will be studied by AAS and PSA respectively.

1.1. Toxic effects of heavy metal

Heavy metals increasingly contribute to the pollution of the environment. Environmental contamination is caused by toxic elements in the environment which results in toxic effects thereby causing several human illnesses [10]. The toxicity of heavy metals at higher levels of exposure is well known, but a current concern is a possibility that continual exposure to relatively low levels of heavy metals may lead to chronic adverse health effects. Even though, continuous exposure to lower amounts of toxic metals might cause severe toxic effects, data on the exposure to higher concentrations of toxic elements has already been well established. Efforts have been made to reduce the exposure to heavy metals yet several people are still expose to potential toxicity of heavy metals through industrial activities [11]. Heavy metals have the potential to accumulate and cause serious health effects [12], to the human body (nervous system, kidney, and liver) and also serve as agents of cancers [13]. Oxidative stress, inhibition of enzyme activities, reduction in oxidative metabolism are some of the toxic effects of heavy metals [14]. Moreover, DNA damage, depletion of protein and lipid peroxidation could be caused through radical formation [15]. Infants are particularly sensitive to Pb toxicity, therefore Pb present in their main nourishment (i.e. breast milk) needs to be estimated. The Pb present in breast milk can be estimated by electrothermal atomic absorption spectrometry [16]. Through the food chain, higher levels of toxic metals enter living organisms.

1.2. *Atomic Absorption Spectroscopy (AAS)*

Traditional analytical methods for analyzing metals are atomic absorption spectroscopy/emission spectroscopy (AAS, AES) [17]–[18]. Heavy metal-containing samples can be analysed by sensitive methods such as AAS after acid digestion [19]. Even though these traditional analytical methods are sensitive, they are labor-intensive and expensive [20]. Atomic Absorption Spectrophotometer analysis relies on proportionality of concentration to absorbance according to Beer Lambert's law [21]. Flame AAS is a very useful method for determining the presence of heavy metals in environmental samples [22].

1.3. *Electroanalytical methods*

Different types of stripping methods are applied for heavy metal analysis among the electroanalytical techniques. The development of Differential Pulse Anodic Stripping Voltammetry is meant to improve detection by compensating capacitive current (i >). Redox reaction of trace impurities higher salt-containing aqueous systems are responsible for faradaic current (if). A blank aqueous solution may inevitably present impurities that might contribute i~. In Anodic Stripping Voltammetry, the oxidation potential of every element is determined at the height of the peak current (i). However, it is important to know that overlap with stripping peaks that are of interest is caused by background current (ibd). Usually, the concentration of the element to be determined should produce an equal faradaic current. The working electrode potential in Potentiometric Stripping Analysis depends on the stripping time which is equivalent to the electroactive species to be determined. When the metal to be determined is being stripped off the electrode surface, there is no background current flow in the working electrode [23], which makes PSA less sensitive to non-targeted electroactive species. Voltammetry and Potentiometric stripping analysis (PSA) have proved useful techniques often used for toxic element estimation [24] - [26]. Even though electrochemical stripping methods are considered cost-effective and easy to use, results from electroanalytical methods are very comparable to other analytical instruments such as AAS.

The preconcentration step is the main unique parameter that makes stripping voltammetry different from other electroanalytical methods. In most applications involving analysis of metals, pre-concentration is carried out with electroanalysis of the target metal cations to the respective metals (and some special cases to metal oxides) and deposition on the surface of the working electrode. Electroanalysis employs preconcentration of the target metal species onto the surface of the working electrode. After deposition, the accumulated metals are oxidized (other metal-oxides reduced) to the respective cations and stripped back into the solution. One of the common applications of PSA is the determination of heavy metals such as Co, Zn, Cd, and Pb in the environment to curtail toxicity to humans.When the target metal is deposited onto the electrode surface, a thin film or an amalgam is formed. Heavy metal analysis reduction on inert electrodes (such as carbon, platinum, or boron-doped diamond) follows target metal monolayer formation preconcentration from bulk-phase of the metal [27]. The Glassy Carbon (GC) electrode is a widely used material in stripping analysis. Since the sensitivity of bare GC in the potentiometric stripping analysis of metals is low, the GC surface is usually subjected to preliminary (ex-situ) surface modification and/or in situ modification to achieve the desired surface properties. Thin films of metals, conducting polymers, selective organic reagents, clay minerals, and ion-exchangers have been reported for surface modification of GC. Occasionally, more than one modifying layer is used. Metal films (mercury, bismuth, gold, antimony, copper) facilitate the accumulation of metal cations and the stripping procedure of deposited metals [28]. The behavior of heavy metals depends on the chemical forms instead of the total metal concentration. These elements are part of the biogeochemical cycling [29]. Therefore, this research seeks to develop a reliable method that can accurately determine heavy metals in aqueous solutions for their competitive kinetic study in complex matrices.

EXPERIMENTAL

2.1. *Materials and reagents*

All electrochemical analyses were carried-out by electrochemical workstation (Autolab, Eco Chemie, Utrecht, The Netherlands), driven by GPES 4.9 software (Eco Chemie). Ag/AgCl/KCl(saturated), Platinum, glassy carbon electrodes were purchased. The AAS measurements were performed on the Perkin Elmer Atomic Absorption Spectrometer PinA Acle 9007 using the flame analyzer. HNO_3 (69%) was purchased from Sigma Aldrich, Hungary. Spirulina platensis—Spirulina maxima cells (in dried form) were obtained from the Academy of Sciences, Czech Republic. Analytical grade purity chemicals were used in this experiment. GC carbon was purchased from BAS-Inc, Tokyo-Japan. Hydrochloric acid (37%) was purchased from VWR Prolab Chemicals, France. The following heavy metals salts of hydrated $ZnSO_4$, nitrate salts of $Cu(NO_3)_2{\bullet}3H_2O$, $Pb(NO_3)_2$, $Cd(NO_3)_2$, and $HgCl_2$ were bought in Hungary from Sigma Aldrich.

2.2. *Sample and sampling location*

Soil samples from five different locations Empan Mu, Nassara, and Mpamprome in Konongo (6 ° 37 '0 "North, 1 ° 13' 0") were collected to analyze two main pollutants namely, chromium and Arsenic. For each sampling location, 2 Kg soil was collected, pre-treated, and dried for 24hrs at a constant temperature of 105 ^{o}C in an oven. The dried soil samples were digested in aqua regia ($ccHNO_3^+$ ccHCl). The physical and chemical characteristics of samples of these soils are shown (Table 1).

2.3. *Samples and physicochemical parameters of the soils*

FIG. 1. LOCATION OF SOIL SAMPLES STUDIED

TABLE 1. PHYSICOCHEMICAL PARAMETERS OF THE SOILS

Parameter	**E**	**N**	**M**
pH	6.8	6.2	6.7
Metal-binding capacity	medium	medium	medium
Salt content (%)	n.d	n.d	n.d
Specific surface area	n.d	n.d	n.d
CEC (mEQ/100 g)	6	4	5
Sand (%)	82	79	80
Silt (%)	18	15	16
Clay (%)	10	12	9
Organic matter (%)	2	1	1
CaCO3 content (%)	3.0	2.9	2.6
Upper limit of plasticity	29	29	29
Soluble Fe in Aqua regia (mg/kg)	35000	27510	31500
Soluble Mn in Aqua regia (mg/kg)	621	410	583

Sample area; E= Empan Mu; N=Nassara; M= Mpamprome; n.d= not detectable

2.4. *Soil extraction, AAS measurements and Microwave (MW)-assisted digestion of soil samples*

The Lakanen and Erviö leaching test was employed for Phytoavailability studies [30]. In summarizing the procedure, dried soil was extracted for 1hr in a 40 mL of 0.02 M solution of EDTA. The pH of the EDTA solution was 4.65 which was measured with OP-212/2 pH meter (Radelkis Ltd., Budapest, Hungary) and adjusted with ammonia. When the sample digestion was completed, prior to washing of the residues, the digested samples were centrifugated (Fig. 2). According to the procedure by Lakanen and Erviö (1971), digestion of the dried soils to obtain the pseudo-totals were performed in aqua regia by MW-assisted digestion (Fig.2).

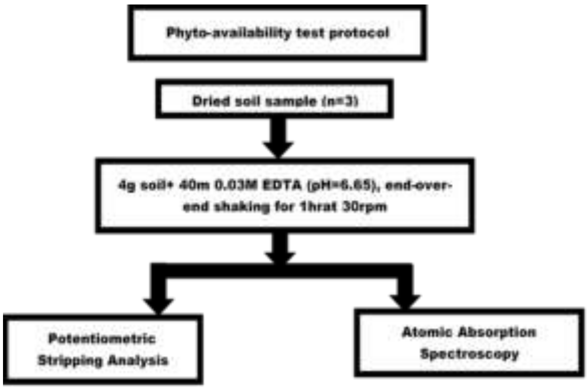

FIG.2. PHYTOAVAILABILTY TEST IN SOIL SAMPLES ACCORDING TO LAKANEN AND ERVIÖ (1971)

Before both elements(As, and Cr) concentrations were measured, the dried soils and the residual soil samples were digested in aqua regia by the Ethos Plus 1 equipment (Milestone S.r.l., Sorisole, Italy) based on EU Standard EN 13346 (2000) [31].

In summary, 1.0 g of each soil sample was taken from the homogenized samples and transferred into 100-mL PTFE digestion vessels (n = 5). Into a 100-mL PTFE digestion vessel, 1.0g of each dried homogenized soil is measured followed by the addition of 8.0ml of aqua regia. The MW-assisted digestion program procedure is as follows: 500 W in 4 minutes; 750 W in 5 minutes and, 800 W in 12 minutes. Prior to decanting of digested samples into PP tubes, the samples were properly cooled after digestion at higher temperatures of up to 170 °C. Finally, dilution with UPW to obtain 5v/v% HNO_3 was performed. Atomic Absorption Spectroscopy, Perkin Elmer using the flame analyzer was used for Chromium and Arsenic determination. AAS methods utilized 1% HNO_3 whiles all electrochemical analyses were performed in 0.1M HCl_2 solution. The temperature of all the measurements of the experiments was maintained at 20 ºC. Additionally, an equal volume of each sample was flamed and analyzed in the AAS measurements. All working solutions were prepared from stock solutions by diluting with deionized water. Before equipment are used, working apparatus were rinsed twice in nitric acid (1%)

2.5. General conditions of PSA for zinc, cadmium, copper and lead analysis

The investigation used the system with 3-electrodes which included a Glassy Carbon electrode with a modified mercury film surface. The reference electrode was an Ag/AgCl/KCl(saturated) electrode whiles Platinum electrode was the counter electrode (Fig. 1). The electrochemical workstation with the following parameters; Autolab, Eco Chemie, Utrecht, The Netherlands, driven by GPES 4.9 software(Eco Chemie) was used for electrochemical analysis. In each analysis, 50µL of the sample to be analyzed was used in all the electrochemical measurements. The mercury solution used for the mercury film formation on the electrode surface was 0.5mM $HgCl_2$ and 0.1 M HCl was used as the working electrolyte.

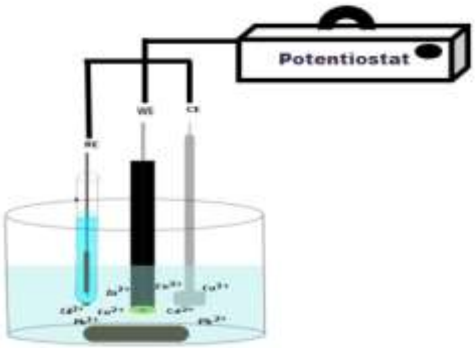

FIG. 3. POTENTIOSTAT CONNECTED TO THE ELECTROANALYTICAL CELL

The Potentiometric Stripping Analysis utilizes mercury modified electrode as oxidizing agent.

Electrode modification in PSA analysis uses mercury already diluted as oxidizing agent which is capable minimizing the risk arising from contamination. All measurements were performed at room temperature (20±1 ºC) in a 5 mL electrochemical cell. For the PSA, the analyzed sample must be in soluble form. The instrumental setup of the electrochemical cell for Zn, Cd, Cu, and Pb determination by PSA have been illustrated (Fig. 1)

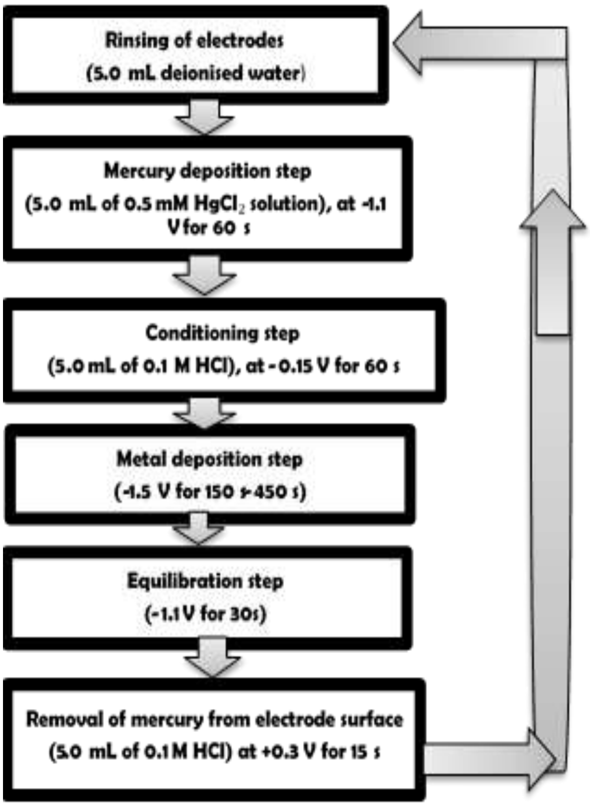

FIG. 4. EXPERIMENTAL CONDITIONS AND PROCESS ILLUSTRATION

After the sample was properly filtered, Zn, Cu, and Pb concentrations were measured in 0.1M HCl solutions by the method of standard addition. Each of these metals, Cu, Zn, and Pb concentration was 50 mg/L whiles the concentration of Cd varied from 25- 500 mg/L in all respective samples. Standard solutions of all the four metals were prepared from high-grade metal salts. To obtain quantitative recoveries of the metal ions on the Glassy Carbon Electrode, the pre-concentration procedure was optimized for various analytical parameters such as pH, sample volume and amount of $HgCl_2$ solution, matrix effects, etc. The percent of metal adsorbed on the Glassy Carbon Electrode was calculated from the amounts of metal in the starting sample and amounts of metal stripped from the Glassy Carbon Electrode according to the electrochemical reaction;

$$\boldsymbol{E_{cell} = E^{o}{}_{cell} + \frac{RT}{zF} InQ_{r}} \qquad (1)$$

Where;

- E_{red} is the half-cell reduction potential at the temperature of interest,
- $E^{o}{}_{red}$ is the standard half-cell reduction potential,
- E_{cell} is the cell potential (electromotive force) at the temperature of interest,
- $E^{o}{}_{cell}$ is the standard cell potential,
- R is Universal gas constant
- T = temperature in K
- z is the number of electrons transferred in the cell reaction or half-reaction,
- F is the Faraday constant, the number of coulombs per mole of electrons
- Q_r is the reaction quotient of the cell reaction

To obtain accurate results, clean equipment, proper storage of standard solutions in dark drawers, clean working surfaces, and storage of samples in refrigerators among other things were strictly followed. Care was also taken according to safety protocols and environmental regulations during heavy metal usage and waste handling. Additionally, to avoid these heavy metals from returning into the environment, used-up samples were collected in waste bottles and properly disposed of.

2.6. Adsorption of dried biomass of Spirulina platensis—Spirulina maxima cells

Approximately 1.0g/L of dried biomass of Spirulina platensis—Spirulina maxima cells were agitated gently in solution of heavy metals for 24hrs at room temperature.

The concentration of Cd ranged from 25 to 250 mg/L whiles Zn, Pb and Cu were 50mg/L. After the incubation period elapsed, the heavy metal concentrations of the supernatants were measured by both AAS and Potentiometric Stripping Analysis. The adsorption by the dried biomass was calculated (Eqn. 2):

$$\boldsymbol{Adsorption\ (\%\ removal\ efficiency) = \frac{Ci - Ce}{W}\ x\ V} \qquad (2)$$

Where; q = adsorbed amount of heavy metals (mg/g),
C_o = initial heavy metal concentration (mg/L),
C_e = heavy metal concentration in the adsorption equilibrium (mg/L),
V= volume of the solution (L),
m = mass of bio-sorbent (*Spirulina platensis—Spirulina maxima* cells) (g). Each experiment was in triplicates.
The removal efficiency of the biosorbent (*Spirulina platensis—Spirulina maxima*) at equilibrium was determined using Eqn. (3):

$$\boldsymbol{Adsorption\ (\%\ removal\ efficiency) = \frac{Ci - Ce}{Ci}\ x\ 100} \qquad (3)$$

where, C_i = initial concentrations (mg/L)
C_e = equilibrium concentrations (mg/L)
V = volume (L) of the adsorbent
W= mass (g) of the adsorbent

The equilibrium adsorption isotherm phenomena were explained by adsorption isotherms of Langmuir and Freundlich. Langmuir's isotherm (Eqn. 4) is as follows:

$$\boldsymbol{q_e = \frac{q_{maxK_L C_e}}{1 + K_L C_e}} \qquad (4)$$

Where; q_e = maximum adsorption capacity (mg/g),
K_L = Langmuir's isotherm constant which shows the binding affinity between Cadmium and *Spirulina platensis—Spirulina maxima cells.*

To identify the adsorption parameters, the transformed linearized form of the Langmuir's isotherm (Eqn. 5) is used.

$$\boldsymbol{\frac{1}{q_e} = \frac{1}{K_L q_{max}} \bullet \frac{1}{C_e} + \frac{1}{q_{max}}} \qquad (5)$$

The value of R_L was obtained according to (Eqn. 6)

$$R_L = \frac{1}{1 + C_i K_L} \qquad (6)$$

Where; R is dimensionless Langmuir constant which indicates adsorption possibility either favourable ($0 < R_L > 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

Freundlich's isotherm is represented by (Eqn. 7) whiles the linearized form is shown (Eqn. 8)

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (7)$$

$$Log q_e = Log K_f + \frac{1}{n} Log C_e \qquad (8)$$

where; K_f is Freundlich's constant which measures adsorption capacity,

1/n represents adsorption intensity which intend indicates the adsorption process either, favourable ($0.1 < 1/n < 0.5$) or unfavourable ($1/n > 2$). R^2 describes which model best fits the results of the experiment.
The linear fit must pass through all the points to demonstrate the suitability of the model to the experimental results.
The average relative deviation values from the two methods were compared as PSA to the AAS referent method. According to Eqn. 8, the average relative deviation was calculated. All measurements were in triplicates and the mean values were recorded.

$$\delta = \frac{C_m AAS - C_m PSA}{C_m PSA} x\, 100 \qquad (8)$$

Where; C_m is the concentration of heavy metals Zn, Cu, and Pb ions.

2.7. Statistical analysis

ANOVA was employed in the factorial design verification. Kruskal-Wallis rank-sum test was used to check the violation of assumptions. Var.test and shapiro-Wilk normality were used to check homogeneity and normal distribution respectively. Dunnett's test and Simpson's index were also used to check multiple comparisons of independent samples and concentration accuracies respectively. The vertical error margin of plots was also checked by ErrBars. The R statistical software and DescTools package were used for statistical analysis [32].

RESULTS AND DISCUSSION

3.1. Relationship between linear logarithm and potentiometric stripping step

Conditions examination of constant inverse current, potential of electrolysis, stirring rate of solution, mercury electrodeposition time, were optimized prior to Cd^{2+}, Zn^{2+}, Cu^{2+} and Pb^{2+} determination. Heavy metal concentrations were determined whiles analytical signal and detection limit linearity was established. A Mercury(II) solution prepared with 0.1M HCl was electrodeposited at 1-10µA for 150s onto glassy carbon electrode to form a thin film. Mercury deposition time was studied in relation to reproducibility of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} in solution where PSA signal represented heavy metal concentrations.
When conditions were optimized, best parameters such as; 150s deposition time, and 0% reproducibility which represents coefficient of variance, a linearized function of signal were obtained with lowest detection limit of 0.124 mg/L.

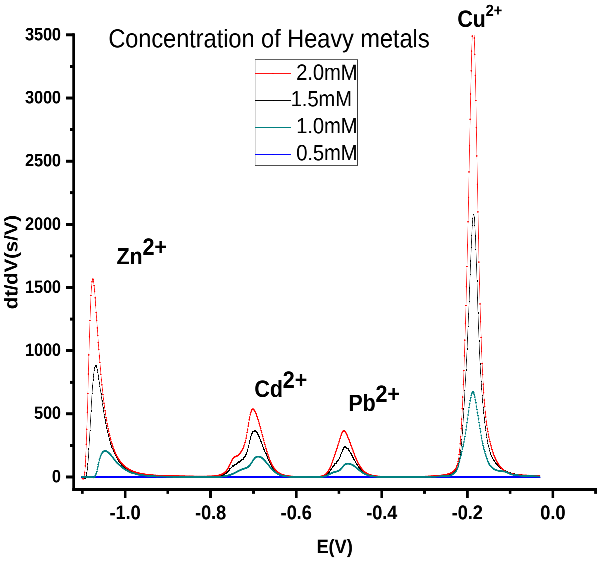

FIG. 5. SIGNAL OF Cu, Zn, Pb, AND Cd IONS DETERMINED SIMULTANEOUSLY

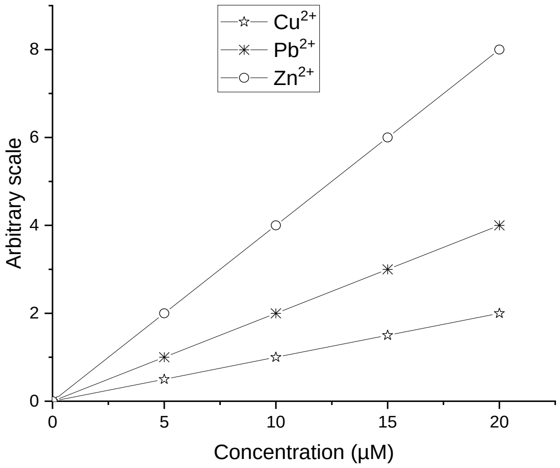

FIG. 6. THE CALIBRATION CURVES FOR ARBITRARY SCALE FOR SIMULTANEOUS DETECTION of Cu^{2+}, $Zn^{2+,}$ AND Pb^{2+}

Spirulina platensis—Spirulina maxima cells were used to investigate adsorption potentials of heavy metals and the effect of increasing concentrations of Cd^{2+} on other heavy metals (Cu^{2+}, $Zn^{2+,}$ and Pb^{2+}). Electrochemical and chemical parameters were optimized to achieve efficient deposition and stripping steps which influence the accuracy the results. The analytical signals had good linearity and were within range. Analytical signals on an arbitrary scale have also been demonstrated (Fig. 5 and Fig. 6). Equations (1) and (2) were used for the calculation of Zn, Co, Cd, and Pb content in analyzed samples. The measured results in aqueous solutions have been presented (Tables 2 and 3) and on Fig. 6 and Fig. 7. The following are the optimized conditions: Mercury deposition potential was performed with 5.0 mL of 0.5 mM oxidant mercury (II) $HgCl_2$ solution) at -1.1 V for 60 s. The conditioning step was with 0.1M HCl at -0.15 V for 60 s. heavy metal deposition step was -1.5 V for 150 s-450 s and equilibration step was also achieved with -1.1V for 30 s. Removal of mercury from electrode surface was with 0.1M HCl at +0.3 V for 15 s. A linear logarithm and stripping relationship was thus achieved as follows; 3.12×10 to 4.20×10^7 cfu mL^{-1}, 2.67×10 to 2.3×10^7 cfu mL^{-1}, 1.31×10 to 2.10×10^7 cfu mL^{-1} for Cu^{2+}, Zn^{2+} and Pb^{2+} respectively.

3.2. Atomic Absorption Spectroscopy and Potentiometric Stripping Analysis results

It is very important to consider analytical instruments that can accurately quantify the levels of contaminants in complex media. In line with this, Electrochemical analytical method was thus selected for this experiment. The two methods, Atomic Absorption Spectroscopy and Electrochemical analytical methods proved robust because neither physical nor chemical parameters affected the results.

TABLE 2. HEAVY METAL CONCENTRATION IN Cd^{2+} (25-500mg/L) BY ATOMIC ABSORPTION MEASUREMENTS (ATOMIC FLAME ANALYSIS)

Initial conc. of Cd^{2+}	Final concentration(%±SD)		
	Zn2+	Pb^{2+}	Cu^{2+}
25	26.00±1.8	32.00±0.9	38.50±1.2
50	22.50±1.8	30.00±1.1	37.10±1.0
75	21.60±1.9	32.00±1.0	47.80±2.1
100	19.50±2.0	11.40±0.8	45.60±2.0
125	17.30±2.4	22.00±1.1	48.80±0.9
150	24.00±1.98	19.00±1.0	47.60±2.5
200	22.80±1.9	28.80±1.5	24.80±1.3
250	24.10±1.9	18.10±1.6	45.00±1.9
300	26.10±1.7	26.60±1.7	42.00±2.0
350	17.40±1.0	16.00±2.2	38.70±1.8
400	18.30±2.0	10.90±0.9	13.40±0.9
450	16.80±2.1	19.90±1.8	18.00±0.8
500	12.30±1.8	15.60±1.3	11.40±.09

TABLE. 3. HEAVY METAL CONCENTRATION IN Cd^{2+} (25-500mg/L) BY ELECTROCHEMICAL MEASUREMENTS (POTENTIOMETRIC STRIPPING ANALYSIS)

Initial conc. of Cd^{2+}	Final concentration(%±SD)		
	Zn2+	Pb^{2+}	Cu^{2+}
25	30.00±1.9	29.00±1.2	39.20±0.9
50	26.60±1.4	29.30±2.0	35.80±1.0
75	25.00±1.5	32.00±2.2	45.80±0.8
100	17.90±2.0	11.40±1.2	47.00±1.3
125	16.90±2.4	23.90±1.7	45.80±0.7
150	24.00±1.6	21.00±0.9	44.40±1.1
200	22.80±1.6	28.80±1.9	25.00±0.8
250	24.10±1.5	18.10±2.1	42.00±1.0
300	24.10±1.5	24.60±0.9	38.70±0.9
350	19.40±1.8	16.00±0.9	36.40±1.2
400	16.80±1.8	10.90±1.4	14.00±1.2
450	16.80±1.9	20.90±0.9	19.40±0.9
500	12.00±2.0	16.40±1.2	11.20±1.4

Both analytical methods produced comparable results by employing both ASS and PSA methods. This adsorption decreased due to toxicity, competition for ion exchange sites of Cu^{2+} at higher concentrations to the *Spirulina platensis*—*Spirulina maxima* cells. Generally, Copper is less reactive as compared to Pb and Zn. These might be some possible reasons for less copper adsorption by Spirulina platensis—Spirulina cells.

The findings of final concentrations for Zn, Cu, Pb with initial concentrations were 50 mg/L in all samples have been represented (Table 2 and Table 3). All measurements from both methods are similar and comparable. From both analytical results, it was demonstrated that when Cd concentration was higher than 300 mg/L, the adsorption of Zn^{2+}, Cu^{2+}, Pb^{2+} decreased by about 5-15% on average. This could be attributed to the effects of a higher concentration of Cd on the other heavy metals. The higher concentration of Cd could have also inactivated Spirulina platensis—Spirulina cells and disfavored adsorption of the other metals. The Cu^{2+} in Cd^{2+} was higher on average compared to that measured in the Pb^{2+} and Zn^{2+}samples. This might be attributed to the fact that the algae absorbed little of the copper from the samples. The results from AAS and PSA are closely related. This served as a confirmation of the final concentrations of all heavy metals in all samples.

3.3 Relative deviation (δ) (%) for Atomic Absorption Spectroscopy and Potentiometric Stripping Analysis

TABLE 4. RELATIVE DEVIATION (δ) (%) BY AAS AND PSA ANALYTICAL METHODS

δ_{Zn} (%)	δ_{Pb} (%)	δ_{Cu} (%)
15.38	-9.38	1.82
18.22	-2.39	-3.50
15.74	0.00	-4.18
-8.21	0.00	3.07
-2.31	7.95	-6.15
0.00	9.52	-6.72
0.00	0.00	0.81
0.00	0.00	-6.67
-7.66	-8.13	-7.86
11.49	0.00	-5.94
-8.20	0.00	4.48
0.00	4.78	7.78
-2.44	4.88	-1.75

The Relative deviation, δ (%) has been calculated (eqn. 8). According to the concentration of analyzed Zn, Cd, Pb, and Cu ions by PSA and AAS techniques, there is a good agreement between the two techniques. The lower SD values also demonstrated good reproducibility of the signals for the measured metal ions. These results indicated the reliability and suitability of the PSA technique for the determination of metals in complex systems and other samples. This implies that accuracy and trueness were maintained in the two analytical methods. In the AAS analysis where dilution was necessary, this could result in a few errors but this did not affect the analysis considerably.

3.4 Adsorption Mechanisms by Langmuir and Freundlich isotherms

By loading the data set of the final concentration of Cd^{2+} from the Zn^{2+} containing solution which is one of the studied elements onto Langmuir and Freundlich isotherms. The data set fitted better with Langmuir isotherm (Fig. 7). The line of linear fit passed through all points. The linear regression coefficient for Langmuir and Freundlich isotherms were $R^2 > 0.999$ and $R^2 > 0.987$ respectively (Fig. 7). This verified a monolayer adsorption phenomenon. In terms of the favourability of the Langmuir isotherm, the value of the dimensionless Langmuir constant (R_L) representing the possibility of adsorption favourability or otherwise was 0.963 which revealed that, the Langmuir isotherm favored the adsorption phenomena. Adsorption intensity (1/n) by Freundlich isotherm is 1.024 which is an indication of the unfavorability of Freundlich's isotherms to the data set.

TABLE 5. ADSORPTION MECHANISM OF CD

Isotherm	Parameter	Value
Langmuir	qmax (mg/g)	150.8296
	K_L (mg/L)	0.000383
	R_L	0.963067
	R^2	0.99901
	1/n	1.024391
	K_f	0.065340
	R^2	0.98735

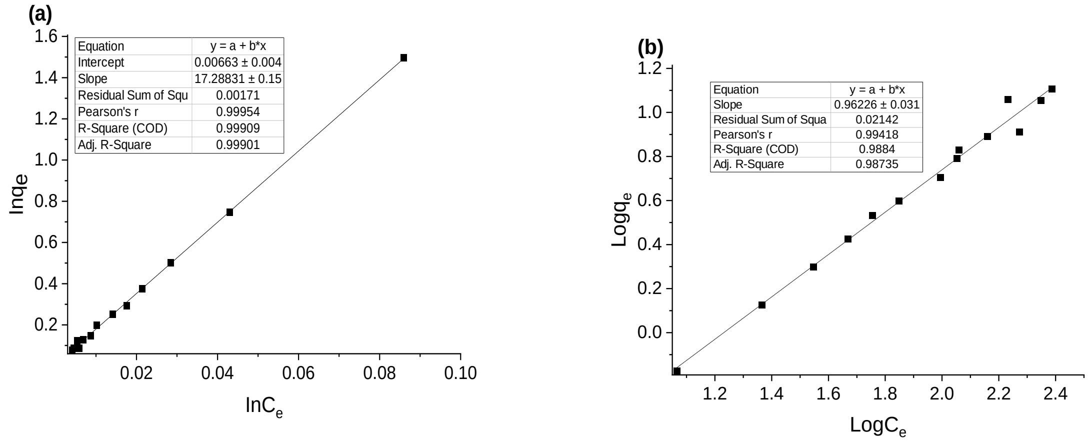

FIG. 7. ADSORPTION ISOTHERM BY (A) LANGMUIR (B) FREUNDLICH

3.5 *Chromium phytoavailability assessment in soils*

The photoavailability studies employ the leaching procedure recommended by Lakanen–Erviö for indirect estimation of heavy metal in soils that can be adsorbed through plants uptake. Higher phytoavailable As species could represent a higher risk of uptake by plants and other living organisms in these soils as well as contamination of nearby water bodies through percolation. On average, the photo available As in Mpamprome and Empan Mu is lower than 10%. This indicates the lower risk of contamination to plants and other organisms and water bodies in the catchment area. However, As in the soil from Nassara exceeded 20% (Fig. 8a) and this could present a higher risk to plants, other living organisms in the soil, and water bodies within the vicinity. By correlating the phytoavailable heavy metal in the soils to the physicochemical parameters such as lower Mn, lower Fe, lower CEC, lower pH and higher OM, the soil from Nassara confirmed our investigation. Often times, complexation of Cr(III) is hindered by aquo complex inertness and thermodynamic stability [34]. During unfavorable conditions such as excessive moisture and higher OM content, physicochemical conditions of the soil could change which affects photoavailability of heavy metal in the environment [33]. This could cause higher release of chromium from the soil systems (Fig. 8).

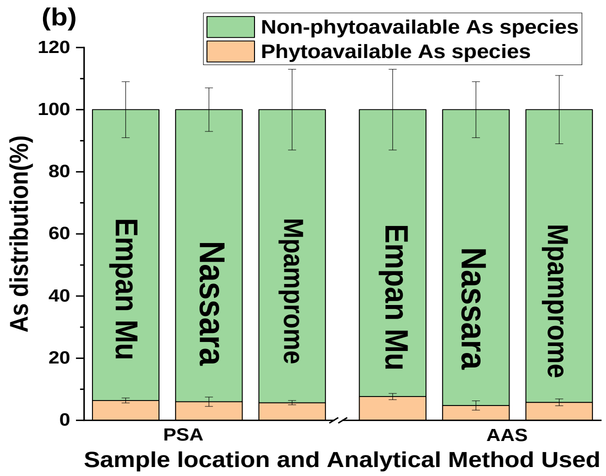

FIG.8. DISTRIBUTION (%) AMONG THE FRACTIONS PHYTOAVAILABILITY TESTS (A) CR (B) AS. RELATIVE STANDARD DEVIATION (%) IS SHOWN AS ERROR BARS FROM CALCULATED DATA (N = 3).

Indirectly, Lakanen–Erviö leaching test provides evidence on inorganic arsenic (iAs(V)) contaminant uptake by plants (Fig. 8). Ethylenediaminetetraacetic acid does not form coordinate compounds with iAs(V). However, Ethylenediaminetetraacetic acid form coordination bonds with compounds containing Fe(III) and Mn(IV). EDTA is a universal extractant that is used (in)direct for the determination of many elements [34]. The non-phytoavailable As species distribution according to Lakanen–Erviö leaching test in the current investigation was <10% on average in all studied soils. Both analytical techniques provided similar and comparable results. The variation from each analytical measurement was < 1% (Fig. 8b) indicating the reliability of the results. A higher phytoavailable heavy species indicate a possibility of pollution of living organisms in the soil system of the location. Moreover, through percolation, water bodies could be contaminated. In the present study, the lower average phytoavailability values indicated a minimal effect of Cr in the studied soils. This could be as a result of higher Cr associated with amorphous Fe(III)/Mn(IV).

TABLE 6. RECOVERY RATES (%) FOR ARSENIC IN SOIL SAMPLES

Sampling location	Atomic Absorption Spectroscopy		
	As Concentration		Recovery (%)
	∑Fraction	Pseudo-total	
Mpamprome	220.21±9	234.25±7	106
Nassara	460.72±5	498.95±5	108
Empan Mu	412.11±5	440.25±6	107
	Potentiometric Stripping Analysis		
Mpamprome	243.25±7	223.93±7	92
Nassara	516.95±3	467.17±4	90
Empan Mu	452.25±4	416.58±7	92

TABLE 7. RECOVERY RATES (%) FOR CHROMIUM IN SOIL SAMPLES

Sampling location	Atomic Absorption Spectroscopy		
	Cr Concentration		Recovery (%)
	∑Fraction	Pseudo-total	
Mpamprome	223.93±8	229.93±6	103
Nassara	467.17±5	489.17±7	105
Empan Mu	416.58±7	431.58±8	104
	Potentiometric Stripping Analysis		
Mpamprome	229.93±7	250.21±8	109
Nassara	489.17±4	471.15±5	96
Empan Mu	431.58±6	432.25±8	100

Comparing the analytical techniques employed for the analysis, the recovery rates for heavy metals were in good agreement with previous studies [33]. In almost all the recovery rates obtained from the potentiometric stripping analysis, the percentage rate values did not exceed 100% except in two instances (Table 6 and Table 7). Although values from the AAS measurement slightly exceeded 100% by >10% in most instances, the results were still within the acceptable limit for soil sample results. Even though a much higher deviation in recovery rate is usually accepted for soil investigations, the present study gave lower deviation from the two methods.

CONCLUSION

Both methods produced good results. However, the findings from the electrochemical method showed reliability, reproducibility, simultaneous determination of metals, and accuracy. The analytical method for the potentiometric chemical stripping is ready for routine studies. Moreso, multi-elements can be determined in the same calibration in the presence of a minimal oxidizing agent and a similar concentration of Mercury(II). Effects of Cd^{2+} (25-500mg/L) in an increasing concentration on Cu^{2+}, Pb^{2+} and Zn^{2+} the presence of Spirulina platensis—Spirulina cells was evident at higher concentrations where there were lower adsorption rates especially with regards to the Potentiometric Stripping Analysis. The study also generated relevant information on the Cr and As phytoavailability in soils for future investigations.

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