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Hexavalent chromium bioremediation using *Hibiscus Sabdariffa* calyces extract: Process parameters, kinetics and thermodynamics

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ABSTRACT

Hexavalent chromium toxicity remains an indispensible toxicity to bioremediation. It has environmental and health impact in areas of hexavalent chromium discharges. This persistent problem associated with hexavalent chromium toxicity had led to employment of both physical and chemical means of control, which suffers major drawbacks. These drawbacks include; incomplete metal removal, high energy requirement, high reagent consumption and high cost of implementation. Bioremediation via bioreduction can be explored using plants rich in antioxidants. Hibiscus sabdariffa is a plant rich in antioxidants. In this study the bioreduction potential of Hibiscus sabdariffa calyces extract in bioremediation of toxic hexavalent chromium (Cr VI) to less toxic trivalent chromium (Cr III) was examined. In a batch mode, the effect of process parameters viz pH, temperature, initial Cr (VI) concentration, contact time and bioreductant concentration was assessed on the bioreduction process. Hexavalent chromium was quantified using diphenyl carbazide complexing agent that forms violet colour. The kinetic and thermodynamic of the process was also investigated. The extract (1 mg/ml) was able to bioreduce 72% of 10 mg/L hexavalent chromium solution in 15 min. The optimized condition of the process was achieved at pH 2.0 and 25 °C. Kinetics studies on the bioreduction revealed pseudo second-order as the main kinetic path the reaction takes with R^2 values of 0.928, 0.993 and 0.997. The extract has the potential to reduce hexavalent chromium which is toxic to trivalent chromium (less toxic).

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Introduction

The increase in documented environmental events had resulted in regulatory measures to remedy past mistakes and protect the environment from future contamination and exploitation [30]. Discharges from textile, leather, tannery, electroplating, galvanizing, dyes and pigment, metallurgical and paint industries as well as other metal processing/refining operations at small and large-scale sector are loaded with considerable quantities of toxic metal ions. [45] stated that these emissions contained high amounts of heavy metals that are carcinogenic, mutagenic and teratogenic to life forms [46]. Various methods aim at remediating chromium (VI) from polluted environment and waste water include; adsorption [17], electrochemical ion exchange [8], membrane separation [12] and chemical reduction [14,48]. Conventional methods suffer certain limitations which include; requirement of a lot of energy, been too expensive and causing injury to the environment [30]. Other limitations are low reduction and incompetent removal of metals from solutions. Treatment is expensive, when membranes and high-pressure equipment's are required as in case of electrochemical ion exchange coupled with demand for electricity to power the process [8]. Now to overcome this limitation, adsorption was employed which is easy operationally and involves low cost. This is true because of availability of raw materials which have the potential of producing high quality water [7]. They add that chemical reduction using KOH and $ZnCl_2$ produces secondary environmental pollution which is undesirable. In the same line [30] demonstrated that lead sulfate precipitates Cr (VI) and produces a harmful secondary pollutant which must be taking care of and dispose of that is the new pollutant must be eliminated and this will require additional cost for it to be removed from the site.

Recently, plants extract were used in the synthesis of iron nanoparticles as reducing agent [11]. Iron salts and polyphenol in plants extract are mixed to form green iron nanoparticles. Some plants extract used include; *Eucalyptus globulus* leaf extract [21] sorghum bran [27] banana peel extract [38] ange peel [20] and *Urtica dioca* leaf extract [10].

In the continued quest for an alternative means of plummeting contamination especially that of hexavalent chromium, several studies were conducted which suggests that Cr (VI) can be removed using natural biomaterials through both direct and indirect reduction mechanisms [29]. Xu et al. [43] studied the reduction of hexavalent chromium by ascorbic acid using potassium dichromate as source of chromium VI ions. The study was able to demonstrate the effect of process parameters where about 70% of the starting chromium concentration was reduced within the first 5 minutes of the reaction. Literature search did not demonstrate the use of *Hibiscus sabdariffa* calyces extract in the bioremediation of chromium (VI). In the present study, the hydroxymethanolic extract of *Hibiscus sabdariffa* was used. The calyces were obtained as a waste product after the production of beverage drinks locally called "sobo". A large volume of this waste product from this process is usually discarded in refuse dump. This extract is rich in antioxidants which are heat labile but have chromium (VI) reducing potential. The reduction of toxic chromium (VI) to less toxic chromium (III) is utilized as an important step in depolluting chromium (VI) contamination [28,33,53]. The calyces are readily available and biodegradable. The significance of key parameters like amount of bioreductant (dose), contact time, initial chromium concentration, optimum pH, kinetics and thermodynamics of chromium (VI) bioreduction were studied.

Materials and methods

Materials

Plant material

The calyces of *Hibiscus sabdariffa* was purchased from a farm at Samaru area (Coordinates 9º 45'0" North, 8º 23'0" East) and authenticated in Department of Biological Science Ahmadu Bello University Zaria where a voucher (1802) was deposited for reference.

Reagents

Potassium dichromate ($K_2Cr_2O_7$) (Merck Germany), Sulfuric acid (98%) (H_2SO_4) (Merck Germany), Concentrated hydrochloric acid, Methanol (CH_3OH) (Guangdong Guanghua Sci. Tech Co., Ltd. Guangdong China, 515000), Ethanol (Guangdong Guanghua Sci-Tech Co. Ltd. Guangdong China, 515000), Diphenylcarbazide ($C_{13}H_{14}N_4O$) (Merck Germany), Sodium hydroxide (NaOH) (Merck Germany). Standard compounds including rutin hydrate, chlorogenic acid, kaempferol, formic acid, were purchased from Sigma Aldrich of St. Louis, MO. Quercetin was purchased from ACROS of Geel, Belgium. Folin Ciocalteu's Phenol Reagent was purchased from MP Biomedicals of Solon, OH. HPLC grade solvents including water, methanol, acetonitrile and hydrochloric acid (HCl) were purchased from Fisher Scientific of Fair Lawn, NJ.

Methods

Extraction

The dried powdered calyces were extracted by cold maceration in 70% methanol by drenching for 24 h. The polarity of methanol for phytochemical extraction is significant considering the vast number of both polar and non-polar compounds obtained and also their non azeotrope nature. Since the study does not involve biological system but rather heavy metal

remediation in soil and water, methanol was used as extracting solvent. The extract was then filtered into freeze drying glass canisters, freeze dried at −52 °C and subsequently, stored at −20 °C until further use [49].

LC-Mass analysis and spectrometric identification conditions

The phytoconstituents of *Hibiscus sabdariffa* calyces were determined using liquid chromatography (LC) tandem mass spectrophotometer (MS) as described by [32]. The methanol extract of *Hibiscus sabdariffa* calyces (HSCE) was reconstituted using the extraction solvent (70% Methanol) and solvents were initially filtered through polytetrafluoroethylene (PTFE) membrane filter with 0.45 μm size. After filtration, the HSCE (5.0 μl) was injected into the LC system and allowed to separate on Agilent zorbax Eclipse XDB-C18, Narrow-Bore 2.1 × 150 mm, 3.5 micron column. The run was carried out at a flow rate of 0.5 mL/mins and oven temperature at 25 °C. The mobile phase consists of 0.1% formic acid in water (solvent A) and 0.1% formic acid in acetonitrile (solvent B) in a linear gradient from A/B 95:5 to 0:100 in 25 min. This ratio was maintained for further 5 min. The mass spectra were acquired with a scan range from m/z 100–3200 after ensuring the following settings: ESI source in positive and negative ion modes; capillary voltage 4000 V (positive) or 3500 V (negative); gas temperature 300 °C; flow rate 10 mL/min; nebuliser gas, 45 psig. MS/MS set in automatic mode applying fragmentation voltage of 125 V. The data was processed with Agilent mass hunter qualitative analysis and molecular feature extraction (MFE). The polyphenolic compounds were identified on the basis of the following information, elution order, and retention time (t_R), fragmentation pattern as well as comparison of these information with standards purchased from reputable vendors, used according to manufacturer's guide and supported with reported literature.

Determination of Cr (VI) concentration (Diphenylcarbazide method)

The chromium (VI) concentration was quantified using diphenylcarbazide. The principle of the assay is based on the quantification of residual chromium (VI) at a given time interval after the incubation of Cr (VI) with the bioreductant (HSCE). Hexavalent chromium reacts with diphenylcarbazide to form a red-violet complex which was subsequently read at 540 nm using a UV-visible spectrophotometer.

Determination of bioreduction potentials Hibiscus sabdariffa

Batch experiment was conducted to assess the bioreduction potentials of the hydroxymethanol extract of *Hibiscus sabdariffa* calyces. Potassium dichromate was used as the sources of the model contaminant chromium VI (Cr^{6+}). Fifty milliliters of Cr (VI) solution was placed in cocked 250 ml Erlenmeyer flask, the pH was adjusted to the required state which was then followed by addition of 50 ml of 0.1 mg/ml hydroxymethanol extract of *Hibiscus sabdariffa* calyces or otherwise specified. The reaction solutions were prepared using deionized water and covered to exclude air penetration. The pH of the Cr (VI) solution was adjusted at the beginning by addition of 0.1M HCl and/or 0.1M NaOH solutions and checked using Agilent 3200P pH meter [24,26,37]. All experiments were conducted at room temperature (i.e 25 ± 1 °C) and in triplicate. The bioreduction process using HSCE was possible at all pH studied during the pilot studies. In the preliminary investigation, it was discovered that both acidic and alkaline pH states of the chromium VI solution changes to neutrality after the addition of the HSCE at the end of incubation period. This suggests the occurrence of a redox reaction. It was further observed the efficiency of the process at the pH of the studies (2.0, 7.0 and 9.0) gave similar outcome. Chromium display different types of pH dependent equilibria in solutions. When there is an adjustment in the pH it causes a corresponding tilt in the equilibrium. Hence at pH below 2 chromium ion ($Cr_3O_{10}{}^{-2}$ and $Cr_4O_{13}{}^{-2}$) species are formed in solution. Consequently, when the pH is adjusted from 2 to 6 the prevailing chromium ions are $HCrO_4{}^-$ and $Cr_2O_7{}^{2-}$ while at pH values above 8, $CrO_4{}^{2-}$ dominate the solution [25]. In the present approach, electron transfer plays a significant role; the reduction of Cr (VI) to Cr (III) requires a large amount of protons [3,18] which are provided by the bioreductant present in HSCE.

$$Cr_2O_7{}^{2-} + 14H^+ \text{ (HSCE)} + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$$

$$CrO_4{}^{2-} + 8H^+ \text{ (HSCE)} + 3e^- \leftrightarrow Cr^{3+} + 4H_2O$$

$$HCrO_4{}^- + 7H^+ \text{ (HSCE)} + 3e^- \leftrightarrow Cr^{3+} + 4H_2O$$

Determination of temperature effect on Cr (VI) bioreduction using HSCE

The effect of temperature on Cr (VI) bioreduction by HSCE was studied using batch experimentation as described above by placing the pH adjusted chromium VI solution in a cocked 250 ml Erlenmeyer flask and varying the reaction temperature; 5 °C, 15 °C, 25 °C and 40 °C in a thermostat waterbath. The residual hexavalent chromium concentration was quantified using 1, 5–diphenylcarbazide method. The pH of Cr (VI) solution was adjusted once by the addition of 0.1M HCl and 0.1M NaOH solutions prior to the addition of the bioreductant [4,13,24] and measured using Agilent 3200P pH meter. The pH was observed to shift from the initial state of acidity/alkalinity to neutrality after the incubation period upon addition of the bioreductant (HSCE) during the pilot studies. Hence continuous monitoring of pH was not carried out. Similar studies have

Table 1
Phenolic compounds obtained from *Hibiscus sabdariffa* calyces using LC-MS in positive ionization mode.

Compound Label	Mass Fragment	Mass (m/z)	Tentative Identification
1	182.98	181.97	Hibiscus acid derivative
2	355.09	354.09	Caffeoylquinic acid derivative
3	279.15	278.15	Quercetin-*O*-pentose
4	205.08	204.07	Hydroxycitric acid derivative
6	778.55		Quercetin-3-*O*-glucosyl-pentoside-7-glucoronide derivative
7	456.36	455.36	Chlorogenic acid derivative
8	384.34	383.32	Feruloyl-quinic acid derivative
9	512.50	511.49	Dicaffeoyl-quinic acid derivative

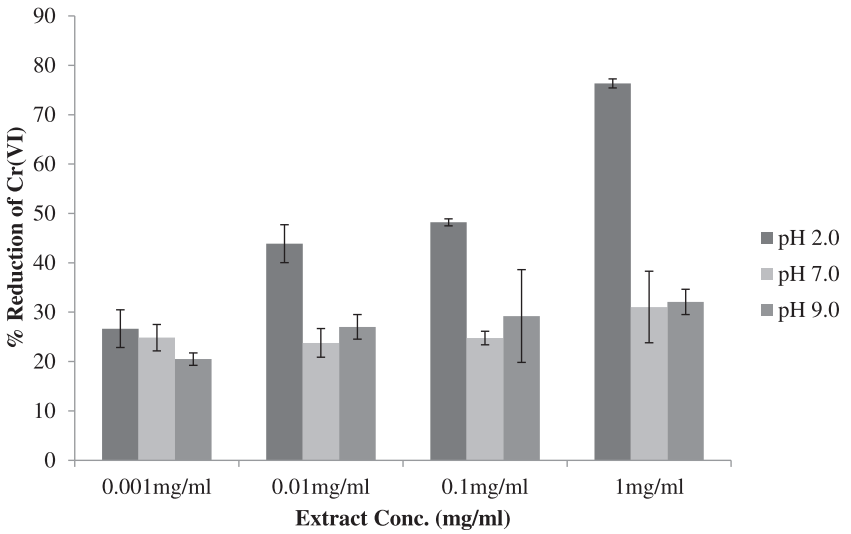

Fig 1. Effect of varying extracts concentrations (bioreductant dose) on bioreduction of chromium (VI). Bioreduction conditions are; Cr (VI) (10 mg/L), Temp 25 °C.

reported the adjustment of pH of the chromium solution at the onset of the studies and once without further monitoring [13,26,37].

Results

Table 1; presents the various phenol and flavonoids detected and identified in *Hibiscus sabdariffa* calyces extract (HSCE) by liquid chromatography-electrospray ionisation tandem mass spectrophotometry LC-ESI MS.

Effect of bioreductant dose

Fig. 1 demonstrates the effect of varying extract concentration (bioreductant dose) on bioreduction of Cr (VI). From the figure, there was steady increase in percentage reduction of Cr (VI) from 25% to 75% and 21% to 30% at pH 2 and pH 9 and at bioreductant doses of 1 mg/ml and 0.001 mg/ml concentration of HSCE. While at pH 7 there was a decrease from 28% (0.01 mg/ml) to 25% (0.01 mg/ml and 0.1 mg/ml) and a slight increase to 30% (1 mg/ml) afterwards.

Effect of initial Cr (VI) ion concentration

The effect of initial Cr (VI) concentration on the bioreduction of Cr (VI) by HSCE was studied. At an extract dose of 0.1 mg/ml, varying concentrations of Cr (VI); 1 mg/L, 10 mg/L, 50 mg/L, 100 mg/L, 250 mg/L and 500 mg/L were incubated. The results attached as Fig. S1 suggest that the residual Cr (VI) concentration increases in a concentration dependent manner i.e as the initial Cr (VI) concentration increase so also the residual Cr (VI) concentration. At pH 2, the increase is such that it increase from 1 mg/L to 10 mg/L and it level up/plateau from 50 mg/L to 500 mg/L in the same manner, at pH 9 a similar outcome was recorded. But at pH 7, there was increase from 1mg/L, 10 mg/L and 50 mg/L from where it level up.

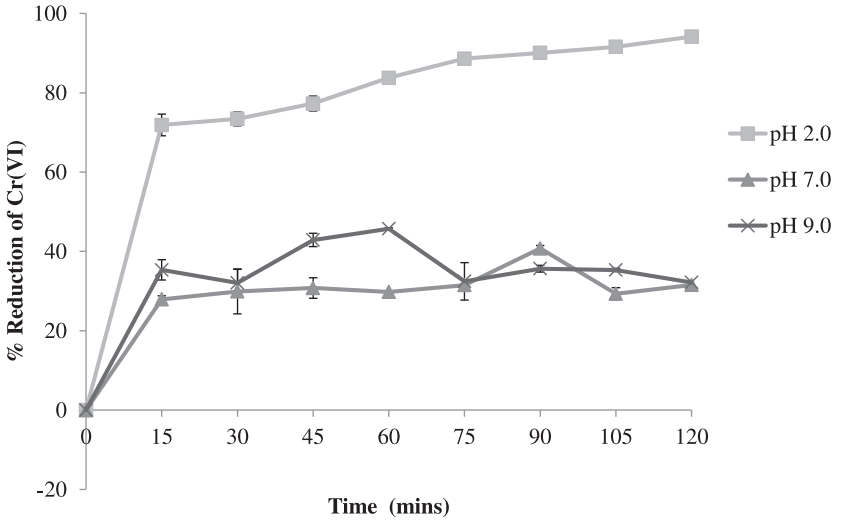

Fig 2. Effect of contact time on bioreduction of Cr (VI) by *Hibiscus sabdariffa* calyces. Bioreduction conditions: 0.1 mg/ml bioreductant, contaminant (10 mg/L).

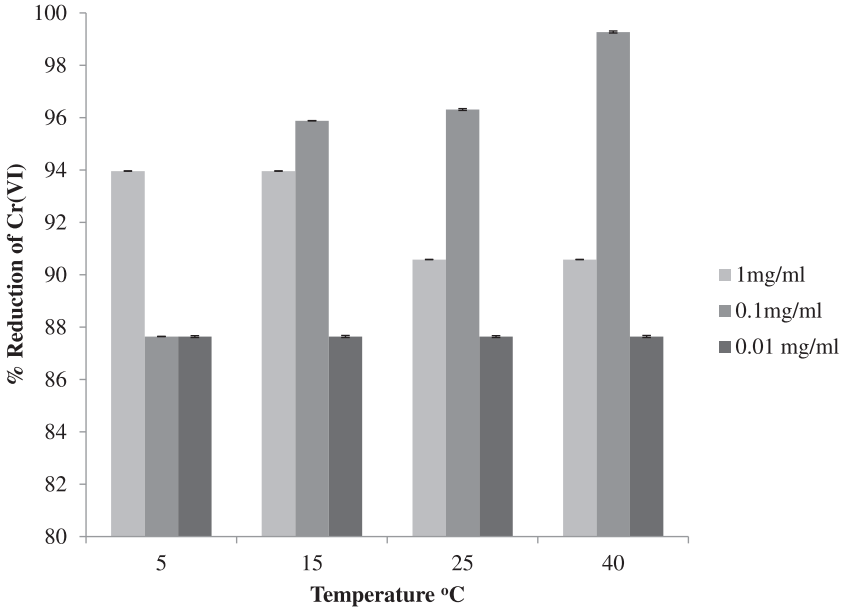

Fig 3. Effect of temperature on bioreduction of Cr (VI) by *Hibiscus sabdariffa* calyces. Bioreduction conditions; 1 mg/ml, 0.1 mg/ml and 0.01 mg/ml bioreductant concentrations, chromate solution (10 mg/L), pH 7.0, incubation time 30 min.

Effect of contact time

The effect of contact time on bioreduction of Cr (VI) at varying pH is demonstrated in Fig. 2. From the plot, there was a sharp increase in the bioreduction of Cr (VI) by HSCE at all pH under study in the initial 15 min; where over 70% decrease in Cr (VI) ions was observed which then gradually build to 90%. The highest percentage reduction was observed at pH 2 while the least reduction in Cr (VI) was recorded by pH 7.

Table 2
Summary of kinetic parameters for bioreduction of hexavalent chromium using *Hibiscus sabdariffa* calyces Extract (HSCE).

Kinetic Model	pH 2	pH 7	pH 9
Pseudo-First-Order			
$\mathbf{q_e}$(mg/ml)	0.750	0.223	0.548
$\mathbf{k_1}$(mg/ml/min)	0.001	0.016	0.001
$\mathbf{r^2}$	**0.013**	**0.538**	**0.124**
$\mathbf{t_{1/2}}(s^{-1})$	693.74	43.32	693.74
Pseudo-Second-Order			
$\mathbf{q_e}$(mg/ml)	**0.101**	**0.088**	**0.080**
$\mathbf{k_2}$(mg/ml/min)	0.097	0.031	0.010
$\mathbf{r^2}$	**0.928**	**0.993**	**0.997**
$\mathbf{t_{1/2}}(s^{-1})$	**7.15**	**22.35**	**69.31**

Table 3
Summary of thermodynamic parameters for bioreduction of Cr (VI) by *Hibiscus sabdariffa* calyces extract (HSCE) (pH 2.0, 7.0 and 9.0).

pH	Temperature (K)	-ΔG° (J/mol)	ΔS° (J/K/mol)	ΔH° (J/mol)
2	**293**	438.34	0.509	-289.2
2	**303**	443.43		
2	**313**	448.52		
7	**293**	591.01	2.074	16.59
7	**303**	611.83		
7	**313**	632.57		
9	**293**	2018.34	3.066	-1120
9	**303**	2048.99		
9	**313**	2079.66		

Effect of temperature

The impact of temperature on bioreduction of Cr (VI) by HSCE is described by Fig. 3. Three different concentrations of bioreductant (HSCE); 1 mg/ml, 0.1 mg/ml and 0.01 mg/ml were studied and the result as presented in Fig. 3. From the plot, over 87% of Cr (VI) ions were bioreduced by HSCE at 5 °C. A steady increase in the bioreduction was recorded with increase in temperature up to 40 °C where 99% of Cr (VI) was bioreduced. Similar observation was recorded when the study was carried out at pH 2.0 and pH 9.0. The outcome of the studies is presented in Table S1.

Kinetic of bioreduction

Data obtained from the batch experiments were fit into pseudo first order and pseudo second order kinetic plots as described by [15], at pH 2.0, 7.0 and 9.0 to evaluate Cr (VI) bioreduction by extract of *Hibiscus sabdariffa* calyces. Their r^2 values were found to be first order; 0.013, 0538 and 0.124; second order; 0.928, 0.993 and 0.997. Table 2 presents the summary of the kinetic parameters.

Thermodynamics

Data obtained from the batch experiment was then used for Van't Hoff's plot for bioreduction thermodynamics. The thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were then evaluated from the plot as described [22]. The change in enthalpy (ΔH^o) and change in entropy (ΔS^o) were calculated respectively from the slope and intercept of the Van't Hoff's plot of $\ln K_c$ against 1/T where kc is obtained using kc = [Product at Time t] / [Reactant at time zero]. Their corresponding correlation coefficients were 0.959 (pH 2.0), 0.954 (pH 7.0) and 0.907 (pH 9.0). The values of ΔS^o and ΔG^o were determined from the intercept and slope of the plots and are presented in Table 3.

Discussion

The resulting waste generated after the removal of the beverage content for use is a sure means of obtaining additional value. The waste was extracted using methanol since the study is targeted against pollution/contamination arising from heavy metals. The identified phytoconstituents using LC MSMS can be classified into phenolics and flavonoids. The phenolics include; Hibiscus acid, caffeoylquinic acid, hydroxycitric acid, feruloyl-quinic acid and dicaffeoyl-quinic acid while the flavonoids include; quercetin-*O*-pentose, quercetin-3-*O*-glucosylpentoside-7-glucoronide derivative [52]. The role of these phytochemicals in the bioreduction of Cr (VI) have been linked to their numerous hydroxyl groups that have radical scavenging activities which are mainly responsible for the conversion of Cr (VI) to Cr (III) as reported [44,1].

In Fig. 1, bioreduction of chromium (VI) was enhanced with increase in concentration of bioreductant (HSCE). This might not be unconnected with increase in antioxidants and free radical-scavenging capacity as the concentration of the bioreductant (HSCE) increases. Antioxidant activities have been associated with the number of free hydroxyl groups present in it [23]. With increase hydroxyl groups due to increased antioxidant concentration, the antioxidant activity increases eventually increasing Cr (VI) reduction efficiency. From the experiment, 0.1 mg/ml dose of the bioreductant was able to bioreduce 7 mg/L of the 10 mg/L chromium (VI) ions at pH 2. The result of this study is similar to the outcomes of [43] in the bioreduction of hexavalent chromium using ascorbic acid.

The residual Cr (VI) ion concentration increase with increase in initial Cr (VI) ion concentration observed from 1 mg/L to 500 mg/L, might be attributed to the presence of more hexavalent chromium ions in solution not reduced by the bioreductant with the increase in the Cr (VI) concentration at constant HSCE concentration. The better bioreduction at lower Cr (VI) ion concentration observed could as well be related to sufficient amount of antioxidants that compete favorably with the metal ion at lower concentration which is not so at higher concentration of the Cr (VI). It has been stated that at higher concentrations of heavy metal ion, there is a slow bioreduction process which translates into increase in residual Cr (VI) concentration [22]. The finding in this study is in harmony with other reports [41] for vitamin C and that of *Sorbaria sorbifolia* [9].

The increase in percentage reduction of Cr (VI) reaching as high as 72% with increase in contact time indicates that hydroxyl groups from the polyphenol and antioxidant had sufficient time to interact with Cr (VI) and reduce it. This effect is similar to earlier reports by [9] for Cr (VI) reduction by *Sorbaria sorbifolia* and also those of gallic acid by [6] for reduction of hexavalent chromium. The observed fluctuation with pH 9.0 was probably due to the activity of different antioxidants at the varying pH level [36] reported that different antioxidants show varying activity at different pH state. In acidic pH, antioxidants activities of phenolic acids have been reported to be more significant while flavonoids are more soluble and show better antioxidant activity at pH 8 [36,47,51].

The observed increase in percentage reduction of Cr (VI) may be related to the fact that at higher temperatures entropy of a system tends to increase leading to increased randomness and reduction in stability of metal ion [19]. This facilitates more interaction and also accelerated dehydrogenation of the antioxidants bringing the heavy metal ion close enough and enhances the reaction rate [19]. At higher temperatures than those of the present study, the integrity of the antioxidants would be lost. Considering other studies, the present findings correlates with reports of [6,42,40] in bioreduction of Cr (VI) using gallic and ascorbic acids. pH is significant in understanding the mechanism of redox reactions. From Fig. 2, there was observed rapid increase in percentage bioreduction of chromium (VI) within the first 15 minutes at all pH studied. This suggests that chromium (VI) bioreduction is such that as the pH increases percentage reduction decreases. This infers that a better reduction was observed at acidic point (72%) even though it is clear that hexavalent chromium reduction occurs in a wide range of pH from acidic to basic/alkaline states (25-35%). This result is significant because most of the reductants reported in literature have either low or no capacity at all to reduce Cr (VI) under alkaline conditions [31]. More than 90% reduction of Cr (VI) by magnetic nanoparticles at pH 2–4 was reported whereas it is 55% at pH 4–7 and only 40% at pH 7–10 [35]. The decrease in reduction efficiency from 72 to 25% when pH increases from 2 to 9, indicate that the reduction was pH dependent [36,39,51] have reported that most antioxidants; phenolic acids are more stable and have better activity in acidic pH while flavonoids are more soluble and have significant antioxidant activity at pH 8.

They further observed that it might also be related to the fact at pH beyond 6.0; the rapture of the heterocyclic ring may occur. The pH values of soil and ground water are between 5 and 9 but most remediation studies reported favorable activity in acidic state. Hence, HSCE could be used in the bioremediation of chromium (VI) contaminated soil and groundwater even in the alkaline region.

Fitting data to kinetic models is significant in the evaluation of bioreduction mechanism and performance [2]. From the correlation coefficient (r^2) values obtained for pseudo first order and pseudo second order models. It can be said that Cr (VI) bioreduction by HSCE presents an excellent linearity with high correlation coefficient; 0.928 pH 2.0, 0.993 pH 7.0 and 0.997 pH 9.0, at the examined condition (pH) when compared with the pseudo first kinetic model; 0.013, 0.538, 0.124 at pH 2.0, 7.0 and 9.0 respectively, which suggest that the rate determining step for Cr (VI) bioreduction by HSCE is governed by chemical reduction.

Thermodynamic considerations are important in throwing more light on the spontaneity of HSCE interaction with Cr (VI) ions. The negative values of ΔG at different temperature demonstrate that Cr (VI) bioreduction process was feasible and spontaneous. The positive values of ΔS indicates that there was increase in randomness in the system during the bioreduction reaction which allows good interaction between the oxidant (Cr VI) and bioreductant (HSCE) that would ultimately lead to the conversion of toxic Cr (VI) to less toxic Cr (III). This finding concurs with the reports of [22]. Based on these deductions in thermodynamics, the reactions were considered to be spontaneous, feasible and exothermic although it was endothermic at pH 7.0.

The outcome of the present study can be compared with the reports of [34], where they recorded 52% reduction in chromium VI ions when reacted with combination of citric acid and manganese over a 24 h period at acidic pH. The same study also recorded 84% reduction efficiency with citric acid alone and same time. The use of tartaric acid/isopropyl alcohol recorded 19% chromium VI reduction efficiency over a 99 h period [5]. Hence the present study can be included in the bioremediation of hexavalent chromium.

Conclusion

Bioremediation via bioreduction using waste from locally produced beverage produced from *Hibiscus sabdariffa* calyces was explored in the remediation of toxic hexavalent chromium. The extract of the calyces is rich in antioxidants that have hexavalent chromium bioreduction abilities. The process parameters were obtained under acidic, neutral and alkaline pH with the optimum bioreduction observed at pH 2 and temperature 25 °C. The pseudo-second order kinetic model best described the kinetics of the bioreduction process. Based on the thermodynamics, the reactions were spontaneous, feasible and exothermic although it was endothermic at pH 7.

Author contribution statement

According to the guide line of Scientific African, we wish to state that each author of this paper have contributed significantly in this work. Below is the role played by each of the authors.

Ahmad Adamu Ambi: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
Abdullahi Balarabe Sallau: Conceived and designed the experiments; Supervision, Writing-Review and Editing.
Mohammed Tijani Isa: took part in designing the experiments; supervision.
Abdulrazak Baba Ibrahim: took part in project supervision.
Musa Bashir, Silas Ekwuribe: performed some of the analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.sciaf.2020.e00642.

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