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Kinetics and thermodynamics of Cr (VI) reduction by *Tamarindus indica* methanol leaves extract under optimized reaction conditions

Babangida Sanusi Katsayal, Abdullahi Balarabe Sallau* and Aliyu Muhammad

Abstract

Environmental contamination with Cr (VI) has recently attracted public attention because of its high concentration in soil and wastewater originating majorly from anthropogenic activities and natural processes. Reduction of Cr (VI) to Cr (III) is a feasible method for minimizing chromium pollution. This work aimed at characterizing the effects of Cr (VI) reduction conditions in a batch experiment such as temperature, hydrogen ion concentration, time, and reactant concentrations, as well as kinetics and thermodynamics of the reaction using *Tamarindus indica* methanol leaves extract as a reductant. Cr (VI) reduction was meaningfully affected by temperature, hydrogen ion concentration, reaction time, and reactant concentrations. The reaction followed the pseudo-second-order kinetic model ($R^2 = 0.997$) at pH of 2; at the neutral and alkaline pH (7 and 9), the reaction predominantly obeyed first order ($R^2 = 0.988$) and pseudo-first order ($R^2 = 0.758$), respectively. Under various hydrogen ion concentrations, the reaction retains negative free energies, enthalpy change, and a positive entropy. The findings from this study suggested the reaction to be spontaneous, exothermic, and orderly unstable. We concluded that phytocompounds present in tamarind methanol leaves extract demonstrated a strong potentials for converting Cr (VI) to Cr (III) and, thus, could be applicable in Cr (VI) contaminated wastewater treatment.

Keywords: Tamarind, Chromium (VI) reduction, Kinetics, Thermodynamics, And Process parameter

1 Background

Weathering and volcanic eruptions are some of the processes that leads to human exposure to chromium [12]. In addition to natural phenomena, anthropogenic activities led to widespread chromium contamination in the environment, particularly in soil and water [7]. Chromium is detected in groundwater and soil predominantly in the trivalent [Cr(III)] and hexavalent [Cr(VI)] forms [22]. Due to its solubility, Cr (VI) diffuses easily through the soil and underground water, thereby considered a potential contaminant in the environment. Cr (VI) is highly toxic [21], soluble, mobile, as well as carcinogenic, mutagenic, and teratogenic [37, 42], while on the other hand, Cr (III) is less toxic, insoluble, immobile [9], and in addition impermeable to the cell membrane [1]. In comparison, Cr (VI) is about 100–1000 times more toxic to human health than Cr (III), partly due to its high solubility and cell permeability [16, 17, 25]. Exposure to Cr (VI) resulted in the formation of various forms of DNA damage, including strand breaks which can lead to cancer as well as other oxidative damage-related disorders [33]. A study with B6C3F1 mice and F344/N rats models shows exposures with drinking water containing Cr (VI) caused an increase in small intestinal cancers at ≥ 20 mg/L and oral cavity cancers at ≥ 60 mg/L, respectively [27, 43].

It is noteworthy that the toxicity of Cr (VI) is attributed to its cellular reduction to Cr (III) via reactive intermediates [2, 17, 29, 38]. Therefore, conversion of Cr (VI) in wastewater and contaminated soil can avert mobility; in consequence, Cr (III) will bind to the organic matter in the soil while precipitating in an aquatic environment

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[25]. This action will drastically reduce the risk of Cr (VI) contamination in drinking water and agricultural products and, hence, moderate the incidences of most of the diseases conditions of this century such as cancer, diabetes, gastrointestinal, and reproductive impairment. Herein, we examined Cr (VI) reduction potentials of *Tamarindus indica* methanol leaves extract, its relationship with antioxidant capacity of the plant, effect of some reaction factors, kinetic and thermodynamic of the reduction reaction. Therefore, findings from this study could be helpful in the treatment of industrial wastewater and Cr (VI) contaminated soil.

2 Methods

2.1 Reagents

Potassium dichromate (Fisher Scientific; Pittsburgh, PA, USA) was used as a source of hexavalent chromium, diphenylcarbazide (Merck Germany), Chromium (III) chloride hexahydrate (Analar 97%, England), sulfuric acid (98%), hydrochloric acid (85%), and sodium hydroxide were all of the analytical reagent grades and obtained from Sigma (St. Louis, MO, USA). Deionized water was used for all solutions and dilutions.

2.2 Extraction of tamarind leaves

Tamarind leaves were collected by a research assistant from Pharmacognosy Research Laboratory, Ahmadu Bello University Zaria. The leaves were washed with clean water and dried before being ground into fine powder. Extraction was carried out by maceration through soaking 500 g leaves powder in 70% methanol for two days. The solution was decanted and filtered through Whatman No. 4 filter paper. The mixture was concentrated to a thick consistency, and the resulting extract was kept in a desiccator for further use.

2.3 Preparation of reagents

The extract solution was prepared by dissolving 0.1 g in deionized water and subsequently diluted to 100 ml to obtain a 1 mg/ml extract solution. Stock Cr (VI) solution (50 mg L^{-1}) was prepared by dissolving 0.05 g of potassium dichromate ($K_2Cr_2O_7$) (294.18 g mol^{-1}) in 1 L of deionized water. The pH of Cr (VI) solution was adjusted to 7.0 using 0.1 M NaOH or 0.1 M HCl before being filtered using a 0.45-µmWhatman filter paper and sterilized. The working solution was prepared by diluting the stock solution with deionized water to give the appropriate concentration (10 mg L^{-1}) of the solution and 0.20 g of 1,5-diphenylcarbazide was added in 100 ml of 95% acidified ethanol and store in sterilized and dried brown colored bottle.

2.4 DPPH radical scavenging activity

The method of Shahidi and Liyana-Pathiranan [40] was used for the determination of scavenging activity of DPPH free radical in the extract solution. A solution of 0.135 mM DPPH in methanol was prepared, and 1.0 ml of this solution was mixed with 1.0 ml of extract solution prepared in methanol containing 0.025–0.5 mg/ml of the plant extracts and standard separately (ascorbic acid). The reaction mixture was vortexed thoroughly and left in the dark at room temperature for 30 min. The absorbance of the mixture was measured spectrophotometrically at 517 nm. The ability of the plant extract to scavenge DPPH radical was calculated by the equation:

$$\text{DPPH radical scavenging activity} = \frac{(\text{Abs control} - \text{Abs sample})}{(\text{Abs control})} \times 100$$

where Abs control is the absorbance of DPPH radical + methanol; Abs sample is the absorbance of DPPH radical + sample extract or standard.

2.5 Hydrogen peroxide scavenging assay

The scavenging capacity for hydrogen peroxide was measured according to the method of Rahmat [35]. A solution of hydrogen peroxide (2 mM) was prepared in 50 mM phosphate buffer (pH 7.4). Hydrogen peroxide concentration was determined spectrophotometrically at 230 nm absorption using molar extinction coefficient for hydrogen peroxide of 81 M^{-1} cm^{-1}. Then, 1 ml of various concentrations (25–250 µg/ml) of extract solution and ascorbic acid in triplicate was transferred into the test tubes and their volumes made up to 4 ml with 50 mM phosphate buffer (pH 7.4) or solvent (methanol). After addition of 6 ml hydrogen peroxide solution, tubes were vortexed and absorbance of the hydrogen peroxide at 230 nm was determined after 10 min, against a blank containing 50 mM phosphate buffer without hydrogen peroxide. Hydrogen peroxide scavenging ability was calculated using the formula:

$$\%\text{Scavenging} = \left(1 - \frac{A_e}{A_o}\right) \times 100$$

where A_o is the absorbance without sample, and A_e is absorbance with sample.

2.6 Determination of Cr (VI) concentration

The experiment for the reduction of Cr (VI) was conducted in batch as described by Chen et al. [6] with some modifications. The reaction mixtures were obtained by adding 100 ml of Cr (VI) solution (10 mg/L) into a 250-ml Erlenmeyer flask, adjusting the pH value, and

adding 100 ml *Tamarindus indica* methanol leaves extract (1 mg/ml) unless otherwise specified. The initial pH of the solution was adjusted with sulfuric acid solution (0.5 M) and/or sodium hydroxide solution (1.0 M). All experiments were conducted at room temperature (25 °C) unless otherwise specified. Cr (VI) was measured spectrophotometrically at 540 nm according to the diphenylcarbazide method.

2.7 Effect of process parameters

The batch experiment explained above was conducted in 250-ml Erlenmeyer flasks with a working volume of 100 ml. The following set of factors was chosen as the standard conditions: 10 mg/L of initial Cr (VI) concentration, pH 7, room temperature (25 °C), and reaction time of 30 min, and one of the parameters was varied at a time, while others were kept constant.

1. Effect of initial extract concentration

To determine the effect of initial *Tamarindus indica* methanol leaves extract concentration on reduction of Cr(VI), 100 ml of Cr (VI) solution (10 mg/L) was reacted with 100 ml of Tamarind extract at different initial concentrations, namely 1.4, 1.2, 1.0, 0.8, 0.6, 0.4, and 0.2 mg/ml, respectively, at pH of 2, 7, 9, and room temperature. The solution was intermittently sampled and centrifuged at 3000 rpm for 5 min, after which the Cr (VI) concentration was quantified using the 1, 5-diphenylcarbazide method.

2. Effect of initial Cr (VI) concentration

To determine the effect of initial Cr (VI) concentration on the reduction of Cr (VI) by *Tamarindus indica* methanol leaves extract, 100 ml of Cr (VI) at initial concentrations of 5, 10, 15, 20, and 25 mg/L was reacted with 100 ml of Tamarind extract at 1 mg/ml, respectively, at pH of 2, 7, 9, and room temperature. The solution was sampled and centrifuged at 3000 rpm for 5 min, after which the Cr (VI) concentration was quantified using the 1, 5-diphenylcarbazide method.

3. Effect of hydrogen ion concentration

The effect of pH on the reduction of Cr (VI) by *Tamarindus indica* methanol leaves extract was determined by varying the pH of the reaction mixture, viz. 2–9 (±0.1), respectively. For each 100 ml solution of Cr (VI) solution (10 mg/L) in 250-ml Erlenmeyer flask, pH was adjusted (change in working volume due to the addition of NaOH or H_2SO_4 was negligible), and then, 100 ml Tamarind extract solution (1 mg/ml) was added. The solution was sampled and centrifuged at 3000 rpm for 5 min, after which the Cr (VI) concentration was quantified using the 1, 5-diphenylcarbazide method.

4. Effect of reaction time

The reaction mixture of the batch experiment at the pH of 2, 7, 9, and temperature of 25 °C was allowed to stand for the different duration (5–65 min) to determine the effect of reaction time on the reduction of Cr (VI) by *Tamarindus indica* methanol leaves extract. The solution was sampled and centrifuged at 3000 rpm for 5 min, after which the Cr (VI) concentration was quantified using the 1, 5-diphenylcarbazide method.

5. Effect of temperature

The reaction mixture of the batch experiment was incubated at different temperatures; 5–45 °C (±10C) under pH 2, 7, and 9 to determine the effect of temperature on the reduction of Cr (VI) by *Tamarindus indica* methanol leaves extract. The solution was sampled and centrifuged at 3000 rpm for 5 min, after which the Cr (VI) concentration was quantified using the 1, 5-diphenylcarbazide method.

2.8 Kinetics studies of Cr (VI) bioreduction

Batch experiments were carried out as described by Chen et al. [6] under optimum conditions to ascertain Cr (VI) reduction kinetics properties.

Reaction order	Kinetic equation
First order	$\log q_t = \log q_e - \frac{k}{2.303}t$ (1)
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{k}{2.303}t$ (2)
Second order	$\frac{1}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$ (3)
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$ (4)
Half-life time	$t_{1/2} = \frac{\ln 2}{k}$ (5)

Other kinetic parameters such as rate constant (k) and equilibrium concentration (q_e) were derived from the equations above.

2.9 Thermodynamics studies of Cr (VI) bioreduction

Batch experiment was carried out under optimum conditions to determine the thermodynamic parameters for the reduction process such as free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) as described by Mekonnen et al. [23] with slight modification.

1. Gibbs free energy

Change in Gibb's free energy ($\Delta G°$) was determined using the equation:

$$\Delta G = -RT \ \ln \ K_c \tag{6}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K).

2. Equilibrium constant

The equilibrium constant K_c was evaluated at each temperature using the relationship:

$$K_c = \frac{\text{Cr (III)}}{\text{Cr (VI)}} \tag{7}$$

where *C*r (VI) is the equilibrium concentration of Cr (VI) in solution in mg L^{-1} and Cr (III) is the amount of Cr (VI) reduced at equilibrium.

3. Enthalpy and entropy

The change in enthalpy ($\Delta H°$) and change in entropy ($\Delta S°$) were calculated, respectively, from the slope and intercept of van't Hoff's plot of $\ln K_c$ against $1/T$. The equilibrium constant K_c can be expressed in terms of the $\Delta H°$ (Kcal mol^{-1}) and $\Delta S°$ (Kcal mol^{-1} K^{-1}) as a function of temperature:

$$\text{In } K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{8}$$

2.10 Statistical analysis

All the experiments were carried out in triplicate and the results presented as mean ± SD.

3 Results

3.1 Relation between antioxidant and Cr (VI) reduction

2,2-Diphenyl-1-picrylhydrazyl radical scavenging activity and hydrogen peroxide radical scavenging activity of Tamarindus indica methanol leaves extract as well as Cr (VI) reduction capacity were determined and correlated (Fig. 1). The study indicated a linear relationship between Cr (VI) reduction and the two radical scavenging activity of the extract. The correlation coefficient of 0.982 and 0.995 was obtained when Cr (VI) reduction was correlated with DPPH and H_2O_2 radical scavenging activity, respectively.

3.2 Effect of process parameters on Cr (VI) reduction

Cr (VI) reduction capacity of *Tamarindus indica* methanol leaves extract at varying concentrations

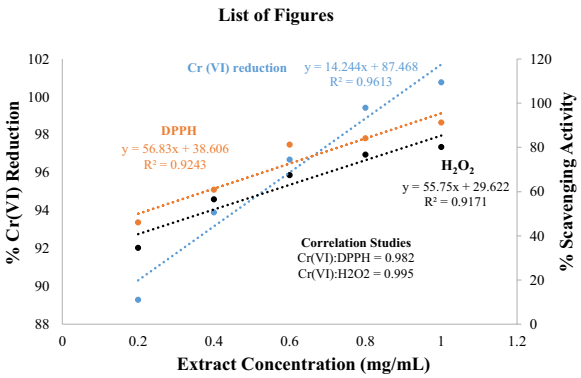

Fig. 1 Relationship between Cr (VI) reduction capacity and antioxidant activity of *Tamarindus indica* methanol leaves extract. DPPH = 2, 2-diphenyl-1-picrylhydrazyl, H_2O_2 = Hydrogen peroxide assay

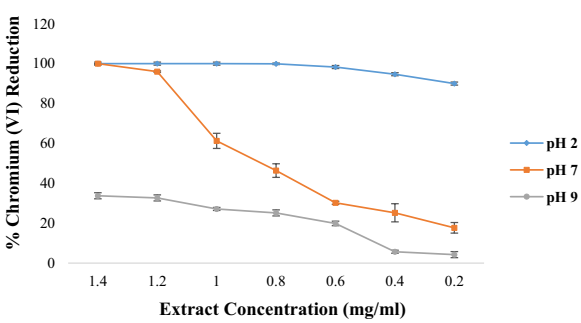

Fig. 2 Effect of initial extract concentration on hexavalent chromium reduction by *Tamarindus indica* methanol leaves extract. (Chromium concentration = 10 mg/L, temperature = 27 °C, time = 30 min, pH = 2.0, 7.0 and 9.0)

was carried out (Fig. 2). The reaction pattern shows a direct relation of the concentration of the tamarind extract with the reduction efficiency. Complete reduction of Cr (VI) was attained by the highest extract concentration (1 mg/ml) at both pH 2 and 7, respectively. Lower reduction efficiency was observed at pH 9 for all the sets of tamarind extract concentrations. Another reaction was carried out at varying Cr (VI) concentrations and fixed extract concentration (Fig. 3). Increase Cr (VI) concentration depicts a decrease in percentage reduction. The reduction has shown to be more effective only at the two lowest concentrations of Cr (VI) (5 mg/L and 10 mg/L) under the defined conditions. As the result indicated, hydrogen ion concentration (pH) also significantly affects Cr (VI) reduction (Fig. 4). Increased hydrogen ion concentration leads to increased Cr (VI) reduction, whereas at lower hydrogen ion concentration Cr (VI) reduction has shown to be slow. Effect of reaction time on Cr (VI) reduction by Tamarind extract was shown (Fig. 5). The result depicts

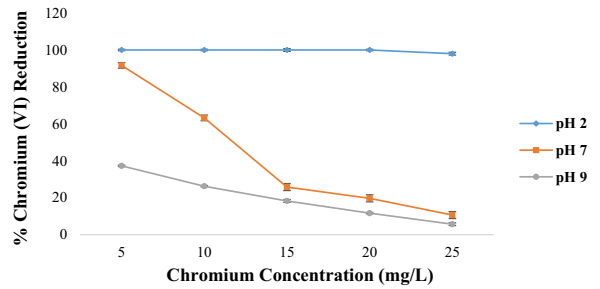

Fig. 3 Effect of initial chromium concentration on hexavalent chromium reduction by *Tamarindus indica* methanol leaves extract. (Extract concentration = 1 mg/ml, time = 30 min, temperature = 27 °C, pH = 2.0, 7.0 and 9.0)

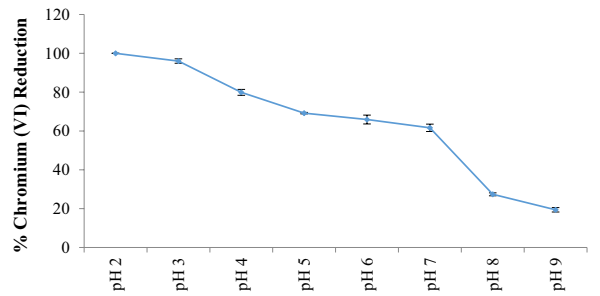

Fig. 4 Effect of pH on hexavalent chromium reduction by *Tamarindus indica* methanol leaves extract. (Extract concentration = 1 mg/ml, chromium concentration = 10 mg/L, temperature = 27 °C, time = 30 min)

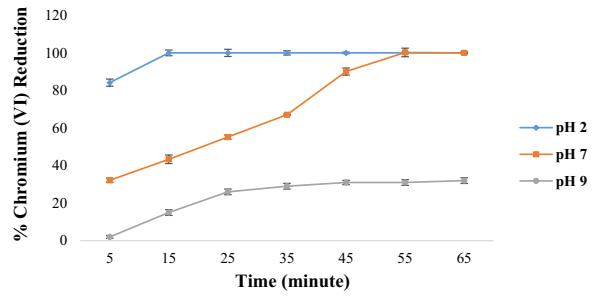

Fig. 5 Effect of reaction time on hexavalent chromium reduction by *Tamarindus indica* methanol leaves extract. (Extract concentration = 1 mg/ml, chromium concentration = 10 mg/L, temperature = 27 °C, pH = 2.0, 7.0 and 9.0)

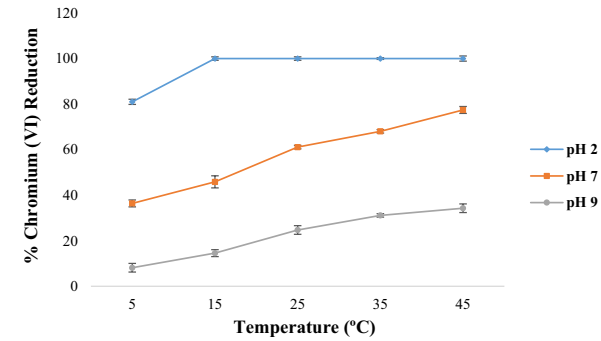

Fig. 6 Effect of temperature on hexavalent chromium reduction by *Tamarindus indica* methanol leaves extract. (Extract concentration = 1 mg/ml, chromium concentration = 10 mg/L, pH = 2.0, 7.0 and 9.0, time = 30 min)

Table 1 Kinetic parameter for hexavalent chromium bioreduction by *Tamarindus indica* methanol leaves extract at pH 2

Kinetic model	Correlation (R^2)	$T_{1/2}$ (min)	K	q_e (mg/L)
First order	0.927	11.36	6.1×10^{-2}	4.985
Pseudo-first order	0.649	45.59	1.5×10^{-2}	6.781
Second order	0.645	42,262.2	1.64×10^{-5}	714.3
Pseudo-second order	**0.997**	10.20	6.2×10^{-2}	11.16

The correlation coefficient value in bold indicated the highest correlation value and the most predominant order of the reaction

R^2 = Correlation coefficient, $T_{1/2}$ = reaction half-life, K = rate constant in different units (first and pseudo-first order in min^{-1} and second and pseudo-second order in mg/L^{-1} min^{-1}), q_e = equilibrium concentration

Table 2 Kinetic parameter for hexavalent chromium bioreduction by *Tamarindus indica* methanol leaves extract at pH 7

Kinetic model	Correlation (R^2)	$T_{1/2}$ (min)	K	q_e (mg/L)
First order	0.985	15.04	6.4×10^{-2}	2.677
Pseudo-first order	**0.988**	1.070	6.5×10^{-1}	860.8
Second order	0.939	3269.34	2.12×10^{-4}	120.5
Pseudo-second order	0.742	450.1	1.54×10^{-3}	19.72

The correlation coefficient value in bold indicated the highest correlation value and the most predominant order of the reaction

R^2 = Correlation coefficient, $T_{1/2}$ = reaction half-life, K = rate constant in different units (first and pseudo-first order in min^{-1} and second and pseudo-second order in mg/L^{-1} min^{-1}), q_e = equilibrium concentration

that Cr (VI) reduction at pH of 2 reached completion after 15 min. At lower pH, an increase in reaction time helps the reaction to reach completion or equilibrium position. After reaching equilibrium, the reaction may flow in a backward direction to favor reactant formation. Cr (VI) reduction was carried out at varying temperatures ranging between 5 and 45 °C after 30 min (Fig. 6). An increase in temperature leads to an increase in percentage Cr (VI) reduction, and complete reduction was achieved at 15 °C at the lowest pH of 2.

Table 3 Kinetic parameter for hexavalent chromium bioreduction by *Tamarindus indica* methanol leaves extract at pH 9

Kinetic model	Correlation (R^2)	$T_{1/2}$ (min)	K	q_e (mg/L)
First order	0.572	27.61	2.5×10^{-2}	1.506
Pseudo-first order	**0.758**	3.300	2.1×10^{-1}	2,179,716.4
Second order	0.426	184.3	3.76×10^{-3}	8.937
Pseudo-second order	0.167	152.3	4.55×10^{-3}	3.680

The correlation coefficient value in bold indicated the highest correlation value and the most predominant order of the reaction

R^2 = Correlation coefficient, $T_{1/2}$ = reaction half-life, K = rate constant in different units (first and pseudo-first order in min^{-1} and second and pseudo-second order in $mg/L^{-1}\ min^{-1}$), q_e = equilibrium concentration

Table 4 Thermodynamic parameters for Cr (VI) bioreduction by *Tamarindus indica* methanol leaves extract at pH 2

Temperature (K)	Δ*G*° (kJ/mol)	Δ*S*° (kJ/K/mol)	Δ*H*° (kJ/mol)
303	− 3.351	0.118	− 52.396
313	− 3.472		
323	− 3.592		
333	− 3.713		
343	− 3.833		

Table 5 Thermodynamic parameters for Cr (VI) bioreduction by *Tamarindus indica* methanol leaves extract at pH 7

Temperature (K)	Δ*G*° (kJ/mol)	Δ*S*° (kJ/K/mol)	Δ*H*° (kJ/mol)
303	− 2.849	0.0972	− 28.066
313	− 2.952		
323	− 3.054		
333	− 3.157		
343	− 3.259		

3.3 Kinetics of Cr (VI) reduction

The kinetic of Cr (VI) reduction by tamarind extract was carried out and the kinetic parameters were evaluated at pH 2, 7, and 9 (Tables 1, 2, 3). Cr (VI) reduction by tamarind extract was shown to predominantly follow a pseudo-second-order kinetic model at a pH of 2, while the reaction is unlikely to follow a second-order kinetic model which shows a very weak reaction rate constant and higher equilibrium concentration. Meanwhile, at the neutral and alkaline pH (7 and 9), the reaction path predominantly followed pseudo-first-order rate.

Table 6 Thermodynamic parameters for Cr (VI) bioreduction by *Tamarindus indica* methanol leaves extract at pH 9

Temperature (K)	Δ*G*° (kJ/mol)	Δ*S*° (kJ/K/mol)	Δ*H*° (kJ/mol)
303	− 1.505	0.081	− 27.916
313	− 1.559		
323	− 1.613		
333	− 1.668		
343	− 1.722		

3.4 Thermodynamics of Cr (VI) reduction

Thermodynamic data on Cr (VI) reduction by tamarind extract at pH 2, 7, and 9 were shown (Tables 4, 5, 6). The study carried out under various hydrogen ion concentrations revealed the reaction to have negative free energy change and enthalpy. In all the conditions, the reactions also displayed a positive entropy which indicated the system to be orderly unstable.

4 Discussion

The solubility of Cr (VI) and toxicity strongly depend on its oxidation state [28]; therefore, its reduction to Cr (III) will mitigate the toxic potency [8]. However, Cr (III) is not only nontoxic but nutritive at a considerable quantity in the biological system [8]. Several treatment methods involving this approach including coagulation, solvent extraction, microbial reduction, and chemical reduction/precipitation have been utilized [28]. Although tremendous success was achieved especially with chemical reduction, at the same time, difficulties and challenges like reagent high costs and secondary contamination remain a problem [32]. Given these shortcomings, we examine the potentials of *Tamarindus indica* methanol leaves extract for Cr (VI) reduction. Tamarind extract has been reported to contain a vast number of antioxidant phytochemicals some of which were reported with efficacy in converting Cr (VI) to a less toxic and immobile form [18]. We first validated the relationship between Cr (VI) reduction and antioxidant capacity by conducting a set of experiments to determine antioxidant capacity of Tamarind methanol leaves extract and relate it to Cr (VI) reduction capacity.

From the data, tamarind extract was able to significantly reduce environmentally toxic Cr (VI) to a less toxic form. This capacity could be due to the presence of high reducing groups such as hydroxy, carbonyls, and carboxyl groups usually found in the plant extract (Fig. 7). Sugars, glycosides, vitamins, natural organic acids such as citric, oxalic, ascorbic, tartaric, and formic acid have been reported for the reduction of Cr (VI) [10], and

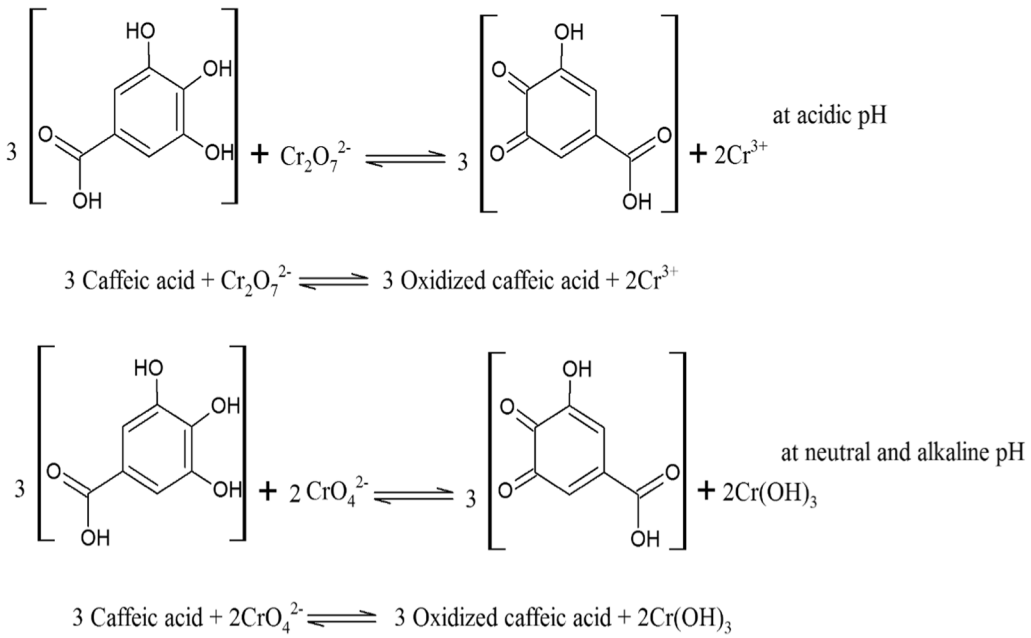

Fig. 7 Molecular mechanism of Cr (VI) reduction by caffeic acid

these compounds were found to be present in tamarind extract [18]. Generally, any compounds bearing aliphatic or aromatic hydroxyl groups may possess the potentials for the reduction of Cr (VI) [3, 36], since it involved steps of single electron/proton transfer, which is a general mechanism of anti-oxidation by phenolics. However, characterization of Cr (VI) reduction shows a rapid pre-oxidative equilibrium between Cr (VI) and substituted phenols to form chromate ester intermediates which decompose with a concomitant transfer of electrons to the Cr (VI) center [20, 39]. Therefore, an increase in percentage Cr (VI) reduced with increasing tamarind extract concentration could be attributed to an increase in the antioxidant groups present in the extract. This is because the number of reductive functional groups increases with the concentration of the extract and its associated antioxidant capacity [4, 13]. Thus, the increase in reductive functional groups can be linked directly to an increase in Cr (VI) reduction. The findings agree with the many earlier works such as Xu et al. [45, 46] and Yong et al. [47] whose reported Cr (VI) reduction using vitamin C, Dubey, et al. [10] on *Sorbaria sorbifolia* aqueous extract, Qi et al. [32] on rutin-Cr (III) complex, and Poonkuzhali et al. [30] on *Aerva lanata* aqueous extract, respectively. On the other hand, the decrease in Cr (VI) reduction with an increase in initial Cr (VI) concentration may be due to the higher Cr (VI) ions in the solution than the available proton/electron-donating groups. Another possible reason is based on the fact that some antioxidant molecules present in the extract can reduce Cr (VI) and release it, while some remained attached to Cr (III) thereby preventing the reduction site from regenerating itself. A formation of tri- or termolecular complex between Cr (VI), tartaric acid, and epigallocatechin was reported [5, 20]. The pattern also coincides with the report of Dubey et al. [10] on *Sorbaria sorbifolia* aqueous extract, Chen et al. [6] on gallic acid, Dutta et al. [11] on zerovalent iron, respectively. The reduction of Cr (VI) by tamarind extract was higher at acidic pH and gradually decreases with an increase in pH value. This may be due to sharp changes in redox potentials (E_o) of the two reacting species owing to high dipole–dipole tension on the bond involved in redox balance. Under acidic conditions, the redox potential of Cr (VI) is greater than + 1.30 V and exists as hydrochromate/dichromate ions ($HCrO_4^-/Cr_2O_7^{2-}$) but drops to 0.36 V under near-neutral conditions as chromate ions (CrO_4^{2-}) [41]. Therefore, hydrochromate/dichromate ions possess a greater tendency to accept electron/proton than chromate ions. Any compound with redox potential lower than that of Cr (VI) species can serve as a reducing agent to Cr (VI), since electron flows from redox pair with more negative potentials to one with more positive potentials [34]. This trend was also reported by Xu et al. [45, 46] and Yong et al. [47] whose reported Cr (VI) reduction using vitamin C, Chen et al. [6] on gallic acid, Dubey et al. [10] on *Sorbaria sorbifolia* aqueous extract, Qi et al. [32] on rutin-Cr (III) complex, Xu et al. [45] on oxalic and citric acids, and Poonkuzhali et al.

[30] on *Aerva lanata* aqueous extract. Tamarind extract was able to reduce Cr (VI) to Cr (III) across varying pHs with higher efficiencies at acidic and neutral pH as other parameters presented alongside pH effects. Cr (VI) reduction efficiency of tamarind extract is also affected by reaction time. Longer reaction time allows the reacting species to have a higher chance for contact at proper sites for reaction to take place [24]. However, the appearance of a plateau may indicate exhaustion of the reacting sites or insufficient activation energy which drives the reaction to completion. The steady increase in reduction with increase in reaction time is in agreement with what was reported for ascorbic acid, gallic acid, vitamin C, *Aerva lanata*, and *Sorbaria sorbifolia*, respectively [6, 10, 30, 32, 45–47]. Temperature favorably affects Cr (VI) reduction efficacy by tamarind extract. Higher reduction observed at high temperatures could be due to energy derived from a more effective collision that can accelerate deprotonation of the reductive groups present in the extract. High temperature increases the number of activated molecules, thereby promoting Cr (VI) reduction [6]. The temperature could also improve the reduction efficiency of Cr (VI) when proton [H+] was insufficient in the reaction mixture. This is also in agreement with all the work cited above in addition to the work of Preethi et al. [31] who reported on *C. sativum*, *A. tenella colla*, *S. hispida*, and *M. verticillata* aqueous extracts, and Iorungwa et al. [15] on sodium metabisulfite, respectively.

The kinetics of Cr (VI) reduction changes from acidic to basic pHs. This is because reaction kinetics is always affected by pH and reactant concentrations [45]. The rate constants at various pH in the predominant orders indicated that the OH increased by 6.2×10^{-2}, 6.4×10^{-2}, and 2.1×10^{-1} times with increasing initial pH from 2.0 to 7.0 and 9.0, respectively. The pH level plays an important role in the reduction of Cr (VI) by tamarind extract, and low pH levels promote Cr (VI) reduction. The reaction predominantly follows pseudo-second-order kinetics, and this is usually when one of the reactant concentrations is by far greater than the other. Therefore, the order of Cr (VI) reduction determined was in respect to limiting reacting species (i.e., Cr (VI)) and could give valuable information for predicting the Cr (VI) disappearance rate when reacted with tamarind extract. It is noteworthy that various antioxidants and electron donors obtainable in tamarind extract may have different reaction rates with Cr (VI), resulting in different rate constants [19, 44]. The reduction rate of Cr (VI) increased with decreasing pH value, and the reduction efficacy was higher under acidic conditions than under neutral or weak alkaline conditions. The kinetic data of the reaction agree with a work previously reported by Chen et al. [6], Hasan et al. [14], and Kim et al. [19]. Under optimum reduction conditions, the negative Gibb's free energy ($\Delta G°$) at different temperatures signifies that Cr (VI) reduction was feasible and spontaneous. Thus, the reacting species possess the minimum energy needed to overcome the reaction activation barrier. The negative enthalpy ($\Delta H°$) value indicates that the reaction was exothermic. The energy of the reacting species put together is higher than the energy of the resulting product, and hence, the net energy is released to the surroundings as heat. The positive entropy ($\Delta S°$) value denotes that there was an increase in the randomness in the system during the reduction reaction. Increasing temperature leads to an increase in the random collision of the reacting species and gaining energy that drives the reaction to completion. The thermodynamic findings on Cr (VI) reduction are in agreement with the work of Niekerk et al. [26], Iorungwa et al. [15], and Mekonnen et al. [23].

5 Conclusions

Reduction of Cr (VI) with *Tamarindus indica* methanol leaves extract was carried out and found to be very effective. The research demonstrated that the reduction capacity is affected by the initial concentration of the reacting species ((i.e., Cr (VI) and extract), pH, reaction time, and temperature. Results obtained show that pH significantly affects the rate of Cr (VI) reduction by tamarind extract with the reaction predominantly following pseudo-second order at pH = 2, and pseudo-first order at pH = 7 and 9, respectively. Thermodynamic studies suggest that the reduction reaction is feasible, spontaneous, and exothermic at all temperature. Further work on individual phytoconstituents of tamarind extract should be carried out to identify the most active reducing molecules and possible application in industrial wastewater treatment.

Abbreviations

$K_2Cr_2O_7$: Potassium dichromate; Cr (VI): Hexavalent chromium; Cr (III): Trivalent chromium; R^2: Correlation coefficient; pH: Hydrogen ion concentration; B6C3F1: Experimental mice model; F344/N: Experimental rats model; H_2SO_4: Sulfuric acid; NaOH: Sodium hydroxide; ΔG: Change in free energy; ΔH: Change in enthalpy; ΔS: Change in entropy; R: Molar gas constant; T: Temperature; K_c: Equilibrium constant; E_o: Redox potential; OH: Hydroxyl group.

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Author contributions
BSK carried out laboratory work, data collection and analysis, manuscript preparation, and corrections. AM contributed to design and manuscript corrections and supervision. ABS was involved in concept and design of the work and supervision. All authors read and approved the final manuscript.

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Availability of data and materials
The datasets used during the current study are available with the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare no conflict of interest regarding the publication of this work.

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References

1. Arundhati P, Sudeshna D, Paul KA (2013) Cr (VI)(VI) reduction by immobilized cells of *Bacillus sphaericus*. Braz Arch Biol Technol 56(3):505–512
2. Bakiyaraj RL, Baskaran A, Chidambaram T, Mahakavi M, Santhoshkumar K (2014) Bioremediation of chromium by *Bacillus subtilis* and *Pseudomonas aeruginosa*. Int J Curr Microbiol App Sci 3(9):715–719
3. Basu A, Saha R, Mandal J, Ghosh S, Saha B (2010) Removal of Cr (VI) by an aromatic alcohol. J Biomed Sci Eng 3:735–741
4. Brewer MS (2011) Natural antioxidants : sources, compounds, mechanisms of action, and potential applications. Compr Rev Food Sci Food Saf 10:221–247. https://doi.org/10.1111/j.1541-4337.2011.00156.x
5. Brose DA, James BR (2013) Cr (VI) reduction by tartaric acid and isopropyl alcohol in mid-atlantic soils and the role of Mn(III, IV)(hydr)oxides. Environ Sci Technol 47:12985–12991
6. Chen ZF, Zhao YS, Li Q (2015) Characteristics and kinetics of Cr (VI) reduction by gallic acid in aqueous solutions. Water Sci Technol 71(11):1694–1700
7. Collins BJ, Stout MD, Levine KE, Kissling GE, Melnick RL, Fennell TR, Walden R, Abdo K, Pritchard JB, Fernando RA, Burka LT, Hooth MJ (2010) Exposure to Cr (VI) resulted in significantly higher tissue chromium burden compared with trivalent chromium following similar oral doses to male F344/N rats and female B6C3F1 mice. Toxicol Sci 118(2):368–379
8. Dalcin MG, Pirete MM, Lemos DA, Ribeiro EJ, Cardoso VL, De Resende MM (2011) Evaluation of Cr (VI) removal in a continuous biological fi lter with the use of central composite design (CCD). J Environ Manag 92(4):1165–1173. https://doi.org/10.1016/j.jenvman.2010.11.022
9. Deepika K, Xiangliang P, Daoyong Z, Chenxi Z, Fahad AA, Golam MM (2015) Bioreduction of Cr (VI) from soil column leachate by Pseudomonas stutzeri. Bioremed J 19(4):249–258. https://doi.org/10.1080/10889868.2015.1029116
10. Dubey SP, Sillanpaa M, Varma RS (2017) Reduction of Cr (VI) using Sorbaria sorbifolia aqueous leaf extract. Appl Sci 7(715):1–10. https://doi.org/10.3390/app7070715
11. Dutta R, Mohammad SS, Chakrabarti S, Bhattacharjee S, Dutta BK, Dutta R et al (2010) Reduction of Cr (VI) in aqueous medium with zerovalent iron. Water Environ Res 82(2):138–146. https://doi.org/10.2175/106143009X426013
12. Flora SD, Camoirano A, Micale RT, La S, Savarino V, Zentilin P et al (2016) Reduction of Cr (VI) by fasted and fed human gastric fluid: chemical reduction and mitigation of mutagenicity. Toxicol Appl Pharmacol 306:113–119. https://doi.org/10.1016/j.taap.2016.07.004
13. Ghasemzadeh A, Ghasemzadeh N (2011) Flavonoids and phenolic acids: role and biochemical activity in plants and human. J Med Plants Res 5(31):6697–6703. https://doi.org/10.5897/JMPR11.1404
14. Hasan SH, Singh KK, Prakash O, Talat M, Ho YS (2008) Removal of Cr (VI) from aqueous solutions using agricultural waste maize bran. J Hazard Mater 152:356–365
15. Iorungwa MS, Wuana RA, Yiase SG, Tor-Anyiin T (2014) A kinetic, thermodynamic and stoichiometric study on the reductive detoxification of Cr (VI) in aqueous phase by sodium metabisulphite. J Environ Earth Sci 4(16):61–72
16. Jin Q, Li W, Rulong L, Feng J, Xiaodi H, Guang-Hou C (2016) An exploratory study on the pathways of Cr (VI) reduction in sulfate-reducing up-flow anaerobic sludge bed (UASB) reactor. Sci Rep 6:23694. https://doi.org/10.1038/srep23694
17. Kanmani P, Aravind J, Preston D (2012) Remediation of chromium contaminants using bacteria. Int J Environ Sci Technol 9:183–193. https://doi.org/10.1007/s13762-011-0013-7
18. Katsayal BS, Sallau AB, Muhammad A, Garba A (2019) Antioxidant potentials of *T. indica* and its environmental application: a mini review. Curr Biotechnol 8:96–103. https://doi.org/10.2174/2211550109666191224124923
19. Kim D, Om J, Kim C (2012) Cr (VI) reduction by water-soluble antioxidants Cr (VI) reduction by water-soluble antioxidants. Chem Sci J 88:1–6
20. Liu K, Shi Z, Zhou S (2016) Reduction of Cr (VI) using epigallocatechin gallate in aqueous solutions: kinetics and mechanism. RSC Adv 6:67196–67203. https://doi.org/10.1039/C6RA02131J
21. Mahmoud MS, Samah AM (2015) Calcium alginate as an eco-friendly supporting material for baker's yeast strain in chromium bioremediation. HBRC J 13:245–254
22. McNeil LS, McLean JE, Parks JL, Edwards MA (2012) Cr (VI) review, part 2: chemistry, occurrence, and treatment. J Am Waterworks Assoc 104:E395–E405
23. Mekonnen E, Yitbarek M, Soreta TR (2015) Kinetic and thermodynamic studies of the adsorption of Cr (VI) onto some selected local adsorbents. S Afr J Chem 68:45–52
24. Mystrioti C, Xenidis AN (2014) Application of iron nanoparticles synthesized by green tea for the removal of Cr (VI) in column tests. J Geosci Environ Prot 2:28–36. https://doi.org/10.4236/gep.2014.24005
25. Narayani M, Shetty KV (2013) Chromium-resistant bacteria and their environmental condition for Cr (VI) removal: a review. Crit Revis Environ Sci Technol 43:955–1009
26. Niekerk WG, Van-Lachmann RE, Hamza M (2007) A kinetic and mechanistic study of the chromium (VI) reduction by hydrogen peroxide in acidic aqueous solutions. Water SA 33(5):619–626
27. NTP (2008) NTP technical report on the toxicology and carcinogenesis studies of sodium dichromate dihydrate (CAS No. 7789-12-0) in F344/N rats and B6C3F1 mice (drinking water studies)
28. Pakade VE, Tavengwa T, Madikizela LM (2019) Recent advances in Cr (VI) removal from aqueous solutions by adsorptive methods. RSC Adv 9:26142–26164. https://doi.org/10.1039/c9ra05188k
29. Peter JW, Elsabe BMM, Maleke O, Abidemi FD, Mary H, Jim B, Robert J, Esta-Van H (2014) Effective bioreduction of Cr (VI) contaminated water in fixed-film bioreactors. Water SA. https://doi.org/10.4314/wsa.v40i3.19
30. Poonkuzhali K, Rajeswari V, Saravanakumar T, Viswanathamurthi P, Park S, Govarthanan M et al (2015) Reduction of Cr (VI) using *Aerva lanata* L.: elucidation of reduction mechanism and identification of active. J Hazard Mater 272:89–95. https://doi.org/10.1016/j.jhazmat.2014.03.001
31. Preethi J, Chitra L, Vennila K (2017) Plant extract as environmental-friendly green catalyst for the reduction of Cr (VI) in tannery effluent. Environ Technol 3330:1–22. https://doi.org/10.1080/09593330.2017.1329355
32. Qi Y, Jiang M, Cui Y, Zhao L, Liu S (2015) Novel reduction of Cr (VI) from wastewater using a naturally derived microcapsule loaded with rutin-Cr (III) complex. J Hazard Mater 285:336–345. https://doi.org/10.1016/j.jhazmat.2014.12.008

33. Quievryn G, Goulart M, Messer J (2001) Reduction of Cr (VI) by cysteine: significance in human lymphocytes and formation of DNA damage in reactions with variable reduction rates. Mol Cell Biochem 222:107–118
34. QuiIntana M, Curutchet G, Donati E (2001) Factors affecting chromium (VI) reduction by Thiobacillus ferrooxidans. Biochem Eng 9:11–15
35. Rahmat AK, Muhammad RK, S. S. and M. A. (2012) Evaluation of phenolic contents and antioxidant activity of various solvent extracts of *Sonchus asper* (L.). Hill Chem Cent J 6:12–21
36. Rivero-huguet M, Marshall WD (2009) Chemosphere influence of various organic molecules on the reduction of Cr (VI) mediated by zero-valent iron. Chemosphere 76(9):1240–1248. https://doi.org/10.1016/j.chemosphere.2009.05.040
37. Saranraj P, Sujitha D (2013) Microbial bioremediation of chromium in tannery effluent: a review. Int J Microbiol Res 4(3):305–320
38. Sathishkumar K, Murugan K, Benelli G, Higuchi A, Rajasekar A (2016) Bioreduction of Cr (VI) by Pseudomonas stutzeri L1 and *Acinetobacter baumannii* L2. Ann Microbiol. https://doi.org/10.1007/s13213-016-1240-4
39. Satish BN, Dillip KP (2015) Free radicals, natural antioxidants, and their reaction mechanisms. Res Adv 5:27986
40. Shahidi FS, Liyana-Pathiranan CM (2005) Antioxidant activity of commercial soft and hard wheat (*Triticum aestivum* L.) as affected by gastric pH conditions. J Agric Food Chem 53:2433–2440
41. Sillerova VH, Chrastny E, Cadkova MK (2014) Isotope fractionation and spectroscopic analysis as an evidence of Cr (VI) reduction during biosorption. Chemosphere 95:402–407
42. Šillerová H, Komarek M (2013) New low cost sorbents for Cr (VI) batch and column experiments. In: E3S web of conferences. https://doi.org/10.1051/e3sconf25006
43. Stout MD, Herbert RA, Kissling GE, Collins BJ, Travlos GS, Witt KL, Melnick RL, Abdo KM, Malarkey DE, Hooth MJ (2009) Cr (VI) is carcinogenic to F344/N rats and B6C3F1 mice after chronic oral exposure. Environ Health Perspect 117(5):716–722
44. Xiong U, Hu XI, Ong AI, Igu J, Xiaoan IL (2005) Kinetics of the reduction of chromium (VI) by vitamin C. Environ Toxicol Chem 24(6):1310–1314
45. Xu Z, Bai S, Liang J, Zhou L, Lan Y (2013) Photocatalytic reduction of Cr (VI) by citric and oxalic acids over biogenetic jarosite. Mater Sci Eng 33(4):2192–2196. https://doi.org/10.1016/j.msec.2013.01.040
46. Xu X, Li H, Li X, Gu J (2004) Reduction of Cr (VI) by ascorbic acid in aqueous solutions. Chemosphere 57:609–613. https://doi.org/10.1016/j.chemosphere.2004.07.031
47. Yong LIU, Xin-hua XU, Ping HH (2005) Remediation of Cr (VI) in solution using vitamin C. J Zhejiang Univ Sci 6B(6):540–542. https://doi.org/10.1631/jzus.2005.B0540

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