

## Article

# Reduction of Hexavalent Chromium Using *Sorbaria sorbifolia* Aqueous Leaf Extract

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**Abstract:** Aqueous plant leaves extract (PLE) of an abundant shrub, *Sorbaria sorbifolia*, was explored for the reduction of hexavalent chromium, Cr(VI), to trivalent chromium, Cr(III). The effect of contact time, pH, PLE quantity, ionic strength, hardness, temperature and effective initial Cr(VI) ion concentration were tested; Cr(VI) reduction followed the pseudo-first order rate kinetics and maximum reduction was observed at pH 2. Significantly, Cr(VI) reduction efficacies varied from 97 to 66% over the pH range of 2 to 10, which bodes well for PLE to be used for the reduction of Cr(VI) also at a higher pH. PLE-mediated Cr(VI) reduction displays considerable efficiency at various ionic strengths; however, hardness strongly affects the reduction ability. Higher temperature significantly enhances the Cr(VI) reduction. This study reveals the potential use of PLE as a green reducing agent in aqueous extract for the efficient reduction of Cr(VI) to Cr(III).

**Keywords:** hexavalent chromium; aqueous stream; reduction; kinetics; *Sorbaria sorbifolia* extract

## 1. Introduction

Chromium is a naturally occurring transition metal, found in contaminated soils, groundwater and drinking water, with the two most common oxidation states of chromium being trivalent, Cr(III) and hexavalent, Cr(VI). Cr(III) is an essential element in human nutrition and plays an important role in carbohydrate, protein and lipid metabolism [1], whereas Cr(VI) is soluble, relatively more mobile than Cr(III) [2] and toxic; Cr(VI) is a known carcinogen and mutagen [3,4]. The erosion of natural chromium deposits, oxidation of Cr(III), anthropogenic activities (dyeing, electroplating, leather tanning) and other industrial applications have been responsible for chromium contamination in the environment [5].

Many remediation strategies have been advanced to deal with Cr(VI) pollution, including adsorption [6], ion exchange [7], chemical precipitation [8], membrane filtration [9] and reduction [10–17], among others. The reduction of Cr(VI) is among the most widely used strategies in view of the redox activity of chromium. Reductive remediation approaches can address the toxicity of Cr(VI) by transformation into Cr(III), that can be easily removed after precipitation with alkaline substances [8]. Several synthetic and natural electron-rich compounds are capable of reducing Cr(VI): Fe(II) bearing clay minerals, zero-valent aluminum and Mn(II) have been reported as reducing, and being catalyzing agents in the reduction processes of Cr(VI) [10–12]. Natural organic acids including citric, oxalic, ascorbic, tartaric and formic acid have also been examined for the reduction of Cr(VI)

from contaminated aqueous and soil matrices [13–16]. In general, compounds bearing aliphatic or aromatic hydroxyl groups have been found suitable for the reduction of Cr(VI) [15,17].

Most of the remediation-by-reduction strategies described in the literature entail a sharp decrease in reduction rates for a higher pH, but they are effective only at lower pH levels, which thus presents a challenge for more alkaline Cr(VI) contaminated sites [15]. Sarkar et al. report 100% Cr(VI) reduction efficiency at pH 2.25 that becomes negligible at pH > 7.5 [12]. Similarly, Lan et al. observed that montmorillonite and illite significantly catalyze the reduction of Cr(VI) by citric acid at pH < 5.0; in contrast, their effectiveness are dramatically diminished at pH 5.0 [18].

Aqueous plant extracts have been extensively utilized for the synthesis of metal nanoparticles via the reduction of noble metal ions [19,20]; the presence of multiple hydroxy and carboxylic acids groups serve as mild reduction and capping agents [21,22]. Thus, the use of an aqueous plant extract (PLE) for the reduction of Cr(VI) to Cr(III) is a viable strategy. A local abundant shrub, *Sorbaria sorbifolia*, was selected for this study, since it grows rapidly and contains polyhydroxy constituents in its aerial part i.e., Kaempferol 3-arabofuranoside ( $C_{20}H_{18}O_{10}$ ), Astragalin ( $C_{21}H_{20}O_{11}$ ), Quercetin 3-glucuronide ( $C_{21}H_{18}O_{13}$ ), Isorhamnetin 3-glucoside ( $C_{22}H_{22}O_{12}$ ), Scutellarein ( $C_{21}H_{18}O_{12} \cdot H_2O$ ), Chlorogenic acid ( $C_{18}H_{18}O_9$ ), Arbutin ( $C_{12}H_{16}O_7$ ) and Sorbifolin ( $C_{16}H_{12}O_6$ ) [23–25]. Importantly, the reductive capability of its aqueous extract for the conversion of Cr(VI) to Cr(III) has been hitherto unexplored. One of the primary objectives of the present study is to conduct the reduction of Cr(VI) over a wide-range of pH and diverse environmental settings. In this article, aqueous plant extract mediated reduction of Cr(VI) is investigated and the effects of the concentration of plant extract, pH, ionic strength, temperature, initial concentration of Cr(VI) ions and hardness are examined.

## 2. Materials and Methods

### 2.1. Reagents

Potassium dichromate ( $K_2Cr_2O_7$ ), sodium chloride (NaCl), calcium carbonate ( $CaCO_3$ ), sulphuric acid ( $H_2SO_4$ ), sodium hydroxide (NaOH), 1,5-diphenylcarbazide (DPC) and acetone were purchased from Sigma-Aldrich Co., St. Louis, MO, USA. All chemicals used in the study were of reagent grade and used without further purification. All solutions were prepared using 18 M $\Omega$ ·cm Milli-Q water from a Millipore system.

### 2.2. Preparation of PLE

*Sorbaria sorbifolia*'s leaves were collected locally from Mikkeli, Finland. Leaves were separated from other sections of the plant and washed three times with ultrapure water to remove any dirt. Washed plant leaves were dried at room temperature for 12 h and 75 g leaves were boiled in 250 mL ultrapure water in an Erlenmeyer flask (500 mL) for 120 min. After cooling to room temperature, the solution was filtered through a Whatman filter paper (no. 40) and the filtrate was stored at  $-20^\circ C$ , labeled as plant leaves extract (PLE) and used as such for the reduction of Cr(VI) solutions.

### 2.3. Reduction and Analysis of Cr(VI)

The potential of PLE as a green reductant was assessed for Cr(VI). A 1000 mg/L stock solution of Cr(VI) was prepared from  $K_2Cr_2O_7$  in a 1000 mL volumetric flask and stored in a glass bottle at room temperature. PLE was added to 25 mL of freshly prepared Cr(VI) solution (10 mg/L) prepared by diluting the stock solution. Cr(VI) concentration was measured by colorimetric DPC method using a UV-Vis spectrophotometer (Perkin-Elmer Lambda-45, Waltham, MA, USA) at 540 nm [26]. DPC solution was prepared by dissolving 250 mg of DPC in 50 mL acetone and stored in a brown bottle at  $4^\circ C$ . The method combines the acidification of the Cr(VI) solution by  $H_2SO_4$  followed by the addition of DPC. For analysis, 0.25 mL of samples were diluted to 5 mL with ultrapure water and Cr(VI) was analyzed by DPC method after complete color development.

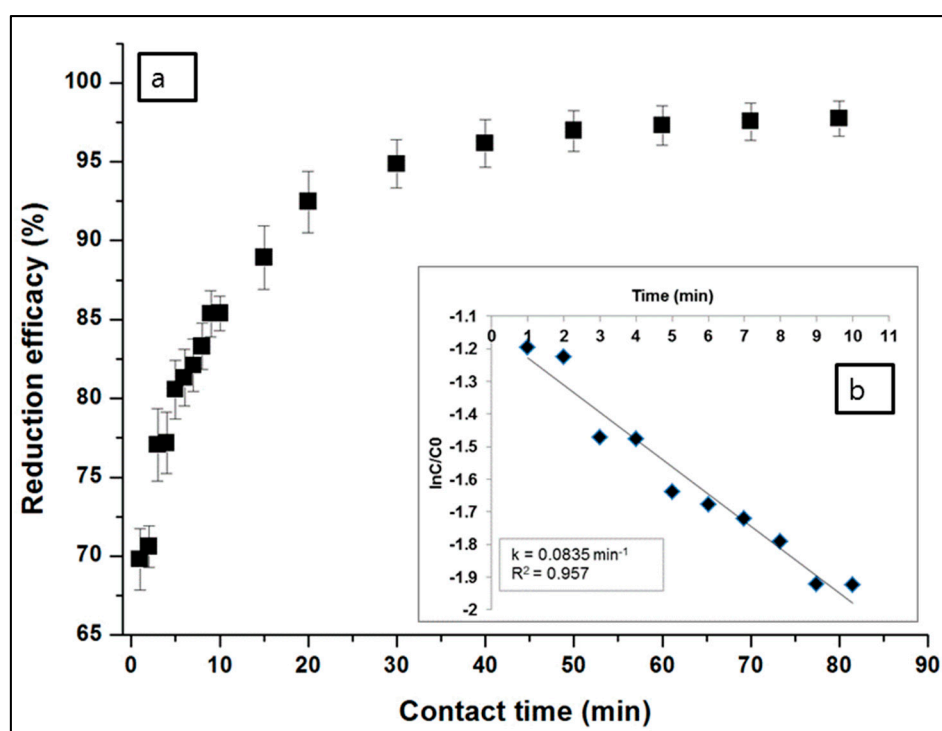
The effect of different parameters was examined to observe the potential of PLE for Cr(VI) reduction. Solution pH (2–10), contact time (0–90 min), PLE quantity (0.5–2.5 mL), ionic strength (0–500 mM), hardness (0.5–5 mM), temperature (278–333 K) and initial Cr(VI) concentration (5–80 mg/L), were evaluated for Cr(VI) reduction using PLE. Solution pH was adjusted with 0.1 M H<sub>2</sub>SO<sub>4</sub> and NaOH. NaCl and CaCO<sub>3</sub> were utilized to adjust the ionic strength and hardness. Experiments were performed in triplicate and the average value and standard deviations are presented. Functionality of PLE was measured by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700, Thermo Fisher, Waltham, MA, USA) using a spectral range of 4000–400 cm<sup>−1</sup> with resolution of 4 cm<sup>−1</sup>.

### 3. Results

#### 3.1. Reduction Efficacies of PLE

##### 3.1.1. Effects of Contact Time and Rate Kinetics

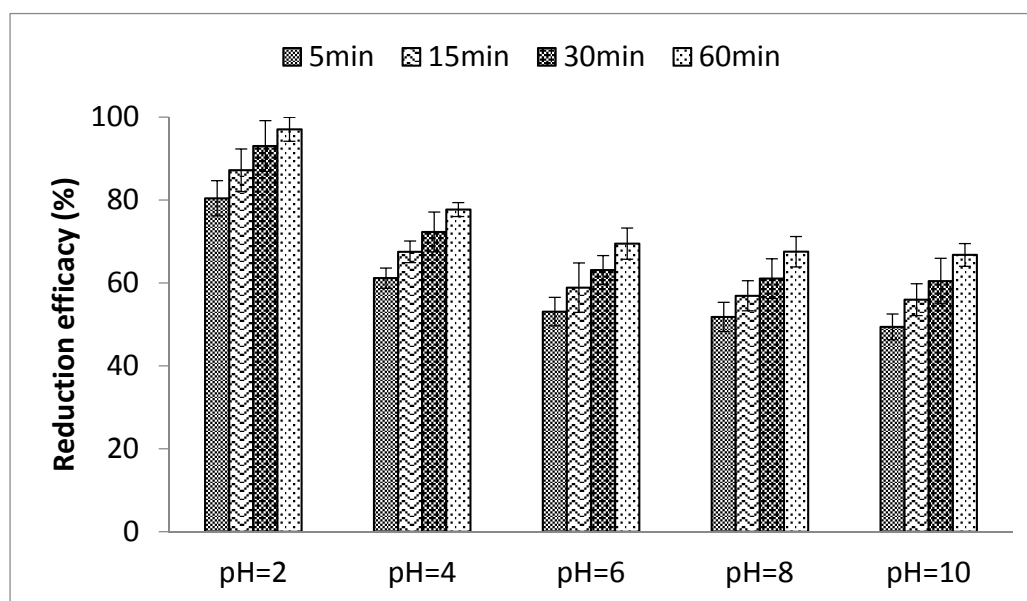
The reduction of Cr(VI) by PLE over varying contact times is presented in Figure 1a. A sharp increase in Cr(VI) reduction efficiency was observed with increasing contact time and more than 90% reduction efficiency was discerned in the first 20 min. Thereafter, the reduction efficiency reached 97% in 60 min, with no further increase in reduction efficiency by increasing contact time. Hence, 60 min contact time was optimized for all other experiments. Pseudo first-order rate kinetics for PLE mediated Cr(VI) reduction was determined.  $\ln(C/C_0)$  was plotted against time and the rate constant was determined from the linear part using regression analysis (Figure 1b). A high correlation coefficient ( $R^2 = 0.957$ ) signifies that the reduction of Cr(VI) by PLE follows pseudo-first order kinetics. The rate constant was obtained from the regression equation and was found to be 0.0835 min<sup>−1</sup>.



**Figure 1.** (a) Effects of contact time,  $[\text{Cr(VI)}]_0 = 10 \text{ mg}\cdot\text{L}^{-1}$ , Cr(VI) volume = 25 mL, contact time = 0–80 min, pH = 2, plant leaves extract (PLE) quantity = 1.5 mL; (b) Pseudo first order rate kinetics of Cr(VI) reduction.

### 3.1.2. Effects of pH

The effects of varying pH on Cr(VI) reduction efficiency is shown in Figure 2. As indicated, pH plays a crucial role on Cr(VI) using PLE. At pH 2, 97% was Cr(VI) was reduced to Cr(III) in 60 min, which decreased to 77% at pH 4. From pH 6 to 10, Cr(VI) reduction efficiencies varied from 69 to 66%, which is an important finding and PLE can also be utilized to reduce Cr(VI) in an alkaline medium. The reduction of Cr(VI) under varying solution pH has been studied previously and most of the reductants have either too low or no ability to reduce Cr(VI) in alkaline media [27,28]. In contrast, PLE could be used as a green reductant to successfully remediate Cr(VI) across a wider range of pH; acidic solution has the maximum reduction efficiency when compared to neutral and alkaline solutions.



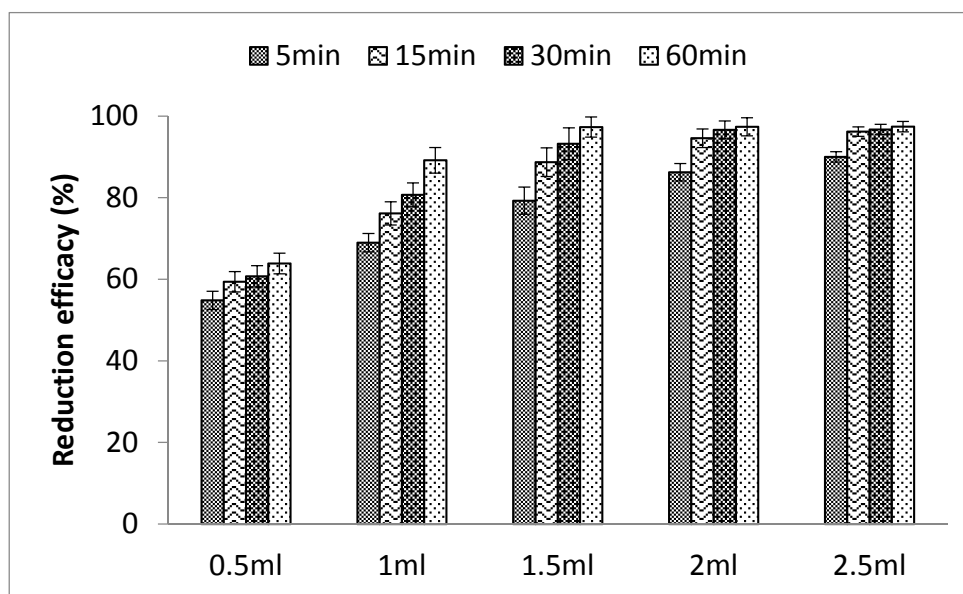
**Figure 2.** Effects of pH:  $[\text{Cr(VI)}]_0 = 10 \text{ mg} \cdot \text{L}^{-1}$ , Cr(VI) volume = 25 mL, contact time = 60 min, pH = 2–10, PLE quantity = 1.5 mL.

### 3.1.3. Effects of PLE Quantity

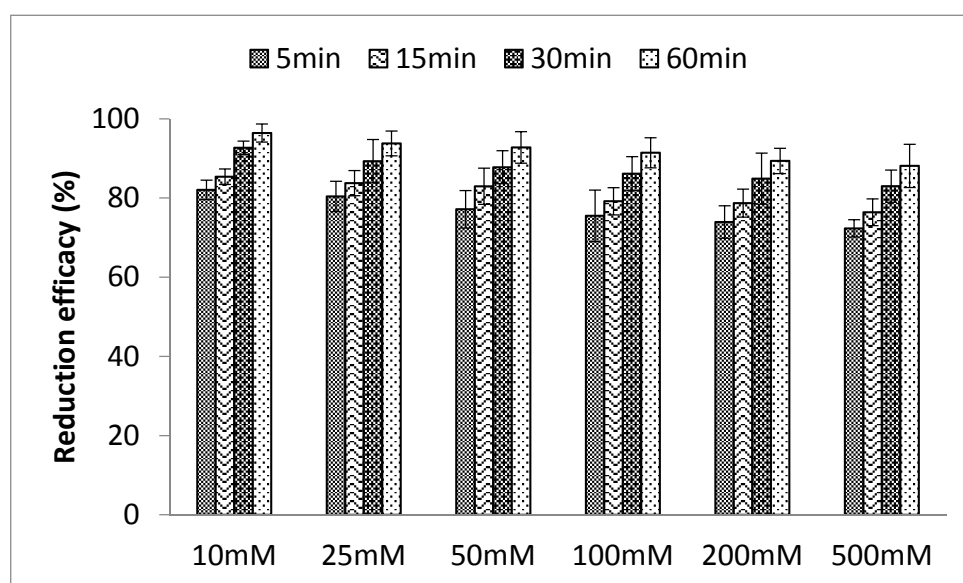
A quantitative range of PLEs were examined to reduce Cr(VI) and the ensuing results are presented in Figure 3; Cr(VI) reduction efficiency increases with increasing PLE quantity. In lower PLE amounts (0.5 mL), 54% of Cr(VI) is converted to Cr(III) within 5 min contact time, which increases to a maximum of 63% in 60 min. Increasing PLE quantity to 1.5 mL, efficiency enhancement varies from 79–97% in 5–60 min, respectively. Further increasing the PLE quantity to the maximum value of 2.5 mL, increases the value to 90%, but reduction efficiency at 60 min is virtually unchanged and remains similar to the maximum value (97%) attained using 1.5 mL of PLE; 1.5 mL of PLE is subsequently used in the other set of experiments.

### 3.1.4. Effects of Ionic Strength

It is imperative to explore the relationship between varying ionic strength and PLE mediated Cr(VI) reduction, as several ionic species may be present in natural water systems. Ionic strength was adjusted by addition of NaCl to acquire the desired ionic strength. Cr(VI) reduction using our green reductant was tested at different ionic strength and contact time. The obtained results presented in Figure 4 reveal that Cr(VI) reduction ability decreased (96–88%) with increasing ionic strength (10–500 mM) but had less effect (~8%) at a wide range of ionic strength solutions and hence, PLE can be utilized for remediation of Cr(VI) from different aqueous sources, including fresh water (~8 to 10 mM) to sea water (~400 mM) content.



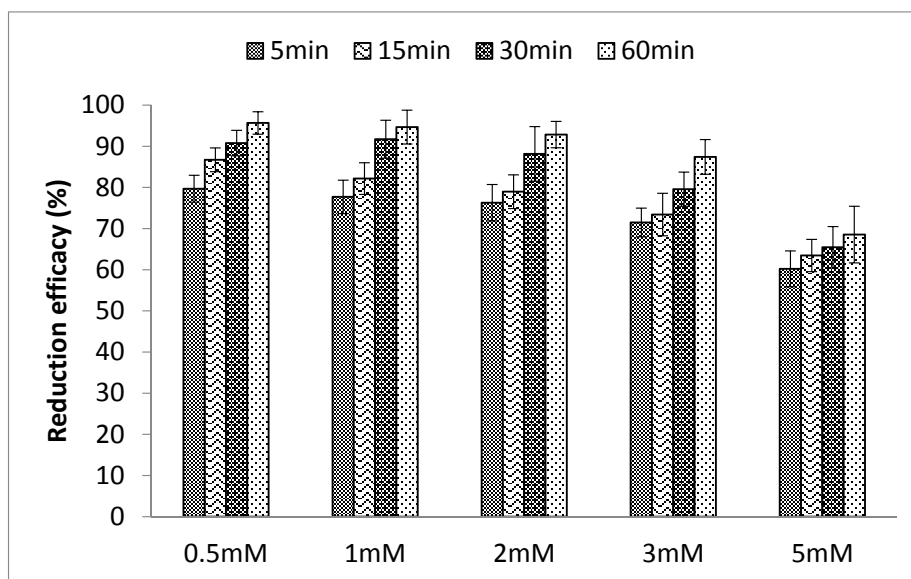
**Figure 3.** Effects of PLE quantity:  $[\text{Cr(VI)}]_0 = 10 \text{ mg}\cdot\text{L}^{-1}$ ,  $\text{Cr(VI)}$  volume = 25 mL, contact time = 60 min, pH = 2, PLE quantity = 0.5–2.5 mL.



**Figure 4.** Effects of ionic strength:  $[\text{Cr(VI)}]_0 = 10 \text{ mg}\cdot\text{L}^{-1}$ ,  $\text{Cr(VI)}$  volume = 25 mL, contact time = 60 min, pH = 2, PLE quantity = 1.5 mL, ionic strength = 10–500 mM.

### 3.1.5. Effects of Hardness

Effect of hardness was also examined for the potential of PLE to affect Cr(VI) reduction. Hardness was adjusted by  $\text{CaCO}_3$  addition to Cr(VI) solutions to acquire the varying hardness levels (0.5–5 mM). The obtained results presented in Figure 5 reveal that Cr(VI) reduction efficiency decreased sharply with increasing hardness of the solution; 92% reduction efficiency is obtainable at 2 mM hardness level which decreases to 68% at 5 mM. Similar observations have been recorded in the literature which indicate that presence of  $\text{Ca}^{2+}$  hardness with carbonate has resulted in a substantial drop in Cr(VI) reduction efficiency [29,30]. It is important to emphasize that the divalent cation ( $\text{Ca}^{2+}$ ) has a more significant effect on Cr(VI) reduction efficiency than monovalent cations ( $\text{Na}^+$ ).

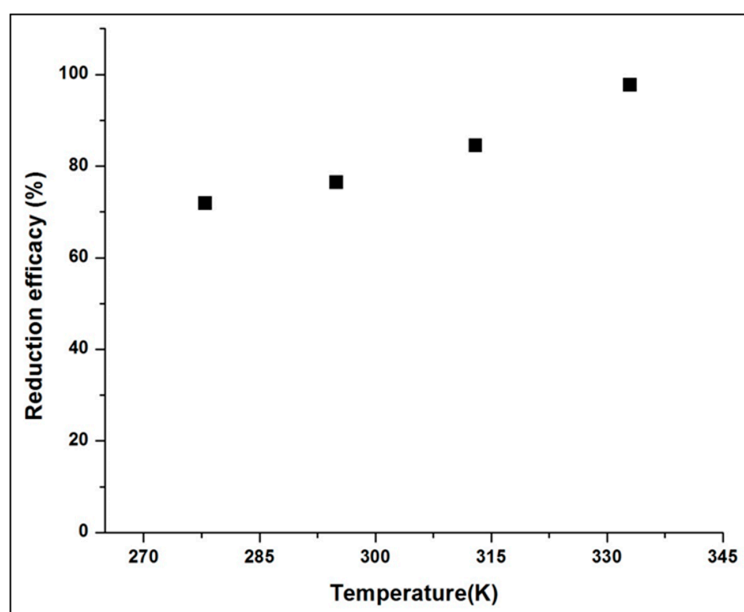


**Figure 5.** Effects of hardness:  $[\text{Cr(VI)}]_0 = 10 \text{ mg}\cdot\text{L}^{-1}$ , Cr(VI) volume = 25 mL, contact time = 60 min, pH = 2, PLE quantity = 1.5 mL, hardness = 0.5–5 mM.

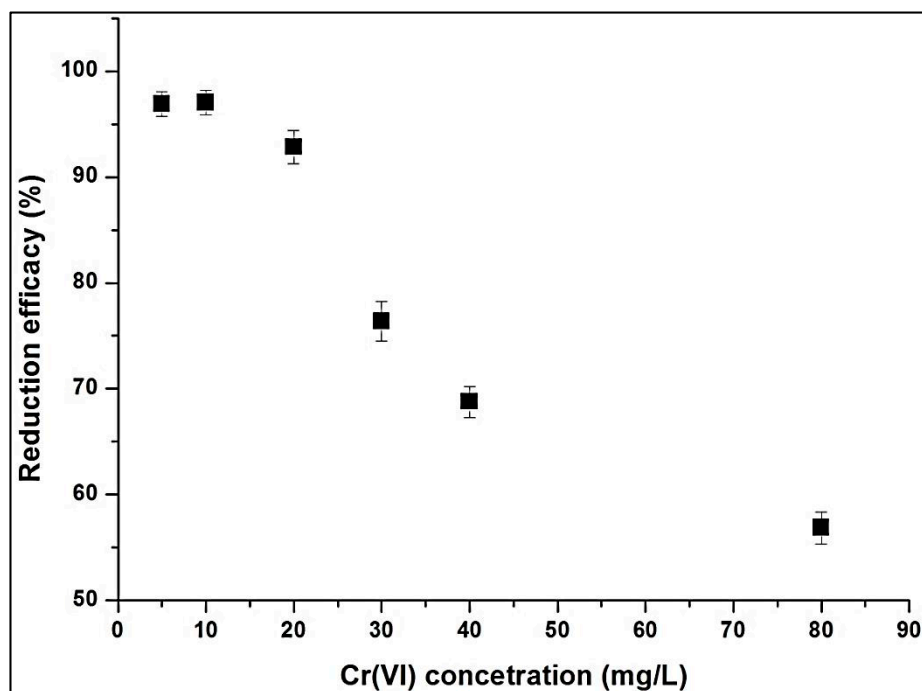
### 3.1.6. Effects of Temperature and Initial Cr(VI) Concentration

Effect of temperature (278–333 K) on Cr(VI) reduction was discerned and the result is presented in Figure 6. Initial Cr(VI) concentration of 30 mg/L was admixed with 1.5 mL of PLE and the mixture was kept at 278–333 K for 60 min. At 278 K, 71% reduction efficiency was observed whereas a significantly higher value of 97% could be attained at 333 K temperature.

The effect of initial Cr(VI) concentration on Cr(VI) reduction efficiency by PLE was examined by varying initial Cr(VI) concentration (5–80 mg/L); more than 92% of reduction efficiency was obtained, which decreased to 56% with increasing Cr(VI) concentration to 80 mg/L (Figure 7).



**Figure 6.** Effects of temperature:  $[\text{Cr(VI)}]_0 = 30 \text{ mg}\cdot\text{L}^{-1}$ , Cr(VI) volume = 25 mL, contact time = 60 min, pH = 2, PLE quantity = 1.5 mL, temperature = 278–333 K.



**Figure 7.** Effects of initial Cr(VI) concentration:  $[\text{Cr(VI)}]_0 = 5\text{--}80 \text{ mg}\cdot\text{L}^{-1}$ , Cr(VI) volume = 25 mL, contact time = 60 min, pH = 2, PLE quantity = 1.5 mL.

### 3.2. Comparison of the Present Study with Other Reductants

Our study demonstrates that reduction efficiency of PLE to convert Cr(VI) to Cr(III) is significant (97–66%) under a wide-ranging pH (2–10) conditions and occurs in an expeditious manner (short time, 60 min) when compared to other reductants documented in the literature (Table 1).

**Table 1.** Comparison of results using various reductants.

Reductants	Initial Cr(VI) Concentration	pH	Contact Time	Reduction Efficiency	References
Ferrous chloride (300 $\mu\text{M}$ )	50 $\mu\text{M}$	7.2	120 min	100%	[10]
Citrate (10 mM)	192.32 $\mu\text{M}$	2.25	24 h	12%	
Citrate (10 mM) + Mn(II) (182.02 $\mu\text{M}$ )	192.32 $\mu\text{M}$	2.25	24 h	52%	
Citrate (10 mM) + clay (3% (w/v))	192.32 $\mu\text{M}$	2.25	24 h	84%	[12]
Citrate (10 mM) + clay (3% (w/v)) + Mn(II) (182.02 $\mu\text{M}$ )	192.32 $\mu\text{M}$	2.25	6 h	100%	
Oxalic acid (300 $\mu\text{M}$ )	50 $\mu\text{M}$	3	20 min	100%	[13]
Ascorbic acid (300 $\mu\text{M}$ )	100 $\mu\text{M}$	7	120 min	100%	[14]
Tartaric acid (12 mM) + Isopropyl alcohol (0.29 M)	2.0 mM	4	99 h	19%	
Russett soil (5 g)	2.0 mM	4	99 h	25%	[15]
Russett soil (5 g) + Tartaric acid (12 mM) + Isopropyl alcohol (0.29 M)	2.0 mM	4	99 h	99%	
<i>Punica granatum</i> -nZVI (Fe(0) (1.53 mM))	50 mg/L	2.73	2 days	96%	[31]
PLE (1.5 mL)	10 mg/L	2–10	60 min	99–66%	Present study

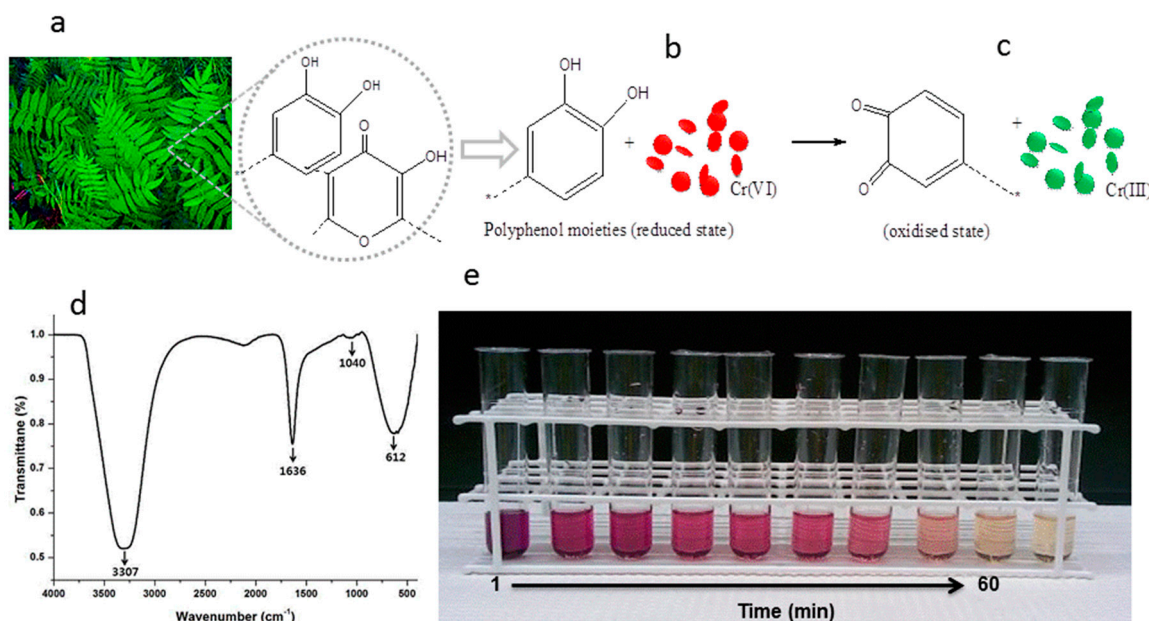
### 3.3. Possible Mechanism for Reduction Efficiency of PLE

The FTIR spectra of PLE sample is recorded in Figure 8d, which clearly shows absorption band at 3307, 1636, 1040 and 612  $\text{cm}^{-1}$ , suggesting the presence of –OH group [32], C=O group [33], C–O group [34], stretching C–H group bending frequencies.

The plant extracts usually contain sugars, glycosides, phenolics and even vitamins. Hydroxyl groups from sugars and phenolics can affect the reduction of metal salts including also vitamins [35–42]. Aerial parts of *Sorbaria sorbifolia* are known to contain a variety of polyphenols, flavonoids and glycosides [23–25]; glycosides are non-reducing sugars, but polyphenols and flavonoids are known antioxidants that serve as reducing agents [36–39] and are thus most likely responsible for the reduction



of Cr(VI) to Cr(III) using 'greener' PLE as a reductant. A schematic presentation delineates the reduction mechanism (Figure 8a–c); captured image for the gradual conversion of carcinogenic Cr(VI) into nontoxic Cr(III) is shown in Figure 8e.



**Figure 8.** (a–c): Schematics describing reduction mechanism of Cr(VI) using polyphenols and flavonoids; (d) Fourier Transform Infrared Spectroscopy (FTIR) spectra of native PLE sample; and (e) Gradual conversion of carcinogenic Cr(VI) into nontoxic Cr(III).

#### 4. Conclusions

An aqueous plant leaf extract of *Sorbaria sorbifolia* was prepared and utilized as a green reductant for reduction of Cr(VI); reduction follows pseudo first order rate kinetics and 97% of Cr(VI) reduced in 60 min contact time. Cr(VI) reduction occurs over a wide pH range (pH 2–10) with maximum reduction efficiency at acidic pH (pH 2). PLE can be utilized for a wide variety of water sources, including fresh to sea water, with a moderate reduction efficiency for Cr(VI); a reduction in efficiency, however, occurs at increasing hardness in PLE mediated reduction. FTIR spectra of crude PLE indicates the presence of hydroxyl and carboxy compounds (polyphenols and flavonoids) in the aqueous extract may reduce Cr(VI) to Cr(III). The ensuing results suggest that PLE can be successfully utilized as a greener strategy for the reductive remediation of Cr(VI) in aqueous matrices.

**Author Contributions:** S.P.D. and M.S. conceived and designed the experiments; S.P.D. performed the experiments; M.S. and R.S.V. analyzed the data; all authors (S.P.D., M.S. and R.S.V.) wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

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