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Green walnut shell as a new material for removal of Cr(VI) ions from aqueous solutions

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ABSTRACT

The removal of aqueous hexavalent chromium (Cr(VI)) by green walnut shell (GWS) was investigated in batch experiments. GWS is a readily available and low-cost horticulture solid waste. The efficiency of this biomass for Cr(VI) removal as impacted by various operational parameters was characterized. Tested parameters are: initial solution pH (pH_0), initial GWS mass loading ([GWS] ($g\,L^{-1}$)), contact time (t (min)), GWS particle size (d (μm)), initial Cr(VI) concentration ($[Cr(VI)]_0$ ($mg\,L^{-1}$)), and ionic strength (I(M)). Results revealed that Cr(VI) chemical reduction (to Cr(III)) followed by adsorption or surface precipitation is the removal mechanism. The optimal operational conditions for Cr(VI) removal from 50 mL of a $[Cr(VI)]_0 = 10\,mg\,L^{-1}$ solution were: $pH_0 = 3.6$, $t = 5$ min, $[GWS] = 6\,g\,L^{-1}$, and $I = 0.1$ M. The corresponding removal efficiency was 95%. The kinetic of the reaction was also studied. Results indicate that using GWS is an affordable, efficient, and applicable method for aqueous Cr(VI) removal and thus a low-cost material for water treatment.

Keywords: Adsorption kinetics; Bioreduction; Chromium removal; Green walnut shell; Low-cost biomass

1. Introduction

Heavy metals are significant pollutants of wastewater. Their toxicity for plants and animals has been largely documented [1,2]. These ionic species originated mostly from industrial and mining processes. Relevant processes include electroplating, metal finishing, metallurgical work, tanning, chemical manufacturing, and battery manufacturing [3,4]. Due to their non-biodegradability, they tend to accumulate in the vital organs of living organisms causing various diseases and long-term disorders, as well as deleterious ecological effects [5]. Some heavy metals are also known to be carcinogens. Accordingly, growing attention is being given to develop affordable, applicable, and efficient technologies for the removal of aqueous metal ions [6]. The removal of toxic heavy metal ions

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from sewage and from industrial and mining effluents has been widely studied in recent years [7–9].

Among heavy metals, chromium (Cr) is a common contaminant in surface water and groundwater resulting from numerous industrial activities such as the preservation of wood, textile dyeing, leather tanning, electroplating, and metal finishing [10]. Hexavalent chromium, which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), poses significantly higher levels of toxicity than the other valence states [11]. Both the common Cr(VI) anions, chromate and dichromate, are strong oxidants [12]. The toxicity of Cr(VI) even in small concentrations, has been studied in the past [13]. The two environmentally stable oxidation states, Cr(III) and Cr(VI), exhibit very different toxicities and mobilities. Cr(III) exhibits little toxicity [14]. In contrast, Cr(VI) usually occurs as the highly soluble and toxic chromate anion (500 times more toxic than Cr(III)), and is a suspected carcinogen and mutagen [15–17].

Conventional technologies for metal-contaminated wastewaters (e.g. Cr(VI) [18]) include chemical precipitation and filtration [2], chemical oxidation or reduction [19,20], electrochemical treatment [21], reverse osmosis [10], solvent extraction [22], adsorption [23,24], and ion exchange [25]. These processes have several disadvantages including high operational cost, incomplete removal, low selectivity, high energy consumption, and generation of a large amount of toxic sludge to be disposed of [26,27]. In recent years, efforts to develop applicable, efficient but affordable technologies for environmental remediation have been intensified [28–32]. Alternative approaches mostly use natural materials as adsorbing agents [33,34]. The expense of individual removal material varies depending on the degree of processing required and local availability [26,35].

Agricultural and horticultural waste materials are abundant and renewable (eco-friendly) potential adsorbents for environmental remediation in general and heavy metal removal in particular [36–39]. Many researchers have tested various biological materials such as non-living bacteria, microalgae, fungi, seaweed, agricultural and horticultural byproducts, and industrial bio-waste as removal material for Cr(VI) ions and some other heavy metals [28,40–42]. It has been reported that Cr(VI) was completely reduced to Cr(III) in aqueous and solid phases by non-living materials of the seaweed [43].

There are some researches on hard walnut shell both in natural state and modified form for water treatment [44–46]. Also, some other researchers used hard walnut shell as a carbon source. In these studies, the extracted carbon is employed as an adsorbent [47,48]. But up to our knowledge there is no investigation on the potential green walnut shell (GWS) for water treatment in the literatures.

The aim of this study was to test the suitability of green walnut shell (GWS) for wastewater treatment using hexavalent chromium as model pollutant. GWS is abundantly available in Iran. Cr(VI) removal by GWS powder was characterized under various experimental conditions (solution pH, contact time, GWS mass loading, GWS particle size, Cr(VI) concentration, and ionic strength). The kinetic of the reaction also was studied.

2. Materials and methods

2.1. Preparation of the solutions

All chemicals used were taken from Merck and were of analytical grade. Chromium trioxide (CrO_3) with deionized water was used in the preparation of solutions. Solutions with the initial concentration of $10\,mg\,L^{-1}$ from CrO_3 were prepared. This concentration was selected because it is within the range of environmentally relevant concentrations [49]. Also for investigating the kinetic of the removal reaction, solutions with various initial Cr(VI) concentrations in the range of 10–40 ppm at the initial $pH = 3.6$ were prepared. $NaNO_3$ was used for ionic strength studies. The solution pH was adjusted with a strong acid (HCl) and/or a strong base (NaOH).

2.2. Preparation of green walnut shell

The raw biomass of green walnut shell was collected from walnut trees in Shiraz, Iran. The biomass was washed with deionized water to remove extraneous materials and then air-dried for a week. The air-dried biomass was ground and sieved to particles of different sizes for subsequent experiments.

2.3. Procedure

In each experiment, an appropriate amount of GWS was placed in 50 mL solution of Cr(VI) with known concentration, initial pH, and ionic strength. Stirring speed of 250 rpm was selected to maintain the GWS particles in suspension. In different time intervals, a 1 mL sample extracted from the solution. The GWS particles were separated by filtration and the Cr(VI) concentration was determined. Each experiment was run thrice and the reported data in the figures are the averaged values.

For determination of point of zero charge, five flasks containing solutions of the same ionic strength and same amount of GWS were prepared. The initial pH (pH_i) values of the solutions were roughly adjusted between 2 and 10. The suspensions were then manually shaken and allowed to equilibrate. The final pH (pH_f) values of the supernatant liquid were recorded.

2.4. Analytical procedure

The analysis of Cr(VI) was carried out by colorimetric method [50] using a UV–Visible Spectrophotometer (UNICO SQ-4802) at $\lambda = 540$ nm. Not only Cr(VI) concentration but also the total concentration of Cr in the aqueous phase was analyzed by Varian (Vista-pro model) Coupled Plasma Mass Spectrometry (ICP-MS). The pH values of the solutions were recorded with a Metrohm 780 pH meter.

3. Results and discussion

For the last few decades, an anionic adsorption of Cr(VI) to cationic functional groups of biological materials has long been misunderstood as an absolute mechanism of Cr(VI) biosorption [40,51,52]. Nowadays "adsorption-coupled reduction" is widely accepted as the true mechanism of Cr(VI) biosorption by natural biological materials under acidic conditions [9,53]. When Cr(VI) comes in contact with biological materials, especially in an acidic solution, the Cr(VI) can be easily or spontaneously reduced to the Cr(III) [54], because Cr(VI) has high redox potential value (above +1.3 V at the standard condition). Often, the reducing agent can act as a sorbent for the resultant Cr(III) ion [55].

The existence of total Cr in the aqueous phase after the treatment implies the occurrence of Cr(VI) reduction to Cr(III) when brought into contact with the green walnut shell powder. According to the study of Park et al. Cr(VI) can be removed from an aqueous system by natural biological materials through both direct and indirect reduction mechanisms. In direct reduction mechanism (mechanism I), Cr(VI) is directly reduced to Cr(III) in the aqueous phase by contact with the electron-donor groups of the biological material, and the reduced Cr(III) forms complexes with biological materials or remains in the aqueous phase. Mechanism II (indirect reduction mechanism) consists of three steps; (I) the binding of anionic Cr(VI) to the positively charged groups present on the biomass surface, (II) the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups, and (III) the release of the reduced Cr(III) into the aqueous phase due to electronic repulsion between the positively charged groups and the Cr(III) ions, or the complexation of the reduced Cr(III) ions with adjacent groups [56].

3.1. Effect of the initial solution pH

The pH of solution is an important parameter which influences the removal of heavy metal ions [57]. The effect of pH on removal of Cr(VI) from the solution was investigated at room temperature (22–28°C) in a 50 mL solution of 10 mg L^{-1} Cr(VI) containing 0.1 g GWS (the particle size was 105–210 micrometers) and 0.1 M $NaNO_3$. The pH of Cr(VI)–GWS suspension was adjusted from 2.3 to 6.7. At the end of each experiment, the concentration of total and hexavalent chromium were measured by ICP and UV–vis spectrophotometer, respectively.

As it is obvious from the Fig. 1, by decreasing the pH of the solution, the efficiency and rate of Cr(VI) removal increases. It seems that protons participate in abiotic reduction reaction of Cr(VI) by GWS. This is in accordance with other researches [43,58,59]. There is a decrease in the removal when the solution pH is raised from 2.3 to 3.6 and thereafter the effect becomes negligible. Similar results were reported by other workers [60,61]. However, increasing the pH from 3.6 to 6.7 seems to have a little effect on the Cr(VI) removal efficiency. On the contrary, as shown in Fig. 2, comparing the total chromium concentration (ICP results) and Cr(VI) concentration (colorimetric method results) in each pH, it was confirmed that the concentration of Cr(III) decreases with increasing the pH, and it was proposed that protons inhibit adsorption reaction between cationic Cr(III) ions and negatively charged functional groups of walnut shell and this phenomenon has been reported in other researches [43].

Another argument for decreasing of metal removal with increasing pH is the decrease of electrostatic attraction. As the pH of the aqueous phase is lowered, a large number of protons can easily coordinate with these functional groups present on the biomass surface. Thus, low pH makes the biomass surface more positive. The more positive the surface charge of the biomass, the faster the removal rate of Cr(VI) in the aqueous phase, since the binding of anionic Cr(VI) ion species with the positively charged groups is enhanced. The low pH also accelerates the redox reactions in aqueous and solid phases, since the protons participate in these reactions [43,62].

3.2. Effect of GWS mass loading

Biomass concentration in the solution affects the specific uptake and hence this effect needs to be taken into consideration in any application of biomass as biosorbents. In order to investigate this parameter, at room temperature (22–28°C) in a 50 mL solution of 10 mg L^{-1} Cr(VI) and 0.1 M $NaNO_3$ and the initial pH of 3.6, results of different amounts of GWS (the particle size was 105–210 micrometers) in the reaction was examined. Fig. 3 indicates the effect of biomass amounts on the removal of Cr(VI) ion. It is obvious that the equilibrium concentration of Cr(VI) in the solution phase was decreased with increasing the GWS amount for a given initial Cr(VI) ion concentration, but changed slightly when the GWS amount was more than 0.3 g in 50 mL. Thus the optimum GWS amount for removal of Cr(VI) was found as 0.3 g in 50 mL of the experimental solution. The increase in the Cr(VI) ion removal with an increase in the GWS amount is due to the increase in surface area and adsorption sites available for reduction.

3.3. Effect of contact time

As shown in the previous plots (Figs. 1–3), for the initial condition of 50 mL solution of 10 mg L^{-1} Cr(VI) and 0.1 M $NaNO_3$ at room temperature (22–28°C), the removal rate of Cr(VI) ions was high initially and it was eventually very slow. The initial rate speed of metal removal was fast and may be explained by the large number of adsorption sites of the GWS. For the initial uncovered surface, the sticking probability was large; consequently removal proceeded with a high rate. The slower removal rate at the end was apparently due to the saturation of active sites with ions which is in accordance with previous study by Jang et al. [61].

3.4. Effect of particle size

Another effective parameter may be the particle size of GWS. Maximum uptake of removing is a function of specific surface or external surface of biomass. In Fig. 4 effect of particle size on removing rate at pH 3.6 in 50 mL solution of 10 mg L^{-1} Cr(VI) containing 0.1 g GWS and 0.1 M $NaNO_3$ is shown.

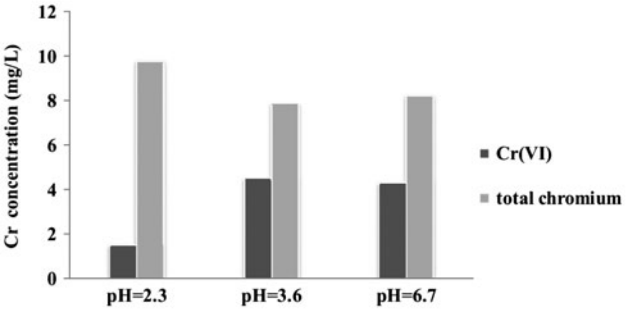

Fig. 2. Total Chromium and Cr(VI) concentrations in different pH values ($T = 22–28$°C, 50 mL solution of 10 mg L^{-1} Cr(VI) containing 0.1 g GWS (105–210 micrometers) and 0.1 M $NaNO_3$).

It is evident from the figure that changing the particle size of GWS from 105–210 to 74–105 μm, has not a significant effect on removal of Cr(VI) ions. It gives an idea that GWS powders are so highly porous which would not have significant effect on Cr(VI) removal at equilibrium.

3.5. Effect of the initial Cr(VI) ion concentration

The effect of Cr(VI) concentration on the removal of Cr(VI) ions was investigated by varying the Cr(VI) concentration (10–40 ppm) at initial pH of 3.6 and 0.1 g GWS in 50 mL solution (Fig. 5). The removal efficiency at each contact time was decreased with an increase in the initial concentration of chromium with

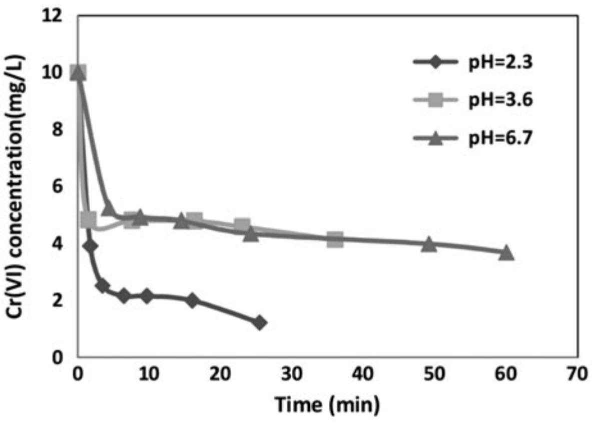

Fig. 1. The effect of initial solution pH on the reaction ($T = 22–28$°C, 50 mL solution of 10 mg L^{-1} Cr(VI) containing 0.1 g GWS (105–210 micrometers), and 0.1 M $NaNO_3$).

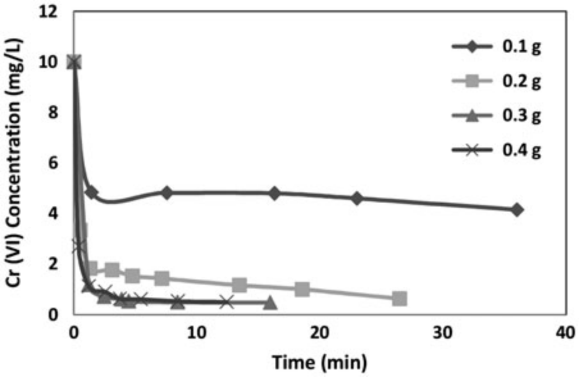

Fig. 3. Effect of green walnut shell amount on the reaction ($T = 22–28$°C, 50 mL solution of 10 mg L^{-1} Cr(VI) containing different amounts of GWS and 0.1 M $NaNO_3$, initial pH = 3.6).

a constant amount of GWS in the solution. Considering the identical removal concentration used in the experiments, a decrease in the Cr(VI) ion removal with an increase in the initial concentration was attributed to limited adsorption sites.

3.6. Effect of ionic strength

Effect of ionic strength on Cr(VI) sorption is shown in Fig. 6 by varying the $NaNO_3$ concentration in the solutions. The initial pH of this experiment was 3.6 and the 50 mL solution of 10 mg L^{-1} Cr(VI) contained 0.1 g GWS, while the $NaNO_3$ concentration varied from 0.01 to 1 M of $NaNO_3$. It is clear from the figure that Cr(VI) removal is approximately independent from ionic strength.

3.7. Determination of the point of zero charge

Five flasks which contained solutions of the same ionic strength (0.1 M $NaNO_3$) and 0.1 g GWS were prepared. The initial pH (pH_i) values of the solutions were roughly adjusted between 2 and 10 by adding either 0.1 M HCl or NaOH solution. The total volume of the solution in each flask was made 25 mL by adding dionized water. The suspensions were then manually, shaken, and allowed to equilibrate for 24 h with intermittent manual shaking. The final pH (pH_f) values of the supernatant liquid were noted. The difference between the initial and final pH values ($\Delta pH = pH_i - pH_f$) was plotted against pH_i. The point of intersection of the resulting curve with the abscissa, at which $\Delta pH = 0$, gave the pH_{PZC} (Fig. 7). The value of pH_{ZPC} of GWS was found to be 4.5. Below this pH, the surface charge of the GWS is positive and above pH 4.5, GWS would have a net negative charge [63].

This result is in accordance with Figs. 1 and 2, as mentioned before positive surface of GWS enhanced the reduction rate at pH = 2.3 (electrostatic interaction between negative chromate ions and surface). But as the initial pH increases, the surface becomes negative (above pH_{PZC}) and this time electrostatic interaction will be introduced between Cr(III) (produced by Cr(VI) reduction) and GWS, so the total concentration of chromium will decrease after the treatment. At pH = 3.6 the total chromium concentration was the least (Fig. 2).

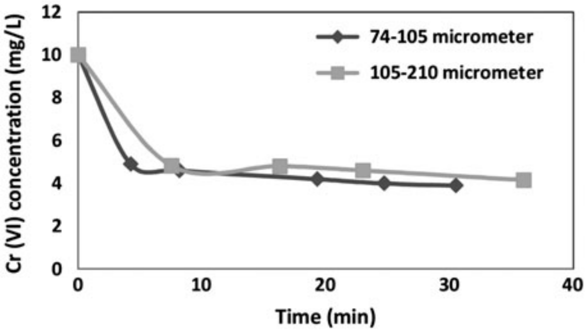

Fig. 4. Effect of particle size on the reaction ($T = 22$–$28\,^\circ C$, 0.1 g GWS in 50 mL solution of 10 mg L^{-1} Cr(VI) and 0.1 M $NaNO_3$, initial pH = 3.6).

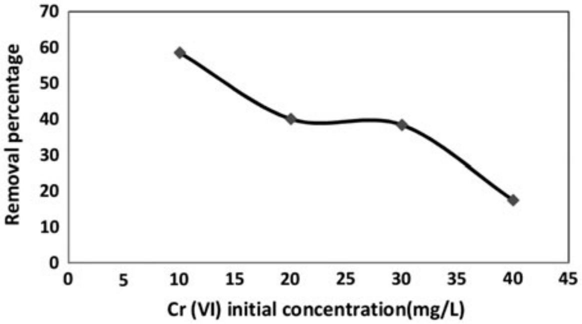

Fig. 5. Effect of initial Cr(VI) ion concentration on the reaction ($T = 22$–$28\,^\circ C$, 50 mL solution of different concentration of Cr(VI) containing 0.1 g GWS and 0.1 M $NaNO_3$, initial pH = 3.6).

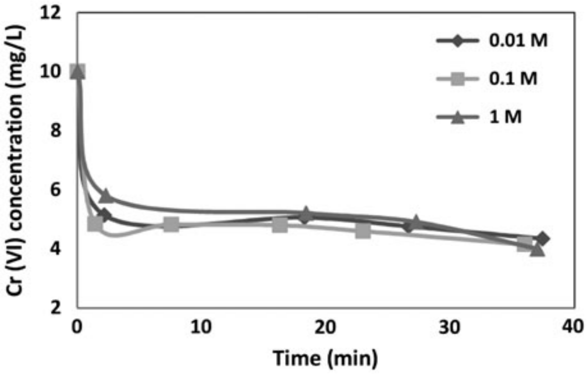

Fig. 6. Effect of ionic strength on the reaction ($T = 22$–$28\,^\circ C$, 50 mL solution of 10 mg L^{-1} Cr (VI) containing 0.1 g GWS and different concentration of $NaNO_3$, initial pH = 3.6).

3.8. Kinetics of hexavalent chromium removal with the GWS

In short, the removal rate of Cr(VI) is increased with a decrease in pH or with increases in Cr(VI) concentration and biomass concentration [41]. In particular, the initial removal rate of Cr(VI) was the first-order with respect to initial Cr(VI) concentration (Fig. 8).

The concentration of Cr(VI) vs. time was examined at various initial Cr(VI) concentrations in the range of 10–40 ppm at the initial pH = 3.6. When removal rates of Ln[Cr(VI)] were plotted vs. Ln[Cr(VI)]$_0$, ([Cr(VI)]$_0$ is the initial concentration), data were plotted on a nearly straight line, indicating that the reaction might be first-order with respect to Cr(VI) concentration (the coefficient of regression, R^2, was 0.993).

The concentration of Cr(VI) vs. time was also examined at various amounts of GWS in the range of 0.1–0.4 g in 50 mL at the initial pH = 3.6. When initial removal rates were plotted vs. amounts of GWS, the plot almost produced a straight line, indicating that the reaction was pseudo-first-order with respect to the amount of GWS (Fig. 9).

The kinetic model could be developed from a concept based on the redox reaction between Cr(VI) and the biomass as Park et al. suggested [41,60].

$$\mathrm{B} + \ \mathrm{Cr(VI)} \rightarrow \ \mathrm{B(oxidized)} + \mathrm{Cr(III)} \tag{1}$$

where B is the biomass. When pH is constant, the rate equation of Cr(VI) reduction is represented as follows: [41,60]

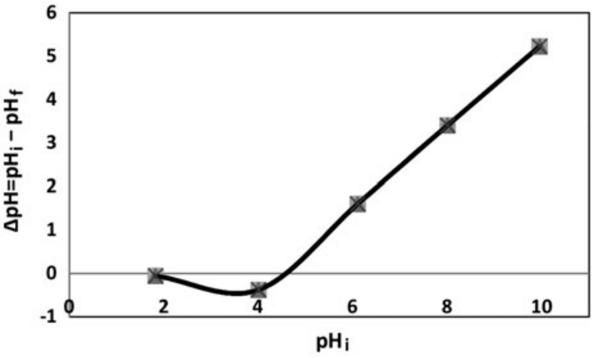

Fig. 7. Determination of the point of zero charge.

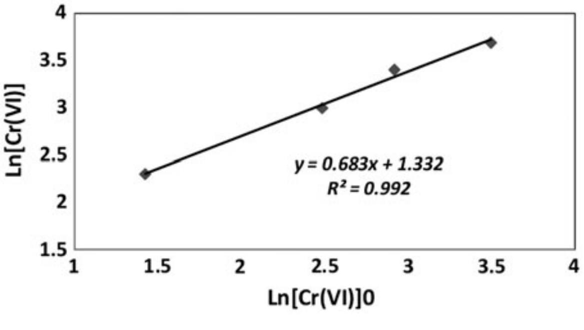

Fig. 8. First-order behavior for Cr(VI) in the reaction.

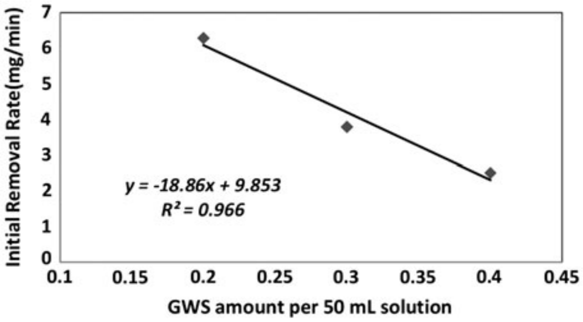

Fig. 9. Pseudo-first-order behavior for GWS in the reaction.

$$\frac{\mathrm{d[Cr(VI)]}}{\mathrm{d}t} = -k\mathrm{[OC][Cr(VI)]}(\mathrm{mmol\,L^{-1}\,h^{-1}}) \tag{2}$$

where OC represents the equivalent organic compound capable of reducing Cr(VI), [mM], and k presents its rate coefficient. For a given time, the concentration of OC is as follows:

$$\mathrm{[OC]} = \mathrm{[OC]_0}(1 - X_{\mathrm{oxi}})\ (\mathrm{mmol\,L^{-1}}) \tag{3}$$

where X_{oxi} represents the fraction of OC oxidized, and can be calculated as follows, when considering equivalent reaction between the OC and the Cr(VI):

$$X_{\mathrm{oxi}}\frac{\Delta\mathrm{[Cr(VI)]}}{\mathrm{[OC]_0}} = \frac{\mathrm{[Cr(VI)]_0} - \mathrm{[Cr(VI)]}}{\mathrm{[OC]_0}} \tag{4}$$

Also, the initial concentration of OC, [OC]$_0$, can be evaluated as follows:

$$\mathrm{[OC]_0} = C^*_{\mathrm{OC}}\mathrm{[B]}\ (\mathrm{mmol\,L^{-1}}) \tag{5}$$

C^*_{OC} indicates the content of equivalent organic compound per unit gram of the biomass, mmol g^{-1}.

Combining Eqs. (2)– (5) gives:

$$\frac{\mathrm{d[Cr(VI)]}}{\mathrm{d}t} = -k\mathrm{[Cr(VI)]}(\mathrm{[Cr(VI)]} + C^*_{\mathrm{OC}}\mathrm{[B]} - \mathrm{[Cr(VI)]_0}) \tag{6}$$

and rearranging Eq. (6).

$$\left(\frac{1}{\mathrm{[Cr(VI)]}} - \frac{1}{\mathrm{[Cr(VI)]} + C^*_{\mathrm{OC}}\mathrm{[B]} - \mathrm{[Cr(VI)]_0}}\right)\mathrm{d[Cr(VI)]} = -\mathrm{k}(C^*_{\mathrm{OC}}\mathrm{[B]} - \mathrm{[Cr(VI)]_0})\mathrm{d}t \tag{7}$$

Table 1
Kinetic model parameters for Cr(VI)removal in aqueous phase

Biomass concentration ($g\,L^{-1}$)	Initial Cr(VI) concentration ($mg\,L^{-1}$)	C^*_{OC} ($mmol\,g^{-1}$)	Overall rate coefficient; k ($\mu M^{-1}\,h^{-1}$)	R^2
2	10	0.24	1.130	0.99
2	20	0.50	0.013	0.95
2	40	0.31	0.009	0.97
4	10	0.28	1.590	0.99
6	10	0.16	2.580	1.00
8	10	0.26	2.620	1.00

Note: Experiments were conducted at pH 3.6 and room temperature.

Finally, the integration of Eq. (7) yields a model equation in the general form, as follows: [41]

$$[\mathrm{Cr(VI)}] = \frac{C^*_{\mathrm{OC}}[\mathrm{B}][\mathrm{Cr(VI)}]_0 - [\mathrm{Cr(VI)}]_0^2}{C^*_{\mathrm{OC}}[\mathrm{B}]\exp(kC^*_{\mathrm{OC}}[\mathrm{B}] - [\mathrm{Cr(VI)}]_0 t) - [\mathrm{Cr(VI)}]_0} \tag{8}$$

where k and C^*_{OC} are model constant parameters and t is a variable.

With the aid of Sigma Plot V 11.00, a weighted least squares linear regression using experimental data obtained in this study gave constant values of k and C^*_{OC} as shown in Table 1. The values were used to describe the Cr(VI) behavior in the aqueous solution when brought into contact with GWS (Fig. 10). The regression value which was found to be 0.99 means that the Cr(VI) removal behavior was well fitted by the simplified reduction equation, explained above.

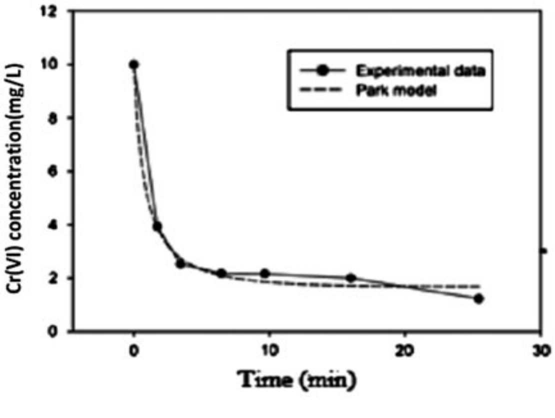

Fig. 10. Comparison of experimental data with simulation results using Eq. (8) (conditions: $10\,mg\,L^{-1}$ initial Cr(VI) concentration, 0.1 g GWS in 50 mL solution, initial pH 2.3). The Cr(VI) removal behavior was well fitted by the simplified reduction equation in a form of $\frac{d[Cr(VI)]}{dt} = -k[OC][Cr(VI)]$.

4. Conclusions

The use of GWS biomass for the detoxification of Cr(VI) from contaminated waters may be a novel and cost-effective alternative for the conversion of toxic Cr(VI) into less toxic or non-toxic Cr(III). The use of GWS is advantageous because it is abundant and cheap. Simplified reduction equation in the form of $\frac{d[Cr(VI)]}{dt} = -k[OC][Cr(VI)]$ was used as a kinetic model for the Cr(VI) biosorption by biomass and successfully predicted the time-dependent concentration of Cr(VI) in the aqueous phase. In conclusion, the main mechanism of Cr(VI) removal by natural biomass is "adsorption-coupled reduction."

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