Grape waste as a biosorbent for removing Cr(VI) from aqueous solution

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ABSTRACT

Grape waste generated in wine production is a cellulosic material rich in polyphenolic compounds which exhibits a high affinity for heavy metal ions. An adsorption gel was prepared from grape waste by cross-linking with concentrated sulfuric acid. It was characterized and utilized for the removal of Cr(VI) from synthetic aqueous solution. Adsorption tests were conducted in batch mode to study the effects of pH, contact time and adsorption isotherm of Cr(VI), which followed the Langmuir type adsorption and exhibited a maximum loading capacity of 1.91 mol/kg at pH 4. The adsorption of different metal ions like Cr(VI), Cr(III), Fe(III), Zn(II), Cd(II) and Pb(II) from aqueous solution at different pH values 1–5 has also been investigated. The cross-linked grape waste gel was found to selectively adsorb Cr(VI) over other metal ions tested. The results suggest that cross-linked grape waste gel has high possibility to be used as effective adsorbent for Cr(VI) removal.

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1. Introduction

Chromium is harmless in its elemental state but it exists in aqueous medium in +III and +VI oxidation states which are toxic to living organisms [1]. Cr(III) is an essential element to living organisms when present in low concentrations but toxic when occur in high concentrations [2]. Cr(VI) is 500 times more toxic and highly mobile than Cr(III) [3]. Its toxicity include cancer as well as kidney, liver and gastric damages [4]. Taking account of its harmful effects, many countries has implemented the maximum permissible level of Cr(VI) in water. The maximum level of Cr(VI) permitted in waste water is $0.5\,mg/dm^3$ in Japan [5] but effluents from textile industries, leather tanning, metal finishing, electric and electronic equipment manufacturing industries, contain higher levels of Cr(VI) [6]. It is essential for such industries to treat their effluents so as to reduce Cr(VI) concentration to acceptable levels before discharging it into environment.

Several methods such as chemical precipitation, ion exchange, membrane separation, and adsorption have been used for waste water treatment [7]. A major drawback of precipitation technique is significant sludge production. Although ion exchange is considered to be a better alternative technique, it is expensive and the majority of ion exchangers have not good selectivity to specified metal ions over other metal ions. Adsorption technique is considered to be

amongst the most favorable processes because of its high efficiency and complete removal of metal ions even at low concentrations [8]. The continuing increase in variety and amount of hazardous chemicals in effluents makes conventional adsorbents inefficient and sometimes even ineffective. Consequently, the development of new and more effective adsorbents has become essential, but at the same time it should be of low cost.

Agricultural materials contain proteins, polysaccharides and lignin which are associated with functional groups responsible for metal ion adsorption [9]. The abundant natural occurrence and presence of large amount of surface functional groups make various agricultural wastes good alternatives to expensive synthetic adsorbents [10]. Different agrowastes like apple and orange wastes as well as rice milling products have been investigated for this purpose [11–13].

In this paper, grape waste has been tested for the adsorption and separation of Cr(VI) ions from water. The grape is one of the major fruit crops worldwide and its harvest is about 60 millions tones per year. About 80% of the harvest is utilized for producing wine and the grape waste consists the 20% of the weight of processed grapes. Wine industry generates about 5–9 million tones grape waste per year, worldwide [14]. Such waste is rich in polyphenol compounds due to which it causes many detrimental effects on the flora and fauna of discharged zones [15]. Its reutilization as an adsorbent for the removal of heavy metal ions can solve not only the disposal problem of this waste biomass but also the problem of the treatment of toxic effluents and increase economic gain to such industries.

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2. Experimental

2.1. Preparation of the adsorbent

The waste of the Muscat berry A (*Vitis vinifera* L.), mainly the skin, generated in the production of wine was kindly provided by the Grape Research Centre of Yamanashi University. Approximate quantity of polyphenols contained in grape skin was measured by means of Folin–Denis method [16]. As tannic acid, gallic acid, pyrogallol, catechol and catechin were used as typical standards for this measurement, the polyphenol content varies depending on the nature of standard used for the calibration. Highest concentration was calculated in case of catechin standard. Although the exact reason for this difference is not clear, highest concentration of polyphenol was obtained using catechin as standard solution followed by tannic acid, gallic acid, pyrogallol and catechol. This investigation confirmed that the grape waste was rich in polyphenol group.

For the preparation of the adsorption gel, 45.3 g grape waste was crushed and mixed with 60 cm^3 concentrated sulfuric acid and stirred for 24 h. During this time cross-linking between the many polyphenol and polysaccharide hydroxyl groups in the grape waste takes place through a condensation reaction by the aid of concentrated sulfuric acid, a dehydrating agent [17]. The product was neutralized by stirring in sodium hydrogen carbonate solution followed by filtration and stirred again in 1 mol/dm^3 HCl solution to recondition the sample. After stirring, the product was filtered and washed with distilled water followed by a hot water wash at 323 K to remove the excess acid. The sample, prepared in this way, was dried overnight in a convection oven at 333 K and the particle diameter was regulated to 100–150 μm by sieving.

Sample solutions for measurement of the total organic carbon (TOC) concentration were prepared by shaking 10 mg of cross-linked grape gel with 10 cm^3 of aqueous solutions at varying pH values over the range of 1–11 at 303 K for 24 h. The pH of the solution was adjusted by adding hydrochloric acid or sodium hydroxide. The TOC concentration was measured by using a Shimadzu model TOC-VSH Total Organic Carbon Analyzer. The TOC concentration of the original grape waste, the feed material, ranged from 248 mg/dm^3 (at pH 1) up to 271 mg/dm^3 (at pH 11) which corresponds to 24.9% and 27.0% of the TOC of the wet sample. However, for the cross-linked grape gel, the TOC value was only 23.1 mg/dm^3 (at pH 1) and 26.6 mg/dm^3 (at pH 11), respectively, which corresponds to 2.3% and 2.6% of the TOC of the wet sample. This result showed that cross-linking helps to combine some water soluble low molecular weight compounds into less water soluble compounds of higher molecular weight and decreases the leakage of low molecular weight compounds thus improving the mechanical strength of the gel.

2.2. Characterization of the adsorbent

Surface functional groups were qualitatively analyzed using a JASCO FT/IR-410 Fourier transform infrared spectrometer. The BET surface area and average pore diameter was measured using a Belsorp 18PLUS-SP (BEL Japan Inc.). The sample was also characterized by X-ray diffractometry (XRD) using a Shimadzu XRD-6300 instrument with Cu Kα radiation.

2.3. Adsorption tests

Batch wise adsorption tests were carried out for individual metal ions by shaking 10 mg of the cross-linked grape waste together with 10 cm^3 of metal solution at 303 K for about 24 h using a thermostated air bath incubator except for kinetic tests. The pH was adjusted with 0.1 mol/dm^3 of HEPES solution and 0.1 mol/dm^3 HCl solutions except in the case of the Cr(VI) solution. Aqueous solution of Cr(VI) was prepared by dissolving analytical grade K$_2$CrO$_4$ into 0.1 M hydrochloric acid. The pH of the Cr(VI) solution was adjusted with 0.1 mol/dm^3 HCl and 0.1 mol/dm^3 NaOH solutions. After adsorption, the adsorbent was removed by filtration and the metal concentration in the filtrate was measured by using a Shimadzu model ICPS-8100 ICP-AES spectrometer. Since the total Cr concentration was measured by means of ICP/AES spectroscopy, the concentration of Cr(VI) was measured by the diphenylcarbazide method using the Hitachi model U-3310 UV spectrophotometer. The concentration of Cr(III) was calculated from the difference between the total Cr and the Cr(VI) concentrations. The % adsorption (*A*%) and the amount of metal adsorbed (q) was calculated as follows:

$$A\% = \left\{ \frac{(C_i - C_e)}{C_i} \right\} \times 100 \tag{1}$$

$$q = \left\{ \frac{(C_i - C_e)}{W} \right\} \times V \tag{2}$$

where C_i (mmol/dm^3), C_e (mmol/dm^3), W (g) and V (dm^3) denote the initial metal concentration, equilibrium metal concentrations, dry weight of adsorbent and the volume of solution, respectively.

3. Results and discussion

3.1. Characterization of the adsorbent

Fig. 1 shows the FTIR spectrum of the cross-linked grape waste gel before and after adsorption of Cr(VI) at pH 4. The broad absorption peak at 3300 cm^{-1} can be attributed to the –OH groups of alcohols, phenols and carboxylic acids. The broad peak at 1242 cm^{-1} can be assigned to the phenolic group. The peak at 3300 cm^{-1} as well as 1242 cm^{-1} existed in cross-linked grape waste gel before adsorption but it disappeared after adsorption of Cr(VI) which shows that phenolic group has been used for the adsorption of Cr(VI) by esterification reaction as described by Nakano et al. [18].

Fig. 2 shows the X-ray diffraction analysis of the cross-linked grape waste gel. The appearance of a broad peak centered at $2\theta = 22.5$ indicated the existence of amorphous silica in the sample.

The surface area and average pore diameter of the gel were measured as 5.34 m^2/g and 63.8 nm respectively.
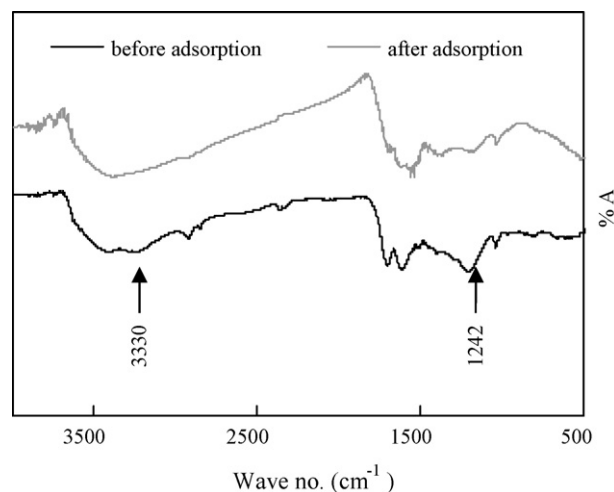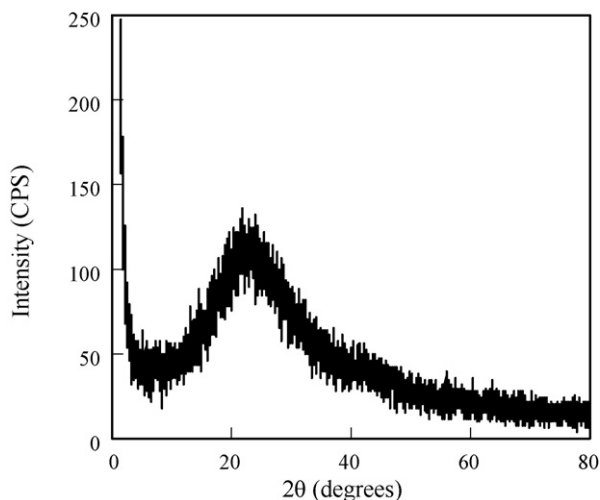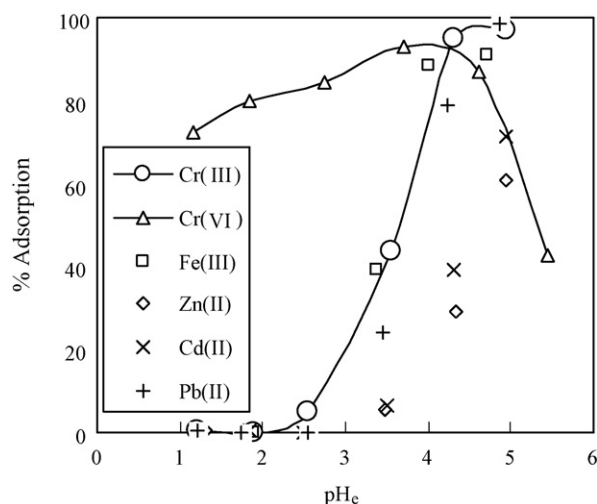

Fig. 1. Fourier transform infrared (FTIR) spectrum of cross-linked grape waste gel before and after adsorption of chromium.

Fig. 2. X-ray diffractogram for cross-linked grape waste gel. Where, CPS = count per second.

Fig. 3. Effect of pH on the adsorption of different metal ions on cross-linked grape waste gel.

3.2. Effect of pH

Fig. 3 shows the effect of the equilibrium pH on the % adsorption of several metal ions on the cross-linked grape waste gel. This figure shows the high selectivity of the present adsorbent for Cr(VI) at pH < 3. The % adsorption of all metal ions investigated in this experiment was found to increase with increasing pH in the range of 1–5 except for Cr(VI). In contrast, the % adsorption of Cr(VI) increased over the pH range of 1–4 and then decreased with further increases in pH. Thus the optimal pH for Cr(VI) adsorption is 4. This contrasting behavior for Cr(VI) adsorption compared to the other metal ions can be attributed to a different adsorption mechanism as shown in Scheme 1 [18].

As mentioned earlier grape waste gel is rich in polyphenol compounds containing functional groups like catechol. Cr(VI) exists in aqueous medium in the $HCrO_4^-$ and CrO_4^{2-} forms, among which the $HCrO_4^-$ form is the dominant species up to pH 5 [19]. Consequently, Cr(VI), existing as oxo anions in water, is considered to be adsorbed on the adsorbent by an esterification reaction with functional groups of catechol as shown in Scheme 1(a), which suggests that a high concentration of H^+ ions facilitates the adsorption whereas a high concentration of OH^- ions suppresses the adsorption reaction, thus accounting for the decrease in the % adsorption of Cr(VI) ion at high pH. This adsorption mechanism is also supported by FTIR data analysis where the absorbance peak existing due to presence of phenolic group in cross-linked grape waste gel has disappeared after adsorption of chromium. On the other hand, the decrease in adsorption of Cr(VI) at low pH is attributed to the reduction of Cr(VI) to Cr(III), as will be described later.

Other metal ions existing as cationic species in water are adsorbed on the cross-linked grape waste gel according to a cation exchange mechanism as shown by Scheme 1(b). According to this reaction mechanism, adsorption of cationic metal species increases with increasing pH as shown in Fig. 3.

3.3. Effect of contact time

Fig. 4 shows the effect of contact time on the % adsorption of Cr(VI) on the cross-linked grape waste gel. It was investigated at pH 1–8 for up to 25 h contact time while keeping other experimental parameters constant. The initial and equilibrium Cr concentration was measured by means of ICP/AES spectroscopy which measures the total Cr ion concentration. At pH 1 and 2, the % adsorption of Cr decreases with increasing contact time after a rapid increase in adsorption whereas at pH 3–8 the % adsorption monotonously increases with increasing contact time till it reaches a constant value. The decrease in % adsorption with increasing contact time at pH 1 and 2 can be attributed to the partial reduction of Cr(VI) to Cr(III) which is not adsorbed at the low pH values of 1 and 2 as shown in Fig. 3. The adsorption rate of Cr(VI) decreases with increasing pH from 3 to 8. This is attributed to the adsorption reaction of the oxo anionic species of Cr(VI) by the esterification mechanism catalyzed by hydrogen ions as described by Scheme 1(a).

(a) Esterification reaction.

(b) Ion exchange reaction
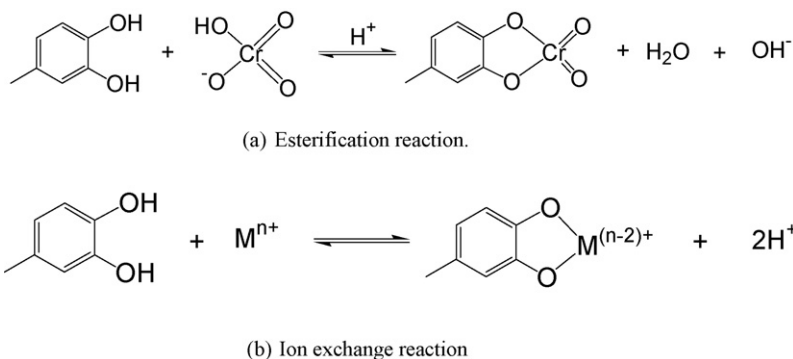
Scheme 1. Adsorption mechanism of (a) Cr(VI) and (b) other metals binding to the catechol group in the grape waste gel.
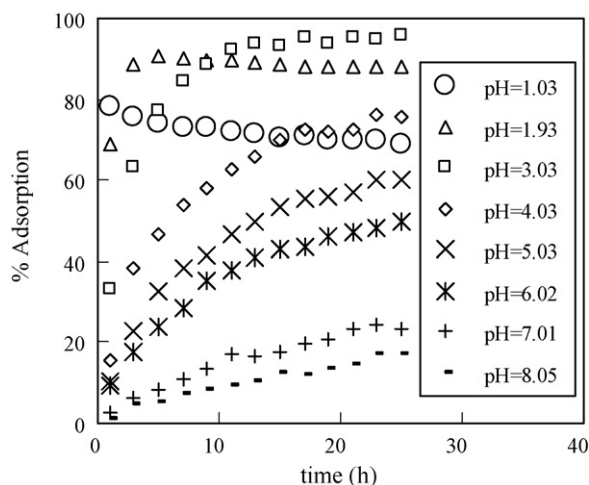
Fig. 4. Effect of contact time on the adsorption of Cr on cross-linked grape waste gel solution at different pH values.

In order to elucidate the possibility of reduction of Cr(VI) after interaction with cross-linked grape waste gel, both Cr(VI) and Cr(III) concentrations in solution were measured as shown in Fig. 5. Fig. 5(a) shows that the Cr(VI) ion was completely removed from the aqueous solution by the cross-linked grape waste gel at pH 1 within the contact time of 60 min. At the same time as Cr(VI) removal, the Cr(III) ion concentration, which was not initially present, was found to increase. This result suggests that Cr(VI) adsorbed on the adsorbent in the form of the anionic species $HCrO_4^-$ by the ester-ification reaction as described above, is reduced to Cr(III) through electron donation from the electron rich polyphenolic aromatic ring according to the following reaction:

$$CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr(III) + 4H_2O \tag{3}$$
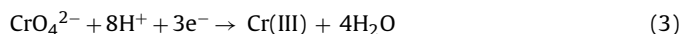
After reduction of Cr(VI) to Cr(III), Cr(III) is released into the aqueous solution again as shown by the increase in Cr(III) concentration with time. Comparison of the results shown in Fig. 5(a)–(d) indicates that the rate of reduction as well as the rate of removal of Cr(VI) decreases with increasing pH. The decrease in the rate of removal of Cr(VI) accompanied by the reduction of Cr(VI) with increasing pH can be interpreted by the catalytic function of the hydrogen ions in the esterification reaction as described by Scheme 1. From the results it is apparent that the adsorption mechanism of Cr(VI) on grape waste gel is an adsorption coupled reduction mechanism as reported in other studies [19,20].

3.4. Adsorption isotherm for chromium(VI)

Fig. 6 shows the adsorption isotherm for Cr(VI) at pH 4. The metal uptake increases with increasing Cr(VI) concentration in the aqueous solution in the low concentration region while it appears to tend to approach constant values in the high concentration region, exhibiting the Langmuir type adsorption.

Consequently, the adsorption isotherm data was fitted with the following Langmuir equation.

$$\frac{C_e}{q_e} = \frac{1}{(\theta b)} + \frac{C_e}{\theta} \tag{4}$$

where q_e = amount adsorbed at equilibrium (mol/kg), C_e = equilibrium Cr(VI) concentration in solution (mol/dm^3)

θ and b are Langmuir isotherm constants, which are related to adsorption capacity and affinity of adsorption, respectively, and were determined from the slope and intercepts of the linear plots of C_e/q_e versus C_e. The experimental data is well fitted by the Langmuir Eq. (4) as shown in Fig. 6(b), where linear relationship is observed with high correlation coefficients ($R^2 = 0.99$). The values of θ and b were evaluated to be 1.91 mol/kg and 653 dm^3/mol, respectively.

The Langmuir constant, 'b', indicates the favorability of reaction. The dimensionless separation parameter R_L [$= \{1/(1 + bC_i)\}$]
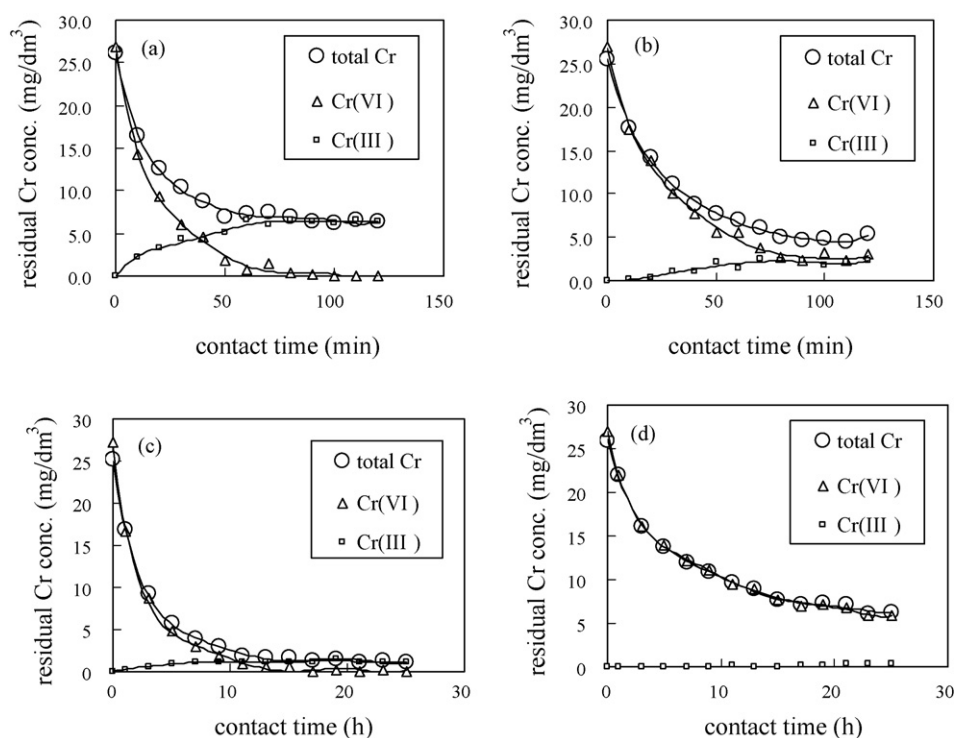

Fig. 5. The variation with time of the concentrations of Cr(VI) and Cr(III) in the aqueous solution during adsorption. (a) pH 1; (b) pH 2; (c) pH 3; and (d) pH 4.
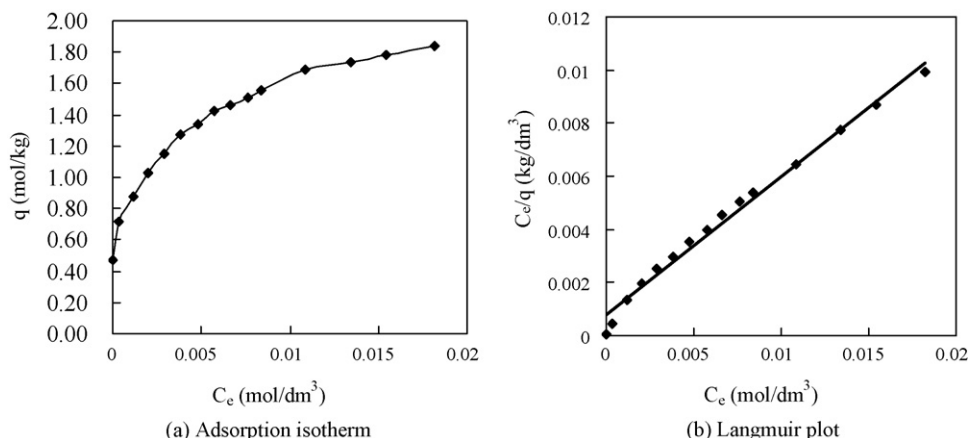
(a) Adsorption isotherm

(b) Langmuir plot

Fig. 6. Adsorption isotherms for Cr(VI).

Table 1
Comparison of the maximum adsorption capacity for Cr(VI) on different adsorbents

Adsorbent	pH	Temperature (°C)	Adsorption capacity (mol/kg)	Reference
Mimosa tannin	2.0	30	5.52	[18]
Persimmon tannin	3.0	30	5.27	[22]
Sugarcane bagasse	3.0	25	1.97	[23]
Quaternary chitosan	4.5	25	1.31	[24]
Cross-linked chitosan	5.5	25	1.01	[25]
Cross-linked grape waste gel	4.0	30	1.91	This work

expresses the essential characteristics of the Langmuir isotherm [21]. Here, C_i is the initial concentration of Cr(VI). The evaluated R_L values at C_i equals to 0.0005, 0.001, 0.01 and 0.02 were 0.75, 0.60, 0.13 and 0.07, respectively, which lie between 0 and 1, indicating the favorable adsorption of Cr(VI) on the cross-linked grape waste gel.

3.5. Comparison of the cross-linked grape waste gel with other adsorbents

Table 1 summaries the comparison of the maximum adsorption capacities for various adsorbents including the cross-linked grape waste gel. This table shows that the polyphenol-containing adsorbents such as mimosa tannin (condensed tannin) [18] and persimmon tannin [22] have higher adsorption capacities than other biomasses such as sugarcane bagasse [23] and chitosan [24,25]. The grape waste gel containing the polyphenolic groups also demonstrated a high adsorption capacity for Cr(VI) comparable to those of the other tannin containing gels. However, compared to other gels, the preparation process of the grape waste gel is simple and economical because the feed material is grape waste itself whereas other tannin gels are produced from expensive pure tannin compounds. Therefore, the utilization of this biomass for the preparation of a more sophisticated adsorbent for Cr(VI) ions for environmental remediation looks highly promising.

4. Conclusions

Cross-linked grape waste gel has been found to be selective to Cr(VI) ion and highly effective for its removal from synthetic aqueous solution. The adsorption of Cr(VI) on the gel was highly pH dependent and maximum adsorption occurred at pH 4. The adsorption capacity was found to increase with increasing solute concentration as described by the Langmuir adsorption model. The maximum adsorption capacity of Cr(VI) was 1.91 mol/kg at pH 4. The Cr(VI) removal occurs by esterification reaction which is confirmed by FTIR measurement. Since most of the industrial wastewaters contaminated with Cr(VI) are highly acidic, cross-linked grape waste gel can be good candidate for waste water treatment. Due to large generation of grape waste every year and the very simple production process of cross-linked grape waste gel, it seams to be a promising adsorbent.

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