Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan

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Abstract

In this study, the technical feasibility of coconut shell charcoal (CSC) and commercial activated carbon (CAC) for Cr(VI) removal is investigated in batch studies using synthetic electroplating wastewater. Both granular adsorbents are made up of coconut shell (*Cocos nucifera* L.), an agricultural waste from local coconut industries. Surface modifications of CSC and CAC with chitosan and/or oxidizing agents, such as sulfuric acid and nitric acid, respectively, are also conducted to improve removal performance. The results of their Cr removal performances are statistically compared. It is evident that adsorbents chemically modified with an oxidizing agent demonstrate better Cr(VI) removal capabilities than as-received adsorbents in terms of adsorption rate. Both CSC and CAC, which have been oxidized with nitric acid, have higher Cr adsorption capacities (CSC: 10.88, CAC: 15.47 $mg\,g^{-1}$) than those oxidized with sulfuric acid (CSC: 4.05, CAC: 8.94 $mg\,g^{-1}$) and non-treated CSC coated with chitosan (CSCCC: 3.65 $mg\,g^{-1}$), respectively, suggesting that surface modification of a carbon adsorbent with a strong oxidizing agent generates more adsorption sites on their solid surface for metal adsorption.
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Keywords: Low cost adsorbent; Surface oxidation; Nitric acid; Sulfuric acid; Electroplating industry; Wastewater treatment

1. Introduction

Presently, there are more than 2000 registered electroplating industries in Bangkok, Thailand. About 1000 m^3 of Cr-contaminated water is generated everyday by a small electroplating industry (with less than 1000 employees). Traditionally, chemical precipitation is the most widely used method in Thailand for Cr(VI) removal (Charerntanyarak, 1999) with the cost required for treating wastewater from a medium size electroplating plant is USD 120 (to produce 800 l water free from Cr).
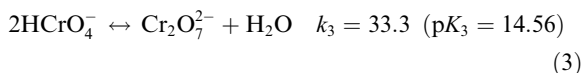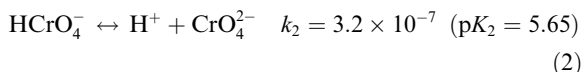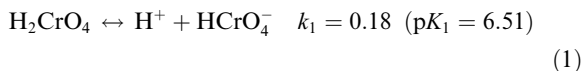
Kongsricharoern (1994) reported that the Cr(VI) concentration in the wastewater effluents discharged from the local electroplating industries in Bangkok was about 25 $mg\,l^{-1}$ and that their current treatment facilities still produce Cr effluent of 10 $mg\,l^{-1}$, far higher than the acceptable limit of the wastewater discharge standards allowed by Thai government and the US EPA (Environmental Protection Agency), which are 0.25 (Pollution Control Department, 2003) and 0.05 $mg\,l^{-1}$ (Nourbakhsh et al., 1994), respectively.

Chromium, which is on the top priority list of toxic pollutants defined by the US EPA, is present in the electroplating wastewater as Cr(VI) in the form of

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oxyanion, such as chromates (CrO_4^{2-}), dichromates ($Cr_2O_7^{2-}$), and bichromates ($HCrO_4^-$). Depending on pH and Cr concentration (Ramos et al., 1994; Kotaś and Stasicka, 2000), the Cr(VI) species exist with equilibrium constant (at 25 °C) as follows:

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^- \quad k_1 = 0.18 \ (pK_1 = 6.51)$$
$$(1)$$

$$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-} \quad k_2 = 3.2 \times 10^{-7} \ (pK_2 = 5.65)$$
$$(2)$$

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \quad k_3 = 33.3 \ (pK_3 = 14.56)$$
$$(3)$$

Due to its high solubility, Cr(VI) is very toxic to living organisms compared to Cr(III) (Selvaraj et al., 2003). If Cr is ingested beyond the maximum concentration ($0.1 \ mg \, l^{-1}$), it can cause health disorders, such as vomiting and hemorrhage (Lalvani et al., 1998). Thus, suggesting that treatment of wastewater prior to discharge is required to avoid these effects.

Various techniques can be employed to treat metal-contaminated water, such as electro-chemical precipitation (Kongsricharoern, 1994), ion exchange (Rengaraj et al., 2001), ultrafiltration (Yurlova et al., 2002), and reverse osmosis (Benito and Ruiz, 2002). But, major drawback with precipitation is sludge production. Ion exchange is considered a better alternative technique for such a purpose. However, it does not appear to be economically appealing because of high operational cost.

Adsorption using commercial activated carbon (CAC) can remove heavy metals from electroplating wastewater, such as Cd (Ramos et al., 1997); Ni (Shim et al., 2001); Cr (Ouki et al., 1997); Cu (Monser and Adhoum, 2002) with adsorption capacities of 8, 10, 32, and 38 $mg \, g^{-1}$ of CAC, respectively. It may be also possible to meet the stringent standard of Cr effluent discharge ($<0.25 \ mg \, l^{-1}$) in Thailand using this treatment method. However, CAC remains an expensive material for heavy metal removal.

To replace CAC, the search for low-cost adsorbents has intensified in recent years. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential as low cost adsorbents, as they represent unused resources.

Due to its heavy metal removal capabilities, recently coconut shell charcoal (CSC) has been developed into one of the promising options. The exchange/sorption properties of coconut shell are due to the presence of some functional groups, such as carboxylic, hydroxyl, and lactone, which have a high affinity for metal ions (Tan et al., 1993). Coconut shell, a hard and thick bony endocarp material, which often presents serious disposal problems for local environments, is an abundantly available agricultural waste from the local coconut industry. According to the statistics of the Thai Ministry of Commerce (1998), about 1.4 million tons of coconut (*Cocos nucifera*) are produced in Thailand annually. Conversion of coconut shell, representing an unused resource, into activated carbon, which can be used as an adsorbent in water purification, would add its economic value, help reduce the cost of waste disposal, and most importantly, provide a potentially inexpensive alternative to the existing CAC.

A preliminary study has been conducted to assess the technical feasibility of using coconut shell-based activated carbon to remove Cr(VI) (Alaerts et al., 1989) from contaminated water. However, the previous study does not provide any information on the surface modifications of CSC to improve its metal removal performance.

In this research, the surface of CSC and CAC are chemically modified with a strong oxidizing agent, like nitric acid and sulfuric acid. Chitosan was also used for coating the surface of CSC and hence, this type of adsorbent was called non-treated coconut shell charcoal coated with chitosan (CSCCC). Using synthetic wastewater, the Cr removal performances of both CSC and CAC are statistically compared. The Langmuir and Freundlich isotherms were also used to understand the adsorption mechanism of Cr removal by CSC/CAC from the solution. The mechanism of Cr adsorption by CSC/CAC and economic point of view of using CSC as an adsorbent compared to CAC for Cr removal are also presented.

2. Materials and methods

2.1. Materials

The adsorbents used in this study were CSC type 12/40 and CAC type PHO 8/35 LBD (Carbokarn Co. Ltd, Bangkok, Thailand). Both adsorbents, made up of coconut shell, are granular in as-received form. Their physical characteristics are listed in Table 1. All chemical solutions were prepared from certified lab grade

Table 1
Physical properties of CSC and CAC

Property	CSC	CAC
Particle size (mm)	0.42–1.70	0.50–2.36
Surface area ($m^2 \, g^{-1}$)	5–10	900–1100
Solid density ($g \, cm^{-3}$)	0.63	0.48
Packing density ($g \, cm^{-3}$)	0.73	0.53
Pore volume ($ml \, g^{-1}$)	0.06	0.73
Unit price (Thai Baht kg^{-1})[a]	15	60
(US\$ kg^{-1})	0.34	1.36

[a] 1US\$ = 43.72 Thai Baht (May, 2003).

chemicals. Potassium dichromate ($K_2Cr_2O_7$) was used as the source of Cr(VI) in the synthetic wastewater. The Cr stock solution (500 mg l^{-1}) was prepared by dissolving 0.7071 g of $K_2Cr_2O_7$ in 500 ml of deionized water, while Cr concentration of synthetic wastewater was varied from 5 to 25 mg l^{-1} by diluting the stock solution. Before being used for adsorption studies, the pH of Cr solution at 20 mg l^{-1} of Cr concentration was measured using a pH meter model pH PRO (Trans, Singapore). Adjustment of pH was carried out using 0.1 N NaOH and/or 0.1 N H_2SO_4. Agitation of the system under investigation was carried out on a rotary shaker type SserikerII PNP (Panapolytech, Bangkok, Thailand), while chromium concentration was analyzed by a spectrophotometer model CECIL/CE 1021 (Cecil Instrument, Cambridge, England).

2.2. Methods

2.2.1. Chemical modification of CSC and CAC
2.2.1.1. Oxidizing with sulfuric acid. For conditioning, CSC/CAC was washed with deionized water until any leachable impurities due to free acid and adherent powder were removed. The samples were then treated with 2% H_2SO_4 (v/v) in an incubator at 110 °C for 24 h and soaked with deionized water until the solution pH was stable. Afterwards, the adsorbent was soaked in 2% $NaHCO_3$ (w/v) till any residual acid left was removed. Finally, the samples were dried overnight in an oven at 110 °C, cooled at room temperature, and stored in a desiccator (Kadirvelu et al., 2001).

2.2.1.2. Oxidizing with nitric acid. After being washed with deionized water and dried overnight, CSC/CAC was oxidized with 65% HNO_3 (w/v). A known volume of the nitric acid was heated in an incubator at 110 °C for 3 h. The adsorbent was then immersed in it (volume ratio of HNO_3 and CSC/CAC = 5:1) and oxidized for 3 h. After cooling, the acid solution was drained and the oxidized adsorbent was washed with deionized water until the pH of rinsing water remained constant. Finally, the samples were dried overnight in an oven at 110 °C and stored in a desiccator (Pradhan and Sandle, 1999; Ramos et al., 2002).

2.2.1.3. Coating with chitosan. To produce CSCCC, chitosan flakes 90% deacetylated,obtained from Eland Co. Ltd. (Bangkok, Thailand), were immersed in 0.5% acetic acid (v/v) and mechanically agitated using a rotary shaker at 150 rpm for 24 h to form a homogenized gel. Afterwards, CSC was dipped into the gel (dose ratio of chitosan and CSC = 1:5) and shaken overnight at 150 rpm. The gel-coated CSC was then washed with deionized water and dried. This process was repeated for three times to form a thick coating of chitosan on CSC. The coated activated beads were removed and neutralized by

putting them in 0.5% NaOH (w/v) solution for 3 h. The chitosan gel beads were then extensively rinsed with deionized water and dried. Hereafter, it was called CSC coated with chitosan (non-treated CSCCC). Similarly, sulfuric acid-treated CSC was also coated with chitosan and this type of adsorbent was called treated CSC coated with chitosan (sulfuric-treated CSCCC).

2.2.2. Batch adsorption experiments
To maximize Cr removal by the adsorbent, batch experiments were conducted at ambient temperature using the optimum conditions of all pertinent factors, such as dose, pH, agitation speed, and contact time (Chakravarty et al., 2002). Subsequent adsorption experiments were carried out with only optimized parameters.

Adsorption isotherm tests were also carried out in the reaction mixture consisting of 1.5 g l^{-1} of adsorbent and 100 ml of Cr solution with varying chromium concentration from 5 to 25 mg l^{-1}.

2.2.3. Cr(VI) analysis
The change in Cr(VI) concentration due to adsorption was determined colorimetrically according to Standard Methods (Clesceri et al., 1998). A purple-violet colored complex was developed in the reaction between Cr(VI) and 1,5-diphenylcarbazide in acidic condition. Absorbance was measured at wavelength (λ) 540 nm. The minimum detectable concentration by this method is approximately 0.005 mg l^{-1} as Cr(VI).

The removal efficiency (E) of adsorbent on Cr(VI) was defined as

$$E(\%) = [(C_0 - C_1)/C_0] \times 100 \qquad (4)$$

where C_0 and C_1 are the initial and equilibrium concentration of Cr solution (mg l^{-1}), respectively.

2.2.4. Statistical analysis
To ensure the accuracy, reliability, and reproducibility of the collected data, all the batch experiments were carried out in duplicate and the mean values of two data sets are presented. In nearly all instances, the accuracy of data was very good, as the relative standard deviation was less than 1.0%. The Cr removal efficiency for all types of adsorbents was within the range of ±1.0%. When the relative error exceeded this criterion, the data were disregarded and a third experiment was conducted until the relative error fell within an acceptable range.

Statistical analysis using the paired *t*-test was performed to evaluate the above data if there was any significant difference in terms of Cr removal efficiency for two categorical variables between an as-received adsorbent (before treatment) and a chemically modified adsorbent (after surface oxidation) for CSC and CAC.

This test was conducted if the Kolmogorov–Smirnov test confirmed the normality of the variable distribution ($p > 0.05$). Otherwise, the Wilcoxon-signed rank test was performed for such a purpose.

Similarly, the analysis of variance (ANOVA) test was employed to analyze data, which has three, or more than three categorical variables, if the distribution of each variable was normal ($p > 0.05$). Otherwise, the Kruskall–Wallis test was employed.

One-way ANOVA test was conducted to find out if there were any significant differences in terms of Cr removal efficiency due to surface modification between treatments in the batch experiments as a whole, but a two-way factorial ANOVA test was performed to compare the mean of Cr removal efficiency between as-received adsorbent and two or more modified adsorbents for both CSC and CAC, while simultaneously detecting if there was any significant interaction between type of surface modification and one of pertinent factors (dose, pH, agitation speed, or contact time). After performing one-way ANOVA test for preliminary evaluation, further statistical analysis was also conducted using the Tukey's HSD test to compare the mean of Cr removal performance of all pairwise adsorbents (CSC and/or CAC). All statistical tests were performed using SPSS 11.00 Windows version with confidence interval of 95% ($p \leqslant 0.05$).

3. Results and discussion

3.1. Coconut shell charcoal

3.1.1. Effect of dose

The dependence of Cr sorption on dose was studied by varying the amount of CSC from 1.5 to 25.5 g l^{-1}, while keeping other parameters (pH, agitation speed, and contact time) constant. Fig. 1 presents the Cr removal efficiency for all types of CSC.

From Fig. 1, it can be observed that removal efficiency of CSC generally improved with increasing dose up to a certain value and then, there is no further increase of adsorption. At 20 mg l^{-1} of Cr concentration, the Cr removal efficiency significantly increased from 50% to 85% when the dose of nitric-treated CSC was increased from 1.5 to 12.0 g l^{-1}. This can be explained due to the fact that the higher the dose of adsorbent in the solution, the greater the availability of exchangeable sites for metal ions.

A significant difference in terms of Cr removal efficiency was also observed between as-received CSC and a chemically modified CSC ($p \leqslant 0.05$; paired t-test). Of the four types of chemically modified CSCs, chemically oxidized CSC with nitric acid has the greatest Cr removal efficiency as compared to others.

It is interesting to note that the saturated values of Cr removal efficiency of the five types of CSC are different from one to another due to the extent of surface modification. Depending on the ability of the oxidizing molecule to diffuse into carbon pores, the acidic surface groups introduced might be preferentially located where there is wide microporosity (El-Hendawy, 2003).

Compared to that with sulfuric acid and/or chitosan, surface modification of CSC with nitric acid substantially increased the negative surface charge of adsorbent, which is a favorable condition for Cr removal. As a result, the negative surface charge of CSC started acquiring more positive charge of Cr(III) ions, making the situation electrostatically favorable for a higher Cr uptake. It is also suggested that the formation of more acidic C=O groups on the surface of CSC due to oxidative treatment enhanced its hydrophilic character and
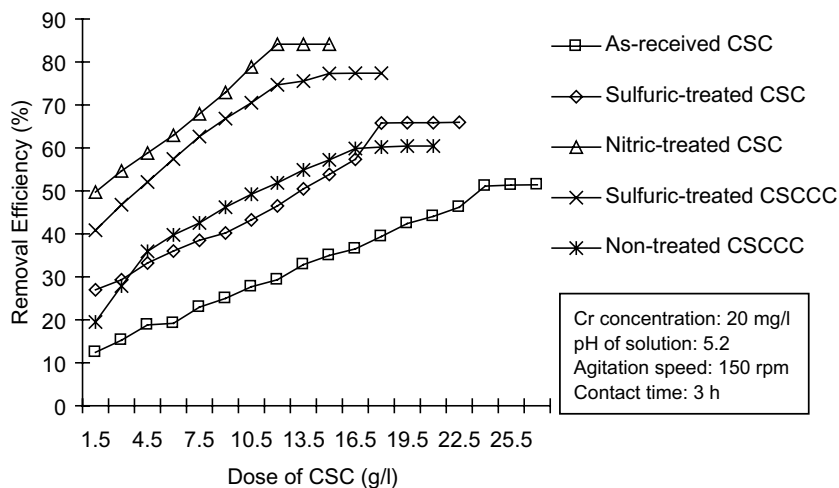

Fig. 1. Effect of dose on the removal efficiencies of all types of CSC.

sorption affinity; thus, promoting more Cr adsorption and pore diffusion.

3.1.2. Effect of pH

Knowledge of the optimum pH is very important since pH affects not only the surface charge of adsorbent, but also the degree of ionization and speciation of adsorbate during reaction. To examine the effect of pH on the Cr removal efficiency, the pH of solution was varied from 2.0 to 9.0.

Fig. 2 shows that the Cr removal efficiency of all types of CSC slightly increased as the pH increased from 2.0 to 6.0. In fact, the removal efficiency of nitric-oxidized CSC increased from 75% to 86% over pH range 2.0–4.0. This phenomenon can be attributed to the fact that a lower pH increases the negatively charged groups on the surface of CSC, which leads to higher Cr uptake.

It was found that there was a significant reduction in Cr adsorption of nitric-treated CSC from 85% to 33% when equilibrium pH was increased from 6.5 to 9.0. It may be due to the fact that the covalent coordination bonds between Cr(III) ions and the surface functional group of CSC, such as carboxylic and hydroxyl, are very weak in basic condition.

It was also noticed that the optimum pH slightly varied between as-received and nitric-oxidized CSC as the latter had a lower optimum pH (pH = 4.0) than the former (pH = 6.0). It can be attributed to the fact that surface modification of CSC with nitric acid increased the acidic site of CSC. Consequently, more surface oxygenated complexes were formed on its carbon surface (Aggarwal et al., 1999).

3.1.3. Effect of agitation speed

In this study, agitation speed was varied from 90 to 190 rpm, while keeping the optimum dose of CSC and the optimum pH as constant. Fig. 3 illustrates the effect of agitation speed on the Cr removal efficiency of CSC.

As can be seen from Fig. 3, the Cr removal efficiency of CSC generally increased with increasing agitation speed. The Cr removal efficiency of nitric-oxidized CSC increased from 76% to 87% when the agitation speed increased from 90 to 150 rpm and the Cr removal efficiency of the adsorbent remained constant for a higher agitation speed. This can be due to the fact that a higher agitation speed increases the degree of physicochemical interaction between negatively charged surface of CSC and Cr(III) ion at acidic conditions, resulting in a higher Cr removal efficiency. It was also found that the Cr removal efficiency was not significantly influenced by the degree of agitation ($p > 0.05$; ANOVA test) for all types of CSC.

An agitation speed of 150 rpm, giving the highest Cr removal efficiency, was selected as the optimum speed for all types of CSC and used for the remaining adsorption studies. An optimum agitation speed is essentially required to maximize the interactions between metal ions and adsorption sites of adsorbent in the solution.

3.1.4. Effect of contact time

The Cr removal was also studied as a function of contact time at the optimum condition of dose, pH, and agitation speed where maximum Cr removal could take place. Results are presented in Fig. 4.

From Fig. 4, it is observed that removal efficiency of CSC increased with an increase in contact time and then, it tends to become constant with a longer period of agitation time. It was noticed that the Cr removal efficiency of nitric-treated CSC increased from 60% to 87% when contact time was increased from 30 to 180 min. Optimum contact time of nitric-oxidized CSC was found
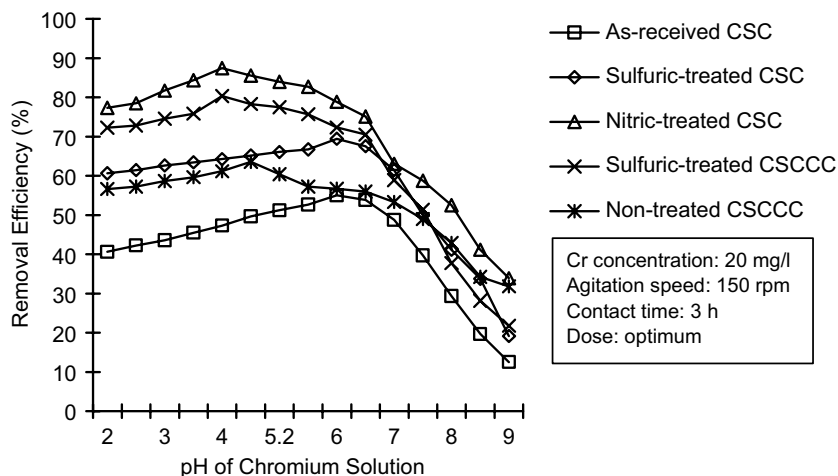

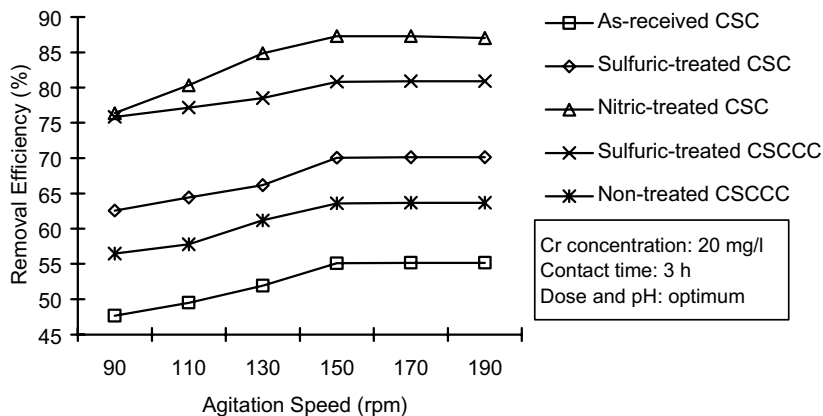Fig. 2. Effect of pH on the removal efficiencies of CSC on chromium.

Fig. 3. Effect of agitation speed on the removal efficiencies of CSC.
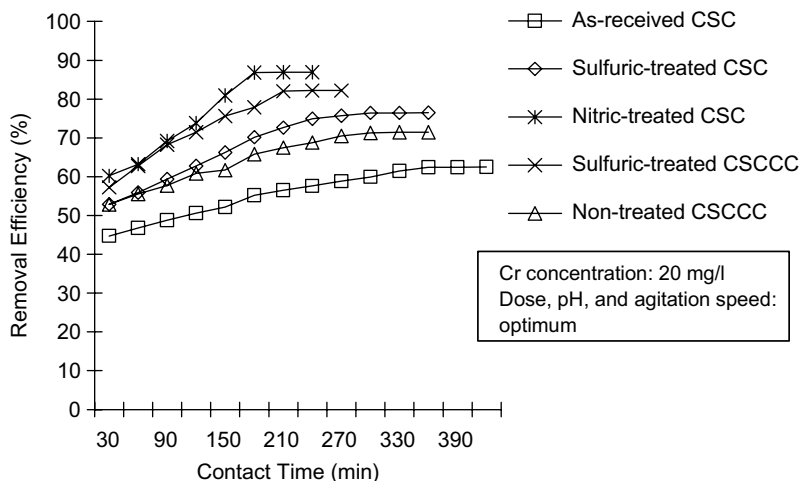

Fig. 4. Effect of contact time on the removal efficiencies of CSC.

to be 180 min compared to that of as-received form (360 min), indicating a shorter contact time for chemically modified CSC.

A significant difference of optimum contact time between CSC in chemically modified form and that in as-received form can be explained due to the fact that optimum contact time was affected by the ratio of the number of adsorption sites to the number of metal species. Due to oxidative treatment, the number of adsorption sites of CSC and its negatively charged surface significantly increased. Consequently, Cr adsorption on CSC proceeded rapidly as more Cr species were adsorbed through columbic forces at acidic condition.

Overall, the contact time required by all types of CSC was relatively short, ranging from 3 to 6 h. As presented in Fig. 4, the Cr removal efficiency for all the adsorbents, such as as-received CSC, for 3 h (55.23%) and 6 h of

contact time (62.42%), respectively, is not much different. Therefore, in order to maximize the cost-effectiveness of adsorption operation, 3 h of contact time was used for the batch experiments. This result is interesting, as equilibrium time is one of the important parameters for an economical wastewater treatment plant.

3.1.5. Adsorption isotherm

3.1.5.1. Langmuir isotherm. The Langmuir model assumes that the uptakes of metal ions occur on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. Langmuir isotherm constants were calculated from the following linearized form:

$$\frac{C_e}{Q_e} = \frac{1}{a_m b} + \frac{1}{a_m} C_e \tag{5}$$

where a_m and b are Langmuir constants determined from the slope and intercept of the plot, indicative of maximum adsorption capacity (mg g^{-1}) of adsorbent and energy of adsorption, respectively, while C_e is the remaining concentration of adsorbate after equilibrium (mg l^{-1}) and Q_e is the amount adsorbed at equilibrium (mg g^{-1}) (Kadirvelu et al., 2001).

The single-solute sorption of Cr by CSC was plotted by varying Cr concentration (from 5 to 25 mg l^{-1}), as the range of Cr concentrations present in the real electroplating wastewater is about 25 mg l^{-1} (before treatment) and 10 mg l^{-1} (after chemical precipitation treatment). The linear plot of $1/Q_e$ and $1/C_e$ shows that the experimental data reasonably well fitted the linearized equation of the Langmuir isotherm over the whole Cr concentration range studied with the average percent deviation of the Langmuir isotherm was lower (0.25%) than that of the Freundlich (1.98%); thus, testifying to the applicability of a monolayer coverage of the Cr on the surface of CSC. The deviations between the experimental data and the value calculated by the Langmuir isotherm can be attributed to the fact that pH affects the amount and type of surface complexes (adsorption sites), which are present on the surface of CSC. The Langmuir constants and corresponding correlation coefficients of all types of CSC are given in Table 2.

According to Kadirvelu et al. (2001), the essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor (R_L), defined by:

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

where b is the Langmuir constant and C_0 is the initial concentration of metal ion. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). Table 2 shows that Cr sorption of all types of CSC in this study is favorable. These results indicate the efficacy of the adsorbent under investigation.

3.1.5.2. Freundlich isotherm. Freundlich isotherm assumes that the uptakes of metal ions occur on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The Freundlich isotherm is expressed as:

$$Q_e = K_f \cdot C_e^{1/n} \tag{7}$$

where K_f and n are constants of Freundlich isotherm incorporating adsorption capacity (mg g^{-1}) and intensity, while C_e and Q_e are the remaining concentration of adsorbate after equilibrium (mg l^{-1}) and the amount adsorbed at equilibrium (mg g^{-1}), respectively. Taking

Table 2
Adsorption capacities (mg g^{-1}) of CSC for Cr(VI) ions

Type of CSC	Langmuir isotherm						Freundlich isotherm			
	Q_e (mg g^{-1})	R^2	a_m	b	R_L	Equation of Q_e	Q_e (mg g^{-1})	R^2	n	Equation of Q_e
As-received	2.18[a]	0.9982	2.1820	0.2092	0.1605	$Q_e = 0.4565C_e/(1+0.2092C_e)$	0.61[fg]	0.988	2.8026	$Q_e = 0.6134C_e^{0.3568}$
Coated with chitosan	3.65[b]	0.9944	3.6519	0.2003	0.1664	$Q_e = 0.7313C_e/(1+0.2002C_e)$	0.92[fh]	0.981	2.5158	$Q_e = 0.9187C_e^{0.375}$
Oxidized with sulfuric acid	4.05[bc]	0.9906	4.0503	0.3010	0.1173	$Q_e = 1.2191C_e/(1+0.3010C_e)$	1.31[fi]	0.971	2.9206	$Q_e = 1.3102C_e^{0.3424}$
Oxidized with sulfuric and coated with chitosan	8.95[d]	0.9995	8.9476	0.1446	0.2166	$Q_e = 1.2943C_e/(1+0.1446C_e)$	1.44[fj]	0.993	1.8210	$Q_e = 1.4351C_e^{0.5492}$
Oxidized with nitric acid	10.88[e]	0.9920	10.8762	0.1487	0.2119	$Q_e = 1.6178C_e/(1+0.1487C_e)$	1.84[fk]	0.963	1.9282	$Q_e = 1.8448C_e^{0.5186}$

Remarks: The Cr adsorption capacities (Q_e) followed by the same letter in the columns 2 and 8 are not significantly different ($p > 0.05$) from each other at the 95% level of confidence interval as determined by the Tukey's HSD test ($n = 20$; df $= 15$; F-value $= 15.75$).

logarithm from the Eq. (7), a linearized form of Freundlich isotherm can be represented as follows:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \qquad (8)$$

Linear plots of $\log Q_e$ versus $\log C_e$ shows that the Freundlich isotherm was also representative for the Cr adsorption by all types of CSC. In this study, however, Langmuir isotherm has a better fitting model than Freundlich as the former have higher coefficient correlations than the latter (Table 2). This can be explained due to the fact that CSC has a small surface area for metal adsorption. Therefore, only monolayer adsorption occurred on its surface, in spite of any surface modification. The application of both models of isotherm was also confirmed by statistical analysis ($p \leqslant 0.05$; regression test).

K_f and n, calculated from the intercept and slope of the above plots, are also presented in Table 2. It is shown that the n values for all types of CSC are $1 < n < 3$, suggesting that the Cr adsorption on CSC is favorable (Kadirvelu et al., 2001).

3.1.6. Adsorption mechanism of CSC

Since the acidic functional groups of CSC, consisting of carboxylic, hydroxyl, and carbonyl, present on its surface, it was assumed that the physicochemical interactions that might occur during Cr removal could be expressed as follows:

$$M^{n+} + n(\text{–COOH}) \leftrightarrow (\text{–COOH})_n M + nH^+ \qquad (9)$$

where (–COOH) represent the surface functional group of CSC and n is the coefficient of the reaction component, depending on the oxidation state of metal ions, while M^{n+} and H^+ are Cr(III) and hydrogen ions, respectively.

Although the oxyanion of dichromate ($Cr_2O_7^{2-}$) was used as the source of Cr(VI) in the synthetic wastewater, under common environmental pH (pH < 6.0), the Cr(VI) exists in the predominant form of $HCrO_4^-$ (Lalvani et al., 1998; Pradhan et al., 1999) with the hydrolysis reaction of $Cr_2O_7^{2-}$ as follows:

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \quad pK_3 = 14.56 \qquad (10)$$
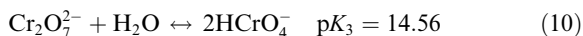
In acidic solution where intimate physicochemical contact between adsorbent and adsorbate occurred, Cr(VI) demonstrates a very high positive redox potential (E^0) in the range of 1.33 and 1.38 V (Kotaś and Stasicka, 2000); thus, implying that Cr(VI) is strongly oxidizing and unstable in the presence of electron donors. The carbon surface of CSC contains carboxylic and hydroxyl groups, which play a role as electron donors in the solution (Tan et al., 1993). Consequently, Cr(VI) oxyanion is readily reduced to Cr(III) ions due to the

presence of electron donors of CSC according to the following reaction of electron transfer:

$$HCrO_4^- + 7H^+ + 3e^- \overset{pH\,5.0–6.0}{\leftrightarrow} Cr^{3+} + 4H_2O \quad E^0 = 1.20\ V \qquad (11)$$
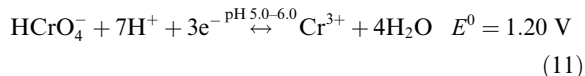
It can be seen from Eq. (11) that the reduction of Cr(VI) oxyanion is accompanied by a large amount of proton consumption in the acidic solution; thus, confirming the decisive role played by H^+ in the Cr(VI) removal. The latter mechanism has also been reported (Ramos et al., 1994; Sharma and Forster, 1994b, 1996; Reddad et al., 2003). It was also reported that the redox potential of the Cr(VI)/Cr(III) strongly depends on pH; at pH $\approx$ 1, $E^0 \approx$ 1.3 V and at pH $\approx$ 5, $E^0 \approx$ 0.68 V (Lakatos et al., 2002), indicating that improving the redox potential of the oxidant will extend the oxidation towards the more resistant surface functionalities.

Since the pH of synthetic wastewater ranges from 5.0 to 6.0, the Cr(III) mostly exists as $[Cr(OH)]^{2+}$ species (Kocaoba and Akcin, 2002; Lakatos et al., 2002) with the hydrolysis reaction of Cr(III) as follows:
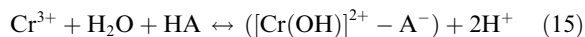
$$Cr^{3+} + H_2O \leftrightarrow [Cr(OH)]^{2+} + H^+ \quad pK_1 = 3.85 \qquad (12)$$
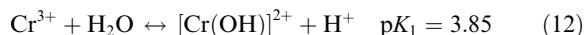
The second mechanism controlling the adsorption of Cr(III) on the carbon surface of CSC is represented as:

$$Cr^{3+} + H_2O \leftrightarrow [Cr(OH)]^{2+} + H^+ \qquad (13)$$

$$HA + [Cr(OH)]^{2+} \leftrightarrow ([Cr(OH)]^{2+} - A^-) + H^+ \qquad (14)$$
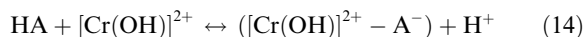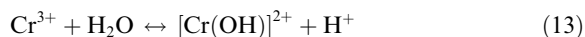
where A represents an adsorption site on the acidic surface of CSC.

Combination of Eqs. (13) and (14) gives the overall adsorption reaction as follows:

$$Cr^{3+} + H_2O + HA \leftrightarrow ([Cr(OH)]^{2+} - A^-) + 2H^+ \qquad (15)$$

Eq. (15) suggests that the Cr adsorption on the surface of CSC is due to columbic forces between the positive charge of Cr(III) and the negative surface charge of CSC. Based on the attractive electrostatics interaction between the electron-donating nature of the oxygen-containing functional groups on the carbon surface of CSC (Lewis base) and the electron-accepting nature of heavy metal ions (Lewis acid), the ion exchange mechanism of Cr might be preferentially considered (Nakano et al., 2001). For instance, a Cr(III) ion may attach itself to three adjacent hydroxyl group, carboxylic group, and oxyl group, which can donate some lone pairs of delocalized π-electrons on the surface to the metal ion for the formation of surface oxide compounds ($[Cr(OH)]^{2+} - A^-$) (Reddad et al., 2003).

Based on the above equation, it is also indicated that as the solution pH increased to 6.0 or the concentration of hydrogen ions decreased (to 10^{-6} M), the

adsorption reaction shifted from left to right, which resulted in the production of more oxygenated Cr complex ($[Cr(OH)]^{2+} - A^{-}$) on the surface of CSC or higher Cr removal efficiency. After equilibrium, it was also found that the pH of the Cr solution decreased after adsorption; thus, indicating that the CSC was hydrophilic and acidic in nature, as more H^{+} was released into the solution.

3.1.7. Effect of oxidative treatment on the surface structure of CSC

The carbon surface of CSC has unsaturated C=C bond, which on oxidation can remarkably generate more oxygen-containing surface functional groups and yield large amounts of surface area available for metal uptake by improving its pore structure (Nakano et al., 2001). The increase in the concentration of potentially accessible carboxyl sites due to surface oxidation was clearly demonstrated by the increase of Cr adsorption capacity in the isotherm studies.

As Cr(VI) reduction mostly took place with the carbons bound to –OH surface functionalities (Lakatos et al., 2002), the oxidation of CSC also resulted in an increase in the concentration of electron donor site. Due to the presence of delocalized π-electrons that is easily transferable in a conjugated system of aromatic bonds, CSC has a remarkable electrical conductivity, as localization of the 2p electrons of the functional group-oxygen ($-COO^{-}$) into the π-conjugated system results in an increase in the negative charge present on the surface and hence, a competition between H^{+} and Cr(III) ions for adsorption sites (El-Hendawy, 2003). Consequently, the availability of relatively high amount of $-COO^{-}$ renders the adsorbent more acidic and have more negative surface charge; thus, increasing the sorptive capacity of the oxidized CSC for Cr(III) ions through attractive columbic interaction.

3.2. Commercial activated carbon

3.2.1. Effect of dose

To investigate the effect of dose, 20 mg l^{-1} of Cr solution was mixed with different doses of CAC (0.5–7.0 g l^{-1}) for 3 h, while keeping other parameters as constants.

It can be seen from Fig. 5 that the Cr removal efficiency of CAC generally increased with an increase in dose up to a certain value and then, there was no further increase of adsorption. It was also noticed that the removal efficiency of as-received CAC significantly increased from 17% to 90% when the dose was increased from 0.5 to 6 g l^{-1}. Beyond the dose of 6 g l^{-1}, there was no increase in Cr removal efficiency.

Similarly, there was no remarkable increase of removal efficiency seen beyond 2.0 g l^{-1} for nitric-oxidized CAC. This indicates that surface modification of CAC with a strong oxidizing agent significantly improved the removal capabilities of CAC as almost 100% Cr removal could be achieved using 2.0 g of adsorbent compared to that of CSC.

It is important to note that the saturated values of Cr removal efficiency of the three types of CAC are different from one to another, depending on the type of oxidizing agent used and the extent of surface modification. It was found that oxidation of CAC with nitric acid generated formation of relatively stronger acidic functional groups, like carboxylic and carbonyl, on the surface of CAC than that with sulfuric acid (Aggarwal et al., 1999), as the former is a stronger oxidizing agent than the latter. As a result, increasing the number of oxygen-containing surface functional group enhanced the sorption affinity of the surface of CAC and hence, its selectivity of polar molecule (El-Hendawy, 2003). Consequently, intensely oxidized carbon surface of CAC substantially possess more adsorption sites available for
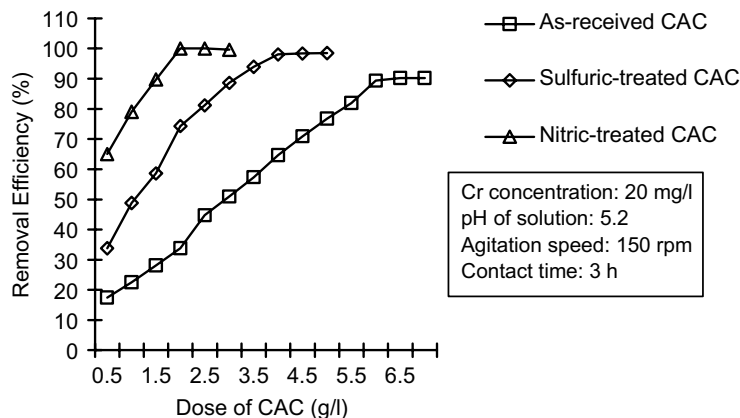

Fig. 5. Effect of dose on the sorption efficiencies of CAC on chromium.

Cr(III) metal ions uptake from the solution (at acidic conditions) through columbic forces. It is concluded that the extent of oxygen-carbon group formation due to surface oxidation plays a major role in the accessibility of Cr species to the oxidized CAC.

3.2.2. Effect of pH

The role of hydrogen ion concentration on the Cr adsorption of CAC was examined at different pH in the range of 2.0–9.0. The results, shown in Fig. 6, reveal that the Cr adsorption by as-received CAC increased from 85% to 95% with an increase in the solution pH from 2.0 to 6.0 and then, decreased to 15% beyond pH 6.0. The remarkable decrease in the adsorption of Cr(VI) reflects a significant reduction in the quantity of negative surface charge on CAC. At acidic pH, the negatively charged surface of CAC attracts positively charged Cr(III) ions by columbic forces. As the negative charge density on the carbon surface of CAC decreases as the solution pH increases, it leads to low Cr adsorption from aqueous solution at pH higher than 6.0. It is concluded that the presence of negative charge on the carbon surface of CAC over the acidic range of pH investigated is the main reason for Cr adsorption.

3.2.3. Effect of agitation speed

The effect of agitation speed on Cr adsorption by CAC was studied by varying the speed from 90 to 190 rpm. Results are presented in Fig. 7.

Fig. 7 demonstrates that the Cr removal efficiency of CAC increased from 83% to 98% when the speed was increased from 90 to 130 rpm. It was observed that
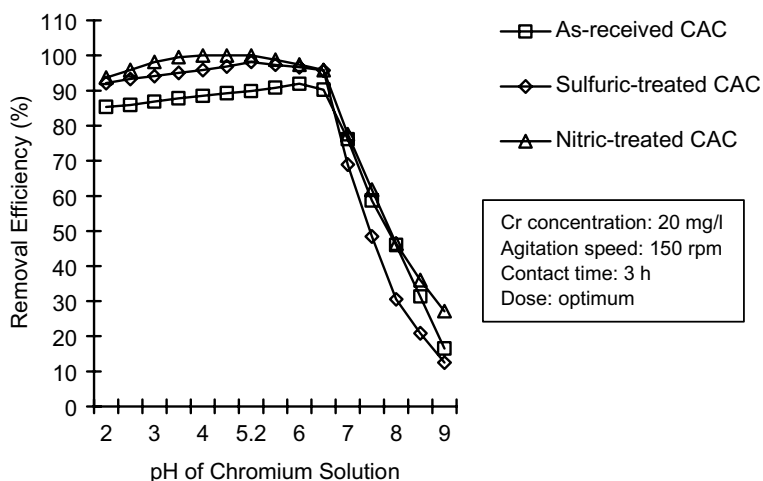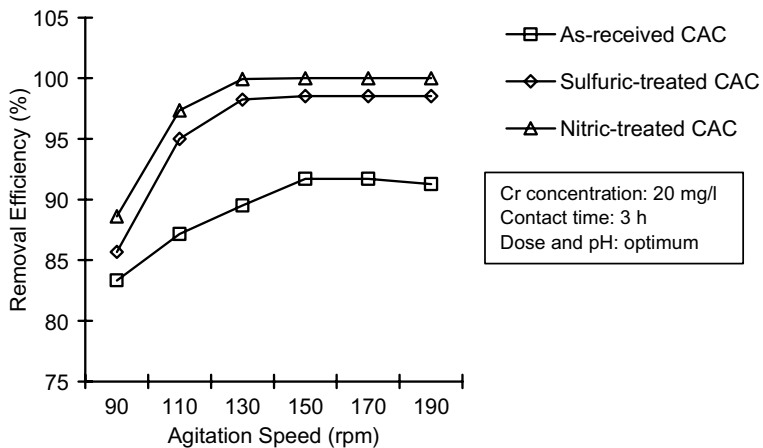

Fig. 6. Effect of pH on chromium sorption by CAC.

Fig. 7. Effect of agitation speed on the removal efficiencies of CAC.

chemically modified CAC could achieve maximum removal efficiency at a lower speed (130 rpm) than as-received CAC (150 rpm). This can be explained due to the fact that the film diffusion did not dominantly control the overall adsorption process. As a result, the increasing agitation speed decreased the boundary layer resistance to mass transfer in the bulk and resulted in an increase in the driving forces of Cr(III) ions (Singh et al., 1998). This result is in agreement with what was cited by Peniche-Covas et al. (1992) on the metals sorption by chitosan for which increasing agitation speed significantly enhances the metal removal efficiency of the adsorbent.

3.2.4. Effect of contact time

The time-dependent behavior of Cr adsorption was measured by varying the equilibrium contact time in the range of 15–120 min. The Cr concentration was kept at 20 mg l^{-1}, while the amount of CAC dose added was 1.5 g l^{-1} for nitric-treated CAC. The adsorption efficiency of Cr is plotted in Fig. 8.

The above figure shows that the Cr removal by as-received CAC increased from 80% to 90% with an increase in contact time until equilibrium was attained within 90 min and thereafter, it became constant. It was also observed that the equilibrium time of CAC modified with nitric acid and/or sulfuric acid, respectively, was achieved within 60 min with almost complete Cr removal. This can be explained due to the fact that oxidative treatments of CAC with strong oxidizing agents increased not only the negative charge of the surface functional group of CAC, but also adsorption sites. Consequently, adsorption on the carbon surface of chemically modified CAC occurred significantly faster than that of as-received CAC.

3.2.5. Adsorption isotherm
3.2.5.1. Langmuir isotherm.
The straight lines of $1/C_e$ versus $1/Q_e$ for all types of CAC were obtained by varying Cr concentration (from 5 to 25 mg l^{-1}). In spite of a larger surface area and surface modification, it is surprising that Langmuir isotherm fits the data well for as-received CAC and sulfuric-treated CAC, as evident from the corresponding regression coefficients (Table 3). It was also found that the average percent deviation of the Langmuir isotherm for both types of CAC was lower (0.32%) than that of the Freundlich (1.89%); thus, hinting towards surface homogeneity of CAC. It is suggested that the surface of CAC is made up of small homogenous adsorption patches, which are very similar to each other. Table 3 also demonstrates that the Cr sorption by all types of CAC in the present study was favorable ($0 < R_L < 1$).

3.2.5.2. Freundlich isotherm.
A plot of $\log C_e$ versus $\log Q_e$ also shows that the Cr adsorption by CAC seems to follow Freundlich isotherm. The n values for all types of CAC are listed in Table 3. This table shows that the value of n is in the range of 2–6; thus, reflecting the suitability of the system under investigation. It was found that the Freundlich isotherm is more applicable for nitric-treated CAC than Langmuir.

3.2.6. Adsorption mechanism of CAC

Since CAC is made up of coconut shell and has the same surface functional groups as CSC, the adsorption mechanism of CAC on Cr is suggested to be the same as that of CSC (Section 3.1.6).

3.3. Comparison of the Cr adsorption capacities of both adsorbents and their cost effectiveness

It was evident from the present study that both chemically modified CSC with nitric acid and/or sulfuric acid coated with chitosan (sulfuric acid-treated CSCCC) have demonstrated outstanding removal capabilities for Cr(VI) (10.88 and 8.95 mg g^{-1}), respectively, which were comparable to that of chemically modified CAC with
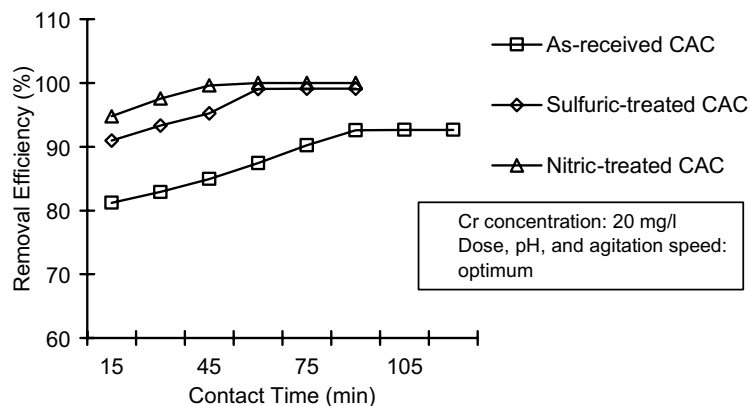

Fig. 8. Dependence of chromium sorption of CAC on contact time.

Table 3
Adsorption capacities (mg g⁻¹) of CAC for Cr(VI) ions

Type of CAC	Langmuir isotherm						Freundlich isotherm			
	Q_e (mg g⁻¹)	R^2	a_m	b	R_L	Equation of Q_e	Q_e (mg g⁻¹)	R^2	n	Equation of Q_e
As-received	4.72[a]	0.9871	4.7216	0.2290	0.1487	$Q_e = 1.0814C_e/(1+0.2290C_e)$	1.33[d]	0.9368	2.7617	$Q_e = 1.3331C_e^{0.3621}$
Oxidized with sulfuric acid	8.94[b]	0.9786	8.9449	1.0244	0.0376	$Q_e = 9.1633C_e/(1+1.0244C_e)$	4.00[e]	0.9731	2.7752	$Q_e = 4.0017C_e^{0.3603}$
Oxidized with nitric acid	10.44[bc]	0.9337	10.4373	4.70×10^3	8.53×10^{-6}	$Q_e = 4.895 \times 10^4 C_e/(1+4.690 \times 10^3 C_e)$	15.47[f]	0.9433	5.7033	$Q_e = 15.4689C_e^{0.1753}$

Remarks: The Cr adsorption capacities (Q_e) followed by the same letter in the column 2 are not significantly different ($p > 0.05$) from each other at the 95% level of confidence interval as determined by the Tukey's HSD test ($n = 12$; df = 11; F-value = 21.43).

sulfuric acid (8.94 mg g⁻¹). It demonstrated that surface modification of adsorbent with a strong oxidizing agent remarkably improved their Cr removal performance.

CAC has a good adsorption capacity for Cr(VI) in as-received form (4.72 mg g⁻¹). It was also found that chemically modified CAC with nitric (15.47 mg g⁻¹) has nearly two times higher adsorption capacity than that of sulfuric acid (8.94 mg g⁻¹). This could be explained due to the fact that nitric was a stronger oxidizing agent than sulfuric acid. Therefore, nitric was more capable of increasing the negative charge of surface oxide complex than sulfuric acid.

Since the cost effectiveness of an adsorbent is one of the important issues that must be considered when selecting an adsorbent, the commercial price of CSC (in Thailand) needs to be compared to that of CAC and another non-conventional adsorbent, such as chitosan. Based on the current commercial price, CSC is a relatively inexpensive material (US$0.34 kg⁻¹) compared to CAC (US$1.37 kg⁻¹). In fact, the commercial price of CSC is considered three-times cheaper than that of chitosan, another type of low cost adsorbent (US$1.14 kg⁻¹).

Due to the very small surface area (10 m² g⁻¹), surface modification of as-received CSC with a strong oxidizing agent, such as nitric acid, needs to be carried out to generate more sites for Cr adsorption and improve its metal removal performance. This process, of course, required extra operational cost due to chemicals. However, improved adsorption capacities of CSC may compensate the cost of additional processing.

Based on the adsorption isotherm study, it can be seen that after oxidative treatments with nitric acid, CSC has a comparable adsorption capacity to CAC. One gram of CSC can sorb about 10.88 mg of Cr(VI), indicating that 10.88 g of Cr(VI) ions in an aqueous solution can be sorbed by 1 kg of CSC, and it costs only US$0.34. Similarly, 1 kg of CAC is able to sorb approximately 15.47 g of Cr(VI) and costs US$1.37. This analysis does not take into account any costs associated with regeneration, or operational costs, such as chemicals, electricity, labor, transportation, and maintenance costs. If the overall costs mentioned previously are assumed to be the same for both adsorbents, the use of CSC for Cr(VI) removal offers more promising benefits than that of CAC, as it can reduce cost inefficiency in the daily operation of wastewater treatment in the local electroplating industry.

The cost effectiveness of using CSC for Cr(VI) removal will also significantly increase if CSC can be chemically regenerated for multiple uses in column operation using effective regenerants, such as sodium hydroxide. It could also be expected that the current commercial price of CSC may decrease, as more local electroplating industries consider using CSC for the treatment of Cr-contaminated wastewater.

Based on the cost evaluation and Cr removal performance mentioned previously, the use of CSC for Cr removal was found to be suitable and is a competitive alternative to the local needs for the treatment of Cr-contaminated water. The easy availability of CSC, reasonable adsorption capacity, potential of Cr recovery, and sludge-free operation are expected to render this Cr removal technique attractive and cut down operational costs. Considering these reasons, the use of CSC for such a purpose in local electroplating industries is strongly recommended.

3.4. Comparison of the present study with other adsorbents in similar batch studies

To justify its viability as an effective adsorbent for Cr(VI) removal, the adsorption capacity of CSC on Cr(VI) needs to be compared to that of other low-cost adsorbents. Table 4 shows a summary of various adsorbents previously studied for Cr(VI) removal. To compare the technical feasibilities of all adsorbents, comparative studies are made in terms of Cr-removal capacity ($mg\,g^{-1}$), optimum pH, and maximum concentration of Cr used ($mg\,l^{-1}$). It is important to note that this comparison has a relative meaning due to some factors, such as different testing conditions (pH, temperature, wastewater composition), type of biomaterial, and methods.

It is clear from Table 4 that appealing materials, such as sphagnum moss peat, chitosan, and CAC type Filtrasorb-400 show outstanding Cr adsorption capacities compared to other less-attractive materials, such as coconut husk fibers, palm pressed fibers, coconut tree sawdust, and coconut shell-based activated carbon. However, a fair and objective evaluation concerning the potential of any material as an adsorbent at commercial level should consider its local availability, as this factor is closely related with cost minimization. For countries, which are not the producers of coconut, the cost of transportation for raw material (coconut shell) may also be involved for the production of CSC/CAC. Local environmental condition also affects the removal performance of CSC on certain metal. For tropical countries, CSC shows a favorable metal removal performance, as adsorption mostly occurs at higher temperature to enhance the rate of particle diffusion of adsorbate in the solution (exothermic reaction). In spite of the two factors mentioned previously, it may be possible to use this kind of technology for international application.

Like other developing countries, Thailand also has abundantly available agricultural waste, such as coconut shells, which have very little economic value and in fact, often create a serious problem of disposal for local environments. To achieve an economically feasible and effective treatment of metal-contaminated water, the utilization of such unused resources from an agricultural waste as an alternative adsorbent for Cr removal is highly desirable. CSC can certainly be classified in this category, of course, after it is chemically modified to improve its removal performance.

Basically, CSC in as-received form has a comparable Cr adsorption capacity ($2.18\ mg\,g^{-1}$) not only to coconut shell-based activated carbon ($2.0\ mg\,g^{-1}$), but also to other materials, such as red mud ($1.6\ mg\,g^{-1}$), clinoptilolite ($2.4\ mg\,g^{-1}$), and sawdust ($3.3\ mg\,g^{-1}$) (Table 4). However, surface modification of CSC with nitric acid significantly enhances its Cr-loading capacity, although CSC has a smaller surface area ($10\ m^2\,g^{-1}$) for metal adsorption compared to coconut shell-based activated carbon ($1000\ m^2\,g^{-1}$) (Alaerts et al., 1989).

Like other adsorbents, the optimum pH range of CSC for effective Cr adsorption lies in acidic pH range between 4 and 6. Most local electroplating industries in Thailand discharge Cr effluents at the low pH. If CSC were to be used for Cr adsorption on an industrial basis, any unadsorbed Cr could be efficiently removed using column operation along with other heavy metals, such as Pb^{2+} and Cd^{2+} (Arulanantham et al., 1989), as these metals may also be well adsorbed.

As for cost information, the commercial price of all adsorbents listed in Table 4 is not completely reported due to the unavailability of the data from previous studies. This can be explained due to the fact that any expenses of individual adsorbent vary, depending on the processing required and its local availability. Thus, a comprehensive comparison among non-conventionaladsorbents is difficult to materialize due to inconsistencies in data presentation.

3.5. Removal performance of CSC at lower Cr concentrations

Although CSC was found to be satisfactorily efficient for Cr removal at $20\ mg\,l^{-1}$ of Cr concentration, it was also demonstrated that CSC has significantly better removal capabilities at lower Cr concentrations (5 and 10 $mg\,l^{-1}$). In fact, further investigation on the removal performance of all types of CSC statistically proved that the adsorption capacity of CSC at $5\ mg\,l^{-1}$ of Cr concentration is comparable (as-received CSC: 4.30, CSC oxidized with sulfuric acid: 8.03 mg of Cr(VI) g^{-1}) to that of CAC in as–received and chemically modified forms at $20\ mg\,l^{-1}$ of Cr concentration (as-received CAC: 4.72, CAC oxidized with sulfuric acid: 8.94 mg of Cr(VI) g^{-1}), as shown in Table 5. It is concluded that CSC is suitable for the treatment of Cr effluents at lower concentrations (5 and 10 $mg\,l^{-1}$).

Similar to that of $20\ mg\,l^{-1}$ of Cr concentration, it was also found that Langmuir isotherm is more applicable for Cr removal by CSC than Freundlich at 5 and 10 $mg\,l^{-1}$ of Cr concen-trations, respectively. This

Table 4
Summary of chromium adsorption capacities of various adsorbents

Type of adsorbent	X/m (mg g^{-1})	Optimum pH	Max. Cr. concentration used (mg l^{-1})	Commercial price (US$ kg^{-1})	Reference
Iron(III)-hydroxide	0.47	5.6	30		Namasivayam and Ranganathan (1992)
Bentonite	0.57	2.0	52	US$0.04–0.12	Khan et al. (1995)
Red mud	1.60	5.2	30		Pradhan et al. (1999)
Coconut shell-based activated carbon	2.00	2.5	20		Alaerts et al. (1989)
As-received CSC	2.18	6.0	25	US$0.34	Present study
Clinoptilolite	2.40	4.0–5.0	10	US$0.03–0.12	Ouki and Kavannagh (1997)
Fly ash-wollastonite	2.92	2.0	16.64		Panday et al. (1984)
Sawdust	3.3	6.0	50		Srivastava et al. (1986)
Coconut tree sawdust	3.46	3.0	20		Selvi et al. (2001)
Chabazite	3.60	4.0–5.0	10	US$0.03–0. 12	Ouki and Kavannagh (1997)
As-received CAC	4.72	6.0	25	US$1.37	Present study
Blast-furnace slag	7.50	1.0	50	US$0.04	Srivastava et al. (1997)
Nitric-oxidized CSC	10.88	4.0	25	US$0.34	Present study
Diatomite	11.55	3.0	1500		Dantas et al. (2001)
Aluminium oxide	11.7	4.0	60		Gupta and Tiwari (1985)
Palm pressed fibers	14.0	2.0	80		Tan et al. (1993)
Anatase (TiO$_2$)	14.56	2.5	100		Weng et al. (1997)
Nitric-oxidized CAC	15.47	4.0	25	US$1.37	Present study
Coconut husk fibers	29.0	2.1	80		Tan et al. (1993)
Leaf mould	43.0	2.0	1000		Sharma and Forster (1994a)
Rice husk carbon	45.6	2.0–3.0	300		Srinivasan et al. (1988)
Non-cross linked chitosan	50	5.0	1000		Schmuhl et al. (2001)
Waste tyre	58.48	2.0	100		Hamadi et al. (2001)
Spheroidal cellulose	89.90	5.0	312	US$1.07	Liu et al. (2001)
Cross-linked chitosan	78	5.0	1000		Schmuhl et al. (2001)
Sphagnum moss peat	119.0	1.5	1000	US$0.02	Sharma and Forster (1993)
Bagasse fly ash	260	1.0	500		Gupta et al. (1999)
Chitosan	273	4.0	500	US$15.43	Udaybhaskar et al. (1990)
Waste slurry	640	2.0	470		Srivastava et al. (1989)
CAC type Filtrasorb-400	53.19	2.0	100	US$20–22	Hamadi et al. (2001)
	57.7	6.0	207		Huang (1977)
	145.0	3.0	1000		Sharma and Forster (1996)

Table 5
Adsorption capacities of CSC for Cr(VI) ions at lower chromium concentrations

Type of chemical modification	5 mg l^{-1} of chromium concentration				10 mg l^{-1} of chromium concentration			
	Langmuir isotherm		Freundlich isotherm		Langmuir isotherm		Freundlich isotherm	
	Q_e (mg g^{-1})	R^2	Q_e (mg g^{-1})	R^2	Q_e (mg g^{-1})	R^2	Q_e (mg g^{-1})	R^2
As-received	4.30[a]	0.9959	3.97[f]	0.9680	3.74[k]	0.9892	3.44[p]	0.9857
Coated with chitosan	6.85[b]	0.8940	6.05[g]	0.8607	5.49[l]	0.9600	4.06[pq]	0.9534
Oxidized with sulfuric acid	8.03[bc]	0.9896	7.49[gh]	0.9882	8.04[m]	0.9858	5.31[qr]	0.9750
Oxidized with sulfuric acid and coated with chitosan	11.42[d]	0.9965	8.46[hi]	0.9730	9.83[n]	0.9586	5.43[qs]	0.9580
Oxidized with nitric acid	14.41[e]	0.9994	11.09[j]	0.9912	14.17[o]	0.9950	5.51[qt]	0.9946

Remarks: The Cr adsorption capacities (Q_e) followed by the same letter in the columns 2 and 4 (for 5 mg l^{-1} of Cr concentration) as well as in the column 8 (for 10 mg l^{-1} of Cr concentration), respectively, are not significantly different ($p > 0.05$) from each other at the 95% level of confidence interval as determined by the Tukey's HSD test ($n = 20$; df $= 15$; F-value $= 17.95$).

indicates that monolayer adsorption taking place on the carbon surface of CSC was not affected by the extent of Cr concentration.

4. Concluding remarks

It is conclusively evident from the batch studies that the use of chemically modified CSC for Cr(VI) removal appears to be technically feasible, eco-friendly, and economically attractive for the treatment of Cr-contaminated wastewater. The advantages of using this adsorbent towards Cr treatment are the simplicity of the required system and the ability to accept a wide variation of effluent concentration.

At the same range of Cr concentration (from 5 to 25 mg l^{-1}), among all types of chemical modifications, CSC modified with nitric acid stands out for having the highest Cr adsorption capacity (10.88 mg of Cr(VI) g^{-1}) compared to other types of CSC, such as sulfuric-treated CSCCC (8.95 mg of Cr(VI) g^{-1}), CSC treated with sulfuric acid (4.05 mg of Cr(VI) g^{-1}), and CSCCC (3.65 mg of Cr(VI) g^{-1}). In fact, it was also found that CSC in as-received form was highly efficient for Cr removal at lower concentrations (5 and 10 mg l^{-1}) with adsorption capacity 4.30 and 3.74 mg of Cr(VI) g^{-1}, respectively, suggesting that the adsorption capacity of CSC at 5 mg l L^{-1} of Cr concentration is comparable to that of as-received CAC (4.72 mg of Cr(VI) g^{-1}) at the same Cr concentration range.

Like CSC, CAC oxidized with nitric acid also demonstrated the most outstanding adsorption capacity on Cr (15.47 mg of Cr(VI) g^{-1}) compared to CAC oxidized with sulfuric acid (8.94 mg of Cr(VI) g^{-1}) and as-received CAC (4.72 mg of Cr(VI) g^{-1}). In fact, in order to achieve a maximum removal efficiency of Cr, nitric-oxidized CAC needed only a smaller amount of dose (2 g l^{-1}), a lower agitation speed (130 rpm), and less contact time (60 min) compared to as-received CAC (6 g l^{-1} of dose, 150 rpm of agitation speed, and 90 min of contact time, respectively). These facts are very interesting, as the dose and contact time required for accomplishing a complete Cr removal are important parameters to achieve an economical wastewater treatment plant in the daily operation of the electroplating industry.

Overall, it has been concluded that surface modifications of both adsorbents mentioned previously with chitosan and/or strong oxidizing agents, such as nitric acid and sulfuric acid, significantly have improved their Cr adsorption capacities. Although CSC and CAC are suitable for treating Cr effluent, it is important to note that their adsorption capacities on Cr(VI) vary, depending on the characteristics of individual adsorbent, the extent of surface modification, and the initial Cr concentration. Considering its low cost, technical feasibility, engineering applicability, and cost effectiveness, it

is suggested that CSC is preferable to CAC for Cr(VI) removal. Therefore, the widespread use of CSC for such a purpose in the local electroplating industries in Thailand is recommended.

Last but not least, since the chemically modified CSC had been capable of performing an efficient and effective Cr(VI) removal, it could be expected that not only local electroplating industries, but living organisms and the surrounding environment benefited also from potential metal toxicity due to Cr(VI). Thus, the use of CSC, an abundantly available unused resource from local coconut industry for Cr(VI) removal, could be expected to be technically feasible, economically viable, applicable for wastewater treatment, and most importantly, contribute to the sustainability of the surrounding environment. All those advantages mentioned above undoubtedly add more credits to the use of coconut shell material for Cr(VI) removal from electroplating wastewater; thus, enabling CSC and/or CAC as one of attractive options.

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