Full Length Research Paper

Chromium (III) sorption from aqueous solutions using activated carbon prepared from cashew nut shells

S. Tangjuank[1]*, N. Insuk[1], V. Udeye[2] and J. Tontrakoon[3]

[1]Program of Science, Faculty of Science and Technology, Uttaradit Rajabhat University, Uttaradit, 53000, Thailand.
[2]Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok, 65000, Thailand.
[3]Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand.

Activated carbon prepared from cashew nut shells using potassium hydroxide activation at 850°C in N_2 and CO_2 atmosphere was used as an adsorbent for the removal of chromium ions from aqueous solutions. The adsorption of Cr(III) ions on activated carbon was studied. The effect of experimental parameters such as, pH of initial concentration of Cr(III) solutions, contact time, dosage of adsorbent and initial concentration of Cr(III) solutions was investigated. The Freundlich and Langmuir isotherm fitted well to data of Cr(III) adsorption. Cr(III) uptake capacity was 13.93 mg/g which was calculated from the Langmuir isotherm.

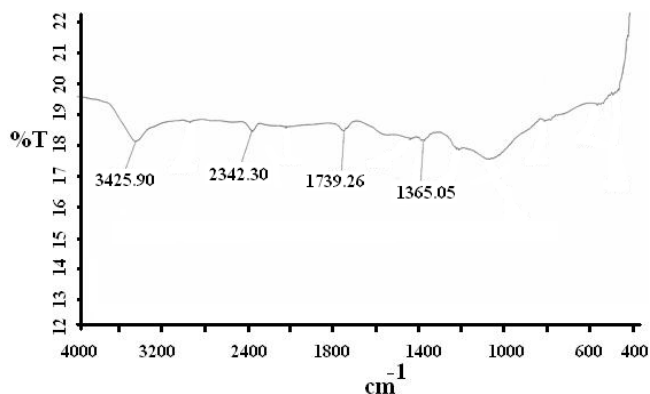**Key words:** Activated carbon, cashew nut shell, trivalent chromium (Cr(III)), adsorption.

INTRODUCTION

Chromium (III) is an essential microelement that can be toxic in large doses(100 mg/L) (Khawaja, 1998). The toxicity of chromium compounds depends on the oxidation state of the metal. Occupational exposure to chromium (VI) has been associated with increased incidence of lung cancer. The efficacy of chelating therapy in chromium poisoning has not been proven (US, 1998). Trivalent chromium compounds are considerably less toxic than the hexavalent compounds and are neither irritating nor corrosive under normal conditions. However, all forms of chromium can be toxic at high levels. People who are allergic to chromium may have asthma attacks after breathing high levels of chromium (III) in air (Song et al., 2000; Alaerts et al., 1989). Repeated or prolonged skin contact may cause irritation. In severe cases, skin allergy can occur with itching, redness and/or an eczema-like rash. Chromium (III) compounds that entered the body can be inhaled or ingested. Both chromium (III) and chromium (VI) have high chronic toxicity to aquatic life. A long-term exposure

to trivalent chromium is known to cause allergic skin reaction and cancer (Bansal et al., 1979). Many studies have investigated the adsorption of trivalent chromium and hexavalent chromium on activated carbon (Ramos et al., 1995; Valdimir and Danish, 2002). Cost Effective adsorbents for environmental treatment of metal containing is required. A low cost adsorbent is defined as by-product or waste material from industrial process and agricultural. Many processes were used for metal removal from wastewater such as ion exchange (Tiravanti et al., 1997), coagulation/flocculation (Song et al., 2004), filtration and membrane (Fabianil et al., 1996; Hafez et al., 2002). Activated carbons prepared from agriculture wastes are more effective due to some specific characteristics with high BET surface area (Kuniawan et al., 2006). Thus, low cost activated carbon can be used as adsorbent for the removal of heavy metals. Few studies performed Cr(III) adsorption on activated carbon. They reported the optimum pH value at 5 and the capacity of adsorption can be fitted to the Langmuir isotherm (Huang and Wu, 1977; Alaerts et al., 1989; Ramos et al., 1995).

In this study, the performance of activated carbon produced from cashew nut shells for Cr(III) sorption from aqueous solution at high level concentration was investi-

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*Corresponding author. E-mail: singhadejt@yahoo.com. Tel.: +6655 411096 ext 1300. Fax: +6655 411096 ext 1312.

Figure 1. FT-IR spectrum of activated carbon derived from cashew nut shells.

investigated. In batched experiments, the influence of initial pH of Cr(III) solution, contact time, dosage of adsorbent and initial concentration of Cr(III) solution were studied. The maximum capacity of the adsorbent using Freundlich and Langmuir isotherms was calculated from experimental data.

MATERIALS AND METHODS

Preparation of activated carbons

The cashew nut shells were obtained from agriculture wastes in Thailand. Chars were prepared from cashew nut shells by carbonization in the absence of air. These chars were well mixed with water and KOH with the weight ratios of KOH/char equal to 4. The mixed chars were dried and heated in furnace from room temperature to 850°C in N_2 and CO_2 atmosphere for 150 min. The activated carbons obtained were thoroughly washed with distilled water several times, dried at 110°C, cooled at room temperature and stored in desiccators.

Characterization of the produced activated carbon

All the produced activated carbon samples were characterized by their physical and chemical properties. FTIR spectrometer (Spectrum GH, Perkin Elmer) was employed to determine the presence of surface functional groups in samples and samples were analyzed as KBr pellets. The crystal structure was characterized by X-ray diffractionmeter (XRD) with Cu Kα radiation (Siemens, D-500). The microstructure of activated carbon was investigated with Scanning electron microscope (LEO, Model 1455VP). The BET surface area of the carbon was obtained from the N_2 adsorption isotherm at 77K with adsorption meter (Micromeritics, Porous Materials, BET-2020). A Shimadzu Varian Spectra A 220 atomic absorption spectrometer was used for Cr(III) ions determination.

Adsorption experiments

The Cr(III) ions batch adsorption experiments were investigated. The high concentration of Cr(III) solution was significantly chosen to carry out for our adsorption experiments as the initial concentration parameter. The 100 mg/L of Cr(III) aqueous solutions were poured into a flask which contained accurately weighted amount of the adsorbent. The activated carbons were weighed in the range from 0.6 - 8.0 g per 100 mL of solutions. Effective parameters such as initial pH, contact time, adsorbent dosage and initial concentration of Cr(III) solutions were studied. The required initial pH of solution was adjusted by adding 0.1 M HCl or NaOH. Then, the flasks were continuously shaken at 200 rpm by auto-shaker for prescribed length of time to equilibrium. After filtration through Whatman filter paper, Chromium ions remaining in the solution were determined by atomic adsorption spectrometer (Varian Spectra A 220).

   The amount of metals ion adsorbed which means that metal uptake(q_e) (Zubair et al., 2008) of the adsorbent was evaluated as in (1).

$$q_e = (C_i - C_e)\ V\ /1000\ w \qquad (1)$$

Where C_i is the initial concentration (mg/L)
C_e is metal concentrations at any time (mg/L)
V is the volume of the heavy metal solution (mL)
w is the mass of adsorbent (g)

The Freundlich equation (Liang et al., 2006; Dastgheib and Karanfil, 2005; Rao et al., 2006; Machida et al., 2005) is in the linearism form as in (2) ;

$$\log q_e = 1/n\ (\log C_e) + \log k \qquad (2)$$

Where q_e is the metal ions adsorbed(mg/g) at equilibrium.
C_e is the equilibrium concentration(mg/L).
k is Freundlich constant with multilayer adsorption.
n is adsorption intensity.

The Langmiur equation (Srivastava et al., 1989) is in the form as in (3);

$$C_e / q_e = 1/ q_{max}\ K_L + C_e /q_{max} \qquad (3)$$

Where q_{max} is monolayer adsorption capacity (mg/g).
K_L is Langmiur adsorption constant.

Langmuir and Fruendlich isotherms were obtained from the experiments.

RESULTS AND DISCUSSION

Characteristics of the adsorbent

Infrared spectroscopy provides qualitative information of characteristic functional groups on the surface. The adsorptive capacity of the activated carbon is also influenced by its surface chemical structure. The FT-IR spectrums of the activated carbon are shown in Figure 1. The absorption at 3425 cm^{-1} was attributed to ν(O-H) vibrations in hydroxyl groups or surface-bonded water. The bands appearing at 2342 and 1739 cm^{-1} are assigned to the C=O stretching vibrations in ketones or carbonyl groups (Boehm, 1994). The band located around 1365 cm^{-1} could be attributed to ν(C-O) vibrations in carboxylate groups. These results agree with the surface chemistries of other agricultural by-products, such
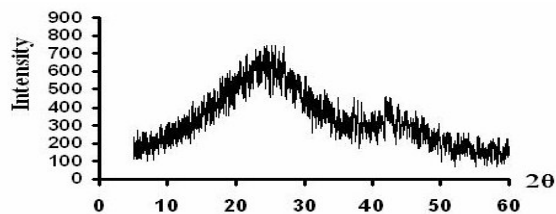
Figure 2. X-ray diffraction of activated carbon derived from cashew nut shells
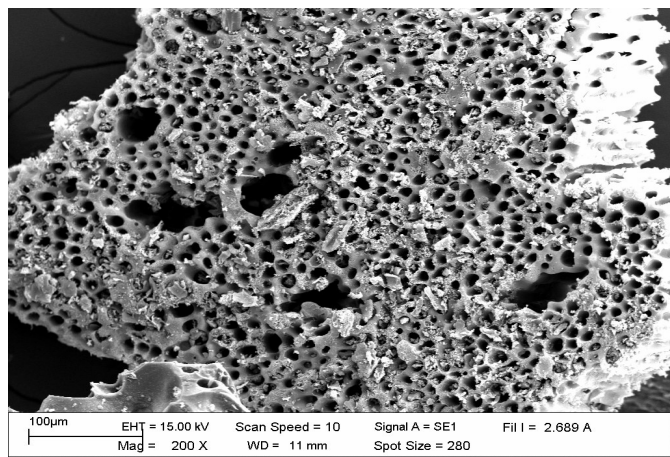

Figure 3. Scanning electron micrograph of activated carbon derived from cashew nut shells.

Table 1. Physical properties of activated carbon derived from the cashew nut shells.

Carbon characteristics	Values
BET Surface area (m^2/g)	1120
Pore volume (cm^3/g)	0.5789
Average pore size (nm)	22.57
Bulk density (g/cm^3)	0.553

such as peach stones (Arriagada et al., 1997) and pistachio-nut shell (Yang and Lua, 2006). Figure 2 shows the X-ray diffraction profile of the activated carbons. The results indicated that the diffraction profiles of all activated carbons exhibited broad peaks and the absence of a sharp peak revealed a predominantly amorphous structure, and two broad peaks seemed to appear at around $2\theta = 26°$ and $43°$ which were similar to the peaks of crystalline carbonaceous structure such as graphite (JCPDS). The porous structure of the activated carbon can be clearly seen from the SEM photographs (shown in Figure 3). The surface shows many uniformly pore structures with honeycomb shape. The availability of pores and internal surface is necessary for an effective adsorbent. The physical properties of activated carbon are represented in Table 1. The effective properties of
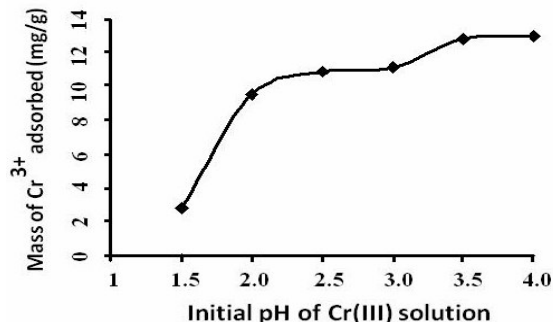
Figure 4. Effect of initial pH on adsorption capacity of Cr(III) solution (initial concentration 100 mg/L, contact time 60 min. and 0.6 g activated carbon/ solution 100 mL).

BET, pore volume, average pore size and bulk density were found to be 1120 m^2/g , 0.5789 cm^3/g , 22.57 nm and 0.553 g/cm^3 , respectively.

Effect of initial pH of solution

Firstly, the pH of the aqueous solution is an important factor in the adsorption process. The effect of initial pH on the adsorption which is exhibited as the amount of metals ion adsorbed on adsorbent (q_e) is shown in Figure 4. The results show that the adsorption values increased from 2.79 to 12.91 mg/g when pH increased from 1.5 to 4.0. The maximum adsorption efficiency of Cr(III) ions regarding pH was obtained in the range of 3.5 - 4.0. It is found that activated carbon effective for the adsorption of Cr(III) was strong at high pH and sharply declined at lower value, since trivalent cation at strongly acidic media are adsorbed as matrix. And at the optimum initial pH, Cr(III) still exhibited trivalent phase and still did not change to another chromium phase such as Cr(VI) (Fahim et al.,2006). The pH of the initial solution is significantly influent to the adsorption process as it controls the electrostatic interactions between the adsorbent and the adsorbate. When pH of Cr(III) increased above 4.0, the precipitates were formed. Because high hindrance between Cr(III) and hydroxyl group of surface bond of adsorbent and other inferences in the solution could hinder the diffusion of Chromium ion into the surface and pore of activated carbon. Thus, the optimum pH for Cr(III) uptake on activated carbon was found to be 3.5 and was selected for all further experiments in this study.

Effect of contact time

The equilibrium time is the one parameter for an econo-mic wastewater treatment. The contact time in the range of 5 - 90 min were studied. The Cr(III) ions uptakes on activated carbon are exhibited in Figure 5. As seen in
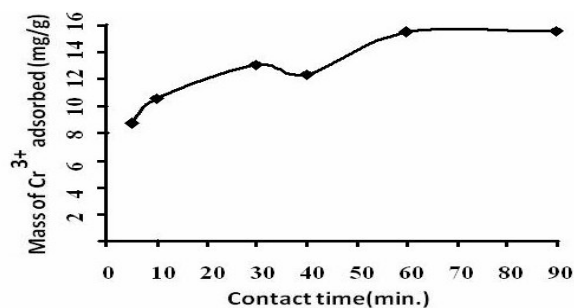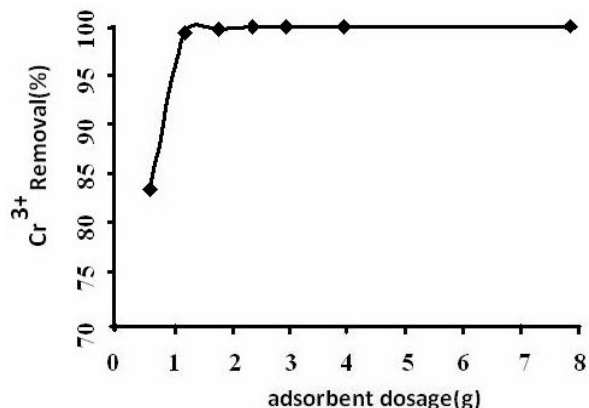
Figure 5. Effect of contact time on adsorption capacity of Cr(III) solution (initial concentration 100 mg/L, initial pH 3.5 of Cr(III) solution and 0.6 g activated carbon/ solution 100 mL).

Figure 6. Effect of adsorbents dosage on % removal of Cr(III) ions for aqueous solutions (initial concentration 100 mg/L, initial pH 3.5 of Cr(III) solution and contact time 60 min).

Figure 7. Effect of adsorbent dosage on adsorption capacity of Cr(III) solution(initial pH 3.5 of Cr(III) solution, contact time 60 min. and initial concentration of Cr(III) solution 100 mg/L).

Figure 5, the equilibrium contact time was 60 min with constant values of pH as 3.5 and 0.6 g of adsorbent. When the contact time increased from 5 - 60 min, the amount of Cr(III) ions uptake further increased and then constant adsorption efficiency continue as 90 min. Further increase in contact time did not show an increase in adsorption. This can be expressed to affinity with sufficient contact time between ions and surface area of adsorbent and shows the affinity of the support toward trivalent chromium cations. At the sufficient contact time between ions and adsorbent, the optimum contact time is 60 min, the ions diffuse to surface and into the pore of activated carbon which have very large number of surface area. When the time increase more than 60 min, the remaining ions adsorbed or diffused into the pore could be saturated. The affinity of metals adsorbed will be decrease. Thus, the affinity of metal adsorbed is upon to appropriated time (Balkaya and Bektas, 2009). Therefore, the contact time 60 min was selected in further experiments.

Effect of adsorbent dosage

The effect of the adsorption of Cr(III) ions on dosage was studied by varying amount of adsorbents while keeping pH(3.5), contact time(60 min), initial concentration of Cr(III) solution(100 mg/L), shaking speed(200 rpm) and temperature(30 °C) constant. A dosage of the adsorbent has a great influence for adsorption process. As seen from Figure 6 which shows the effect of adsorbent dosage on removal of Cr(III), the percentage of Cr(III) removal was increasing with the increase in adsorbent dosage. The removal was increasing significantly as dosage increased from 0.6 - 1.2 g and then tends to constant as almost 100%. The Cr(III) removal values were found to be 84% and more than 99% for adsorbents dosage of 0.6 and 1.2 g, respectively. The effect of adsorbents dosage on adsorption capacity of Cr(III) solution is shown in Figure 7. The results indicate that the
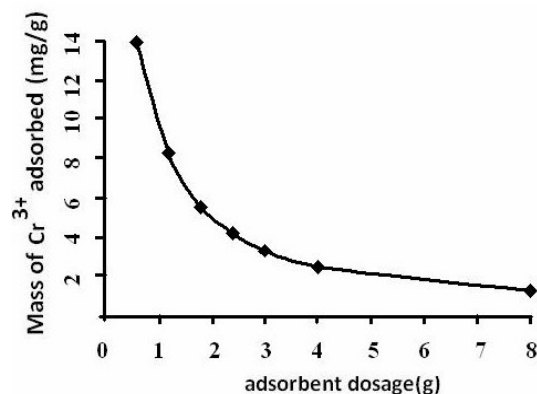
Cr(III) adsorption capacity of activated carbon decreased with increasing adsorbent dosage. This implies that the amount of the number of binding site increased which resulted in a split of the flux of Cr(III) aqueous solution concentration and the solute concentration on the surface area of activated carbon (Huang and Wu, 1975; Montanher et al., 2005). This decrease may be ascribed to the electrostatic interactions and interference of binding site which have an influence to reduce adsorbent densities (Cheng and Yang, 1975).

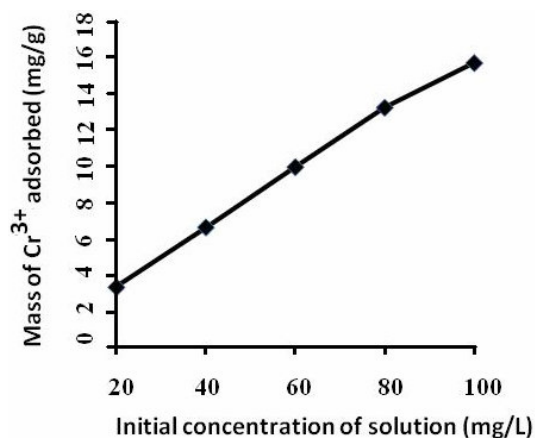**Effect of initial concentration of Cr(III) solution**

The initial concentration of Cr(III) is a very important factor for metals adsorption in aqueous process (Immamuglu and Tekir, 2008; Vadivelan and Kumar, 2005). The effect of initial concentration of Cr(III) solution on adsorption capacity is represented in Figure 8. The concentra-

Table 2. Values of Freundlich and Langmuir constants for the adsorption of Cr(III).

Adsorbate	Freundlich constants			Langmiur constants		
	k	n	r^2 (regres.coeff.)	q_{max} (mg/g)	K_L (L/mg)	r^2 (regres.coeff.)
Chromium(III)	1.32	8.33	96.71	13.93	0.0100	99.46

Table 3. Comparison of the adsorption of various adsorbents for Cr(III).

Adsorbent	Adsorption (%)	Reference
Lignite (Ilgin, Beysehir, Ermenek)	97 - 98	Arslan and Pehlivan, 2008
Activated carbon (Merck)	95	Arslan and Pehlivan, 2008
Makino bamboo	98	Wang et al., 2008
Cashew nut shells	99	Present work

Figure 8. Effect of concentration of Cr(III) solution on adsorption capacity(initial pH 3.5 of Cr(III) solution, contact time 60 min. and 1.2 g activated carbon/solution 100 mL).

varying from 20 to 100 mg/L were studied. It is seen that increasing the initial Cr(III) concentration resulted in increase in Cr(III) adsorbed on activated carbons. This is because at high initial concentration the number of Cr(III) ions available to the surface sufficient area was high. This adsorption indicates that surface saturation replies on initial concentration.

Adsorption isotherm

The adsorption isotherms of trivalent chromium were calculated. Experimental data was fitted to both Freundlich and Langmuir models. In the Langmuir model, monolayer adsorption capacity; q_{max} (mg/g) of activated carbon prepared from cashew nut shells and other para-meters were determined following linearized form of Equation 3. The heterogeneous adsorption capacity; q_e (mg/g) was determined following from Equation 2. The

parameter calculated from the adsorption data is exhi-bited in Table 2. As can be seen from isotherms and regression coefficients, Cr(III) adsorption fitted well with the Langmuir model more than the Freundlich model. The adsorption capacities q_{max} (mg/g) and k_L of the activated carbon for the uptakes of Cr(III) ions were 13.93 mg/g and 0.0100, respectively. The comparisons of the Cr(III) ions adsorption capacity (%) with different adsorbents taken from literature are presented in Table 3. The results of the present work show that the adsorption capacity was higher than those in the other works. Hence acti-vated carbon derived from cashew nut shells would be useful for the economic treatment of wastewater contain-ing chromium metals.

Conclusions

In this work it is shown that, the activated carbon pro-duced from agricultural waste (cashew nut shells) can increase economic return and reduce pollution. The important conclusions can be focused as follow:

- The adsorption process depend on the optimal conditions on the data from the experiments. These are initial pH 3.5 of Cr(III) solution, contact time 60 min and 1.2 g activated carbon/solution 100 mL at 100 mg/L of initial concentration of Cr(III) solution.
- The adsorption parameters play important role in deter-mining Cr(III) uptake capacity.
- The chromium uptake capacity from Langmuir isotherm was 13.93 mg/g which was the theoretical value that is very close to the actual value gotten from the actual experimental value which was reached as 12.91 - 14 mg/g.
- Thus, the activated carbon prepared from cashew nut shells is an efficient adsorbent for Cr(III) removal from aqueous solutions.

ACKNOWLEDGMENT

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