World Applied Sciences Journal 8 (2): 241-246, 2010
ISSN 1818-4952

Enhancement of Chromium (VI) Removal by Pre-Treatments of Cocolumber (*Cocos nucifera*) Sawdust: Vacuum Drying and Plasma Treatments

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Abstract: This study deals with the enhancement of chromium (VI) removal by vacuum drying and plasma pre-treatments of cocolumber (*Cocos nucifera*) sawdust. For fixed adsorbent dose and pH, the effects of important parameters such as initial adsorbate concentration and contact time are determined. Results show that both pre-treatments increased the adsorption efficiency of the sawdust. The adsorption data also fitted well with both Langmuir and Freundlich isotherm models. For an adsorbent dose of 2.0×10^4 mg/L, adsorbate concentration of 5.0 mg/L, contact time of 240 minutes and at a pH of 2, the %chromium (VI) removal for the plasma treatments (oxygen, hydrogen and argon) and for the vacuum drying treatment are 81.2%, 73.5%, 66.4% and 58.7%, respectively. These results are higher compared to 33.9% for the untreated sawdust. Therefore, oxygen plasma pre-treatment of cocolumber sawdust is found to be the most efficient treatment for the removal of aqueous chromium (VI).

Key words: Sawdust · Wastewater treatment · Chromium (VI) · Adsorption · Vacuum drying · Plasma discharge · Isotherms

INTRODUCTION

Water is typically referred to as polluted when it contains harmful contaminants that can affect the chemical and biological equilibrium of the water system. Chromium is one such toxic pollutant due to its carcinogenic effects on human health, especially in its hexavalent form [1]. Its compounds gain access to ground and surface waters through various industrial processes. The maximum limit for chromium (VI) concentration in drinking water is 0.05 mg/L [2].

Sawdust is known to have the capacity to remove dyes, toxic oils and even heavy metals [3]. Previous studies on the removal of chromium (VI) from wastewater indicate that adsorption using sawdust is one of the most highly efficient and cost-effective methods [2,3]. To enhance the efficiency of sawdust in chromium (VI) removal, it can be pre-treated chemically. Chemical pre-treatment of wood has been used to increase the adsorption capacity of wood for chromium (VI) removal. This includes the use of formaldehyde by Baral *et al.* and HCl by Zakaria *et al.* as chemical pretreatments [2,4]. The process of chemically-treating the sawdust can also lead to more chemically wastes that are possibly harmful and therefore studies are still being done for other alternative pre-treatment procedures.

In this study, vacuum drying and plasma treatments of (*Cocos nucifera*), are studied as alternative pre-treatments for the removal of aqueous chromium (VI). Vacuum drying and plasma treatments of sawdust are explored in this work as alternative pre-treatment methods. Coconut lumber (cocolumber) sawdust is chosen because it is inexpensive and quite abundant in tropical countries like the Philippines. Vacuum drying has already been used in experimental and commercial purposes as a conditioning treatment to remove substantial amount of moisture from biomaterials [5,6]. Plasma is known for its wide range of applications

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that include surface modification of materials and thin film deposition [7,8]. For example, a study done by Setoyama has shown that surface modification of wood by plasma treatment results to the formation of free radicals, weight reduction and increased water repellence of wood [9]. Neither of these pre-treatment methods has been extensively studied for sawdust adsorption of aqueous pollutants.

MATERIALS AND MATHODS

The cocolumber sawdust used in this experiment is collected from a local sawmill and is sieved for the size of 210-420 μm. It is then subjected to the pre-treatments without washing. Potassium dichromate ($K_2Cr_2O_7$) is used as source of chromium (VI) ions [10-12]. Adsorption of chromium (VI) is investigated by determining its dependency on varying adsorbate concentration and contact time between the pre-treated sawdust and adsorbate solution, for fixed adsorbent dose and pH.

Pre-treatments of Adsorbent

Microwave Plasma Device: The device used for vacuum drying and plasma treatments is a microwave plasma device. The actual image and schematic diagram of the device are shown in Figure 1. It is composed of a commercial microwave system, with a 2.45 GHz magnetron that serves as the microwave source for plasma production. A borosilicate glass allows microwaves from the waveguide to enter the vacuum chamber where the plasma is generated. Two hexapole configurations of Samarium-Cobalt permanent magnets are placed outside the circumference of the plasma chamber. Three gases are used for the plasma treatment: oxygen, hydrogen and argon.

The vacuum system consists of a diffusion pump and a rotary pump. Pressure measurements are read by an ULVAC WP-01 Pirani Sensor connected to an ULVAC GP-2A Controller for pressures of 3.0×10^{-3} Torr to atmospheric, whereas, ULVAC Type WTI Ionization Gauge coupled to an ULVAC GI-T13 Controller are used for pressures below 3.0×10^{-3} Torr [13].

Vacuum Drying Pre-treatment: Cocolumber sawdust is placed in an electrically grounded $8\times2\times2$ cm^3 substrate holder (Figure 2) inside the vacuum chamber of the microwave plasma device. The rotary pump initiates the vacuum treatment of the sawdust for around 30 minutes at 0.01 Torr just before the diffusion pump is switched on. Further vacuum drying is achieved for 15 minutes and at a pressure of 2.8×10^{-4} Torr, using the diffusion pump.

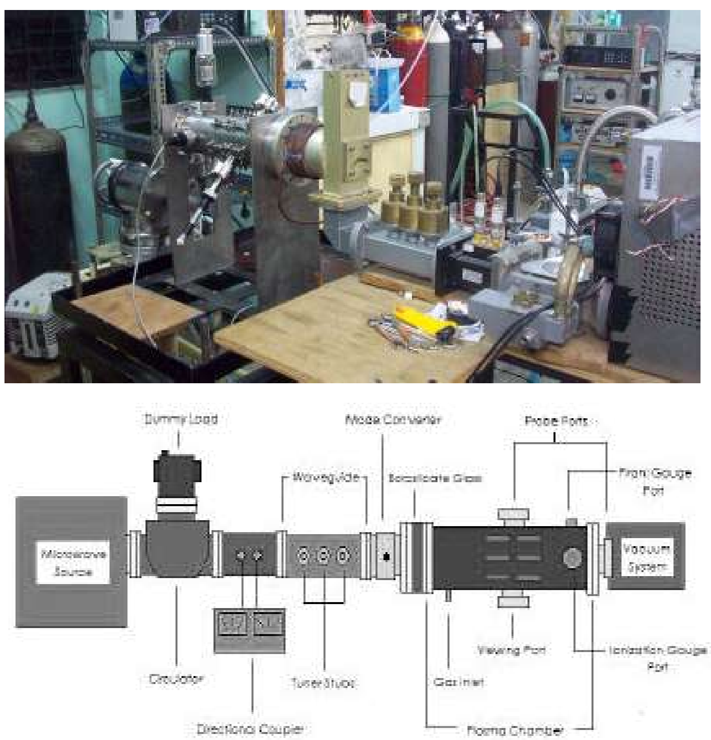

Fig. 1: The Microwave plasma device. (a) Actual image and (b) Schematic diagram

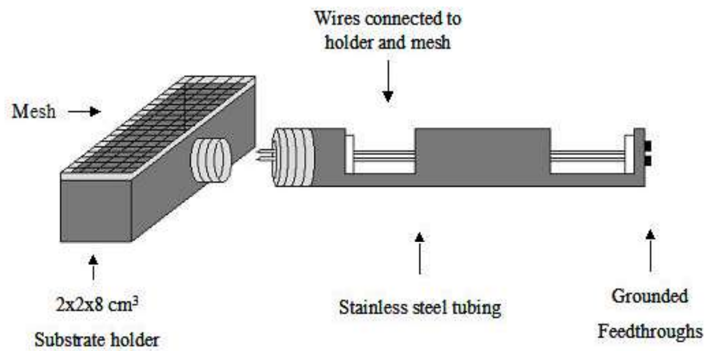

Fig. 2: Schematic diagram of the substrate holder

Plasma Pre-treatment: The other pre-treatment of the cocolumber uses different gas plasmas. In addition to the vacuum treatment, these samples are exposed to plasmas composed of either oxygen-, hydrogen- or argon-discharge for 5 minutes. All plasmas are generated using a forward power of 70 W, with a gas-filling pressure of 0.02 Torr and a fixed base pressure of $2.8\text{x}10^{-4}$ Torr.

Adsorption Experiments: Test solutions are prepared by dissolving the exact amount of $K_2Cr_2O_7$ (adsorbate) in deionized water. Five test solutions are prepared for varying initial adsorbate concentration (2.5, 5.0, 7.5, 10.0 and 12.5 mg/L). For each solution 25 mL volume is transferred into a small bottle with 0.5 g of the sawdust and maintained at an optimum pH of 2 by the addition of 0.1 M HCl or NaOH [1,3,10-12]. The solutions are allowed to stand for 240 minutes before being filtered using Whatman No. 42 filter paper.

Another five test solutions are prepared for varying contact time (5, 30, 60, 120 and 240 minutes) experiment. 25mL of each solution is also prepared with the same initial adsorbate concentration of 5.0 mg/L, adsorbent dose of 20,000 mg/L and a pH of 2. Afterwards, the solutions are also filtered using Whatman No. 42 filter paper.

Equilibrium concentrations of chromium (VI) are determined by reacting the test solutions to 1,5-diphenylcarbazide solution as colorimetric reagent [14]. Absorption is measured using a Perkin Elmer UV-Visible spectrophotometer at 540 nm. Percentage chromium (VI) removal is calculated using Equation 1 where C_o (mg/L) is the initial chromium (VI) concentration and C_t (mg/L) is the chromium (VI) concentration after adsorption [1,15,16].

$$\%Chromium(VI)\text{Re}movel = \frac{C_o - C_t}{C_o} \times 100\% \qquad (1)$$

RESULTS AND DISCUSSION

Effect of Initial Adsorbate Concentration: In Figure 3, the effect on adsorption of initial adsorbate concentration, for fixed adsorbent dose and pH is presented. It can be observed that for all pre-treated sawdust, %chromium (VI) removal generally decreases with increasing adsorbate concentration. This is due to the increasing number of chromium (VI) ions that compete for a finite number of binding sites on the adsorbent surface. After reaching maximum adsorption, any further increase in the adsorbate concentration only saturates the binding sites, therefore decreasing the percentage of adsorbed chromium (VI) ions.

Effect of Contact Time: Effect of contact time between the plasma pre-treated sawdust and the adsorbate solution is shown in Figure 4. Gradual increase in the %chromium (VI) removal with increasing time is observed. After around 120 minutes, little change in the %chromium (VI) removal is seen, which may indicate that the system has already achieved equilibrium. Maximum adsorption of chromium (VI) ions has been reached and no further removal occurs even for longer contact time. Thus, no further experiments were done after 240 minutes.

Vacuum Drying and Plasma Pre-treatments: Results from Table 1 show that vacuum drying increased the %chromium (VI) removal by up to 25% compared with the untreated sawdust. This enhancement could be due to the removal of moisture, resulting to an increase in the hydrophilicity of sawdust [5,6].

Vacuum drying method is effective for enhancing the adsorption efficiency of cocolumber sawdust for chromium (VI). It is considered highly feasible for commercial applications due to its lack of chemical

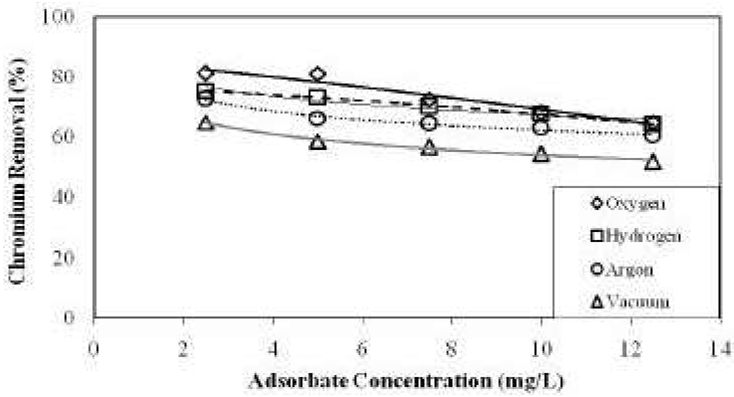

Fig. 3: Effect of increasing initial adsorbate concentration (2.5, 5.0, 7.5, 10.0 and 12.5 mg/L) to %chromium (VI) removal by vacuum and plasma pre-treated sawdust

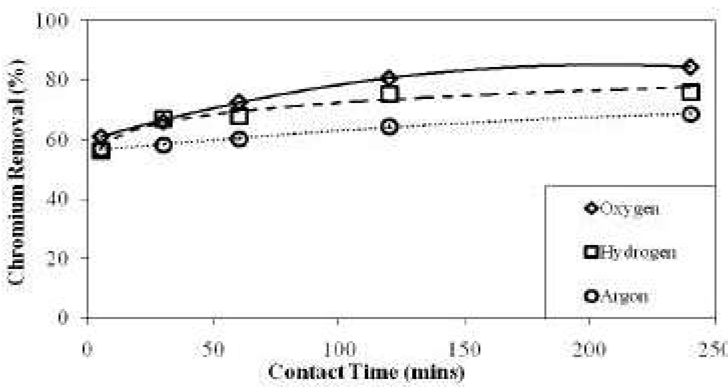

Fig. 4: Effect of increasing contact time (5, 30, 60, 120 and 240 min) between plasma pre-treated sawdust and the adsorbate solution

processing, reduced amount of generated wastes and the existence of commercially available vacuum drying facilities.

Comparison of the plasma pre-treated sawdust with the untreated sawdust has shown a significant increase by as much as 47.3% in chromium (VI) removal. Gases like oxygen and hydrogen dissociate and react with the adsorbent surface when exposed to the plasma. They form new chemical functional groups capable of modifying the hydrophilicity and biochemical activity of the adsorbent. Also, plasma ignited from inert gases like argon can remove certain atomic species from the adsorbent, thereby generating reactive radicals which react with other species to form chemical bonds. Referring to Table 1, oxygen plasma pre-treatment of cocolumber sawdust is found the most efficient for the removal of chromium (VI). Oxygen is known for its very high capacity to etch or modify material surfaces. Surface ablation of the sawdust with the oxygen plasma could have largely increased the adsorbent surface area, thus increasing the available adsorption binding sites [7-9].

Table 1: %Chromium (VI) removal of treated and untreated cocolumber sawdust for 5.0 mg/L adsorbate concentration and 240 minutes contact time

Sawdust	%Chromium (VI) Removal
Oxygen Plasma	81.2
Hydrogen Plasma	73.5
Argon Plasma	66.4
Vacuum Drying	58.7
Untreated	33.9

Adsorption Isotherms: The adsorption mechanism of a system can be described using adsorption isotherm models. Two types of adsorption isotherms are presented in this paper: Langmuir and Freundlich isotherm models. The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. Therefore, all adsorption sites are equivalent and can accommodate, at most, one adsorbed atom. The model is shown in Equation 2 where q_e (mg/g) is the adsorption capacity, q (mg/g) is the Langmuir constant related to

Table 2: Langmuir and Freundlich isotherm constants for chromium (VI) adsorption

		Plasma Treatments			
Isotherms	Parameters	Oxygen	Hydrogen	Argon	Vacuum Drying
Langmuir	b (L/mg)	0.136	0.212	0.159	0.472
	q (mg/g)	14.286	16.667	16.949	11.765
	R^2	0.955	0.997	0.924	0.976
Freundlich	K (mg/g) $(L/mg)^{1/n}$	0.550	0.453	0.373	0.249
	1/n	0.581	0.732	0.732	0.729
	n	1.721	1.366	1.366	1.372
	R^2	0.962	0.992	0.997	0.998

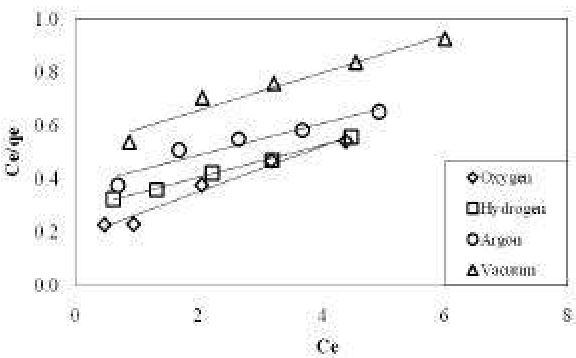

Fig. 5: Langmuir isotherm plots for chromium (VI) adsorption by pre-treated sawdust

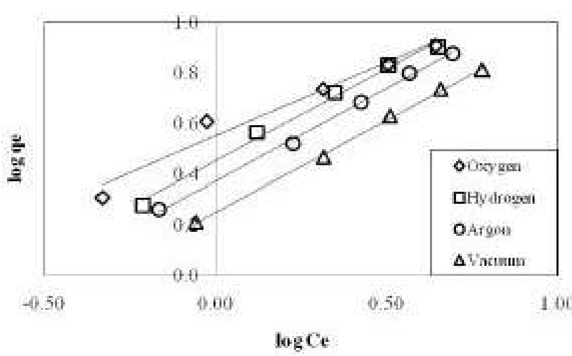

Fig. 6: Freundlich isotherm plots for chromium (VI) adsorption by pre-treated sawdust

maximum adsorption capacity, b (L/mg) is the Langmuir constant related to energy of adsorption and C_e (mg/L) is the equilibrium concentration [1,17].

$$q_e = \frac{q.b.C_e}{1 + b.C_e} \quad (2)$$

The Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption. The model is given in Equation 3 where q_e (mg/g) is the adsorption capacity, K (mg/g) is an indicator of the adsorption, C_e (mg/L) is the equilibrium concentration and $1/n$ (mg/L) is the adsorption intensity [1,17].

$$q_e = K.C_e^{\frac{1}{n}} \quad (3)$$

Data fitted to each isotherm model by linear regression, is often used to find the most appropriate adsorption model. The isotherm constants and the correlation coefficient (R^2) values for Langmuir and Freundlich are listed in Table 2. The Langmuir constants q and b, are calculated using the slope and intercept of the line, obtained from the plot of C_e/q_e vs. C_e (Figure 5), whereas, Freundlich constants K and $1/n$ are determined from the slope and intercept of the line obtained from the plot of ln q_e vs. ln C_e (Figure 6), respectively [18]. It can be observed that for oxygen and hydrogen plasma treatments of sawdust, relatively high and close R^2 values were obtained for the Langmuir and Freundlich models, suggesting that both models may be applicable in demonstrating chromium (VI) adsorption by the pre-treated sawdust. On the other hand, argon plasma and vacuum drying treatments obtained higher R^2 values for the Freundlich model, indicating that chromium (VI) reduction by these pre-treated sawdust follow this isotherm model.

CONCLUSIONS

Studies have shown that vacuum drying and plasma pre-treatments of sawdust using oxygen, hydrogen or argon gas, enhanced the removal of chromium (VI) ions by the cocolumber sawdust. Adsorption of chromium (VI) is found dependent on adsorbate concentration and contact time. Langmuir and Freundlich isotherm models also show good fits with the adsorption data. Vacuum drying and plasma treatments increased the adsorption of chromium (VI) due to the removal of moisture, surface ablations and formation of new chemical functional groups capable of modifying the hydrophilic nature of the sawdust. Compared to a chromium (VI) removal of 33.9% by the untreated sawdust, the plasma treated (oxygen, hydrogen and argon) and vacuum treated sawdust achieved 81.2%, 73.5%, 66.4% and 58.7% removal rates, respectively. Therefore, the most efficient method for the removal of chromium (VI) is thru oxygen plasma treatment of the cocolumber sawdust.

Investigation on further enhancement of the adsorption efficiency of sawdust by variation of plasma parameters can be done. Different criteria such as the heat of adsorption, adsorption temperature and activation energy can also be considered to determine exactly the dominant type of adsorption occurring during chromium (VI) reduction by the treated sawdust [2,4,12]. From the results obtained, initial insights are given as to which isotherm model fits the adsorption data better, based on the measured R^2 values. However, relatively high and close R^2 values were obtained from both models. Therefore, these criteria could give more support to the results and finally aid in determining the more fitted isotherm model to represent chromium (VI) adsorption by each of the pre-treated sawdust.

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