ORIGINAL ARTICLE

Removal of color, COD and lignin of pulp and paper wastewater using wood ash

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Abstract

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Removal of color, COD and lignin of pulp and paper wastewater using wood ash
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This study focused on removal of color, COD, and lignin in wastewater of pulp and paper mill using white wood ash and black wood ash that generated from boilers unit in the pulp and paper mill. Batch experiments were setup for studying the equilibrium time, pH, quantity of wood ash and adsorption isotherm. The results from the equilibrium time experiment concluded that the equilibrium time of the white wood ash is much more rapid than the black wood ash indicated as 2 minutes and 25 minutes, respectively. The effect of pH on the removal of such studied parameters was different for the white and black wood ash. Variation in pH of wastewater at the levels of 2 to 10 had no influence in removal of color (89-93%), COD (66-70%) and lignin (78-82%) when white wood ash was used, whereas the effect of pH on the removal was evident when using black wood ash. The highest removal of color (42.2%), lignin (31.1%) and COD (29.7%) was found when the initial pH was adjusted to 2 and such removal was gradually decreased when pH was raised. The optimum dose of white wood ash for the highest removal efficiency was 20 g ash /L of wastewater. This amount of wood ash can remove color 95%, lignin 80% and COD 69%. The reason for high removal efficiency of white wood ash might occur from the precipitation of lignin by CaO which is the major component of the ash. For the black wood ash, the optimum dose was calculated from the isotherm equation

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of adsorption, both by Langmuir and Freundlich isotherm. These isotherms were applicable to color and lignin, while they were inapplicable to COD. The isotherm for adsorption of color and lignin indicate that the removal mechanism by black wood ash was likely to be physical adsorption. The results indicated that the white wood ash was better than the black wood ash in treating the pulp and paper wastewater.

Key words : lignin, color, COD, wood ash, adsorption, precipitation

บทคัดย่อ

เนตรนภิส ตันเต็มทรัพย์ วันเพ็ญ วิโรจนกูฏ และ สันติ สกลไชย

การกำจัดสี ซีโอดีและลิกนิน ในน้ำเสียของโรงงานผลิตเยื่อกระดาษด้วยเถ้าไม้

ว.สงขลานครินทร์ วทท. 2547 26(ฉบับพิเศษ 1) : 1-12

การศึกษาครั้งนี้มีวัตถุประสงค์เพื่อกำจัดสี ซีโอดี และลิกนิน ในน้ำเสียของโรงงานผลิตเยื่อกระดาษ โดยใช้เถ้าไม้ขาวและเถ้าไม้ดำซึ่งเป็นกากของเสียจากหม้อต้มไอน้ำภายในโรงงานผลิตเยื่อกระดาษดังกล่าว โดยใช้การทดลองแบบแบทช์ เพื่อหาเวลาที่เข้าสู่สภาวะสมดุล สภาพพีเอช ปริมาณของเถ้าไม้ที่เหมาะสมตลอดจนไอโซเทอร์มของการดูดติดผิว จากการทดลองเวลาสัมผัสที่เข้าสู่สภาวะสมดุล พบว่าเวลาที่เข้าสู่สภาวะสมดุลของเถ้าไม้ขาวเร็วกว่าเถ้าไม้ดำมาก โดยเวลาที่เข้าสู่สภาวะสมดุลของเถ้าไม้ขาวเร็วและเถ้าไม้ดำต่างกันคือ 2 นาทีและ 25 นาที ตามลำดับ ผลของพีเอชต่อการกำจัดน้ำเสียของเถ้าทั้งสองชนิดมีความแตกต่างกัน โดยเมื่อปรับสภาพพีเอชให้อยู่ในช่วง 2-10 ก่อนเติมเถ้าไม้ พบว่าพีเอชไม่ส่งผลต่อการกำจัดทั้ง สี ซีโอดี และลิกนินเมื่อใช้เถ้าไม้ขาว แต่สำหรับเถ้าไม้ดำนั้น พีเอชจะส่งผลต่อการกำจัดทั้งสี (89-93%) ซีโอดี (66-70%) และ ลิกนิน (78-82%) โดย ณ พีเอช เท่ากับ 2 นั้นจะได้ค่าการกำจัดสูงสุดคือ 42.2% ลิกนิน 31.1% และ ซีโอดี 29.7% ปริมาณเถ้าไม้ที่มีประสิทธิภาพการกำจัดสูงสุดในเถ้าไม้ขาว คือใช้เถ้าไม้ขาว 20 กรัม/ลิตร น้ำเสีย โดยสามารถกำจัดสี 95% ลิกนิน 80% และ ซีโอดี 69% ตามลำดับ ประสิทธิภาพของการกำจัดคาดว่าเกิดจากการตกตะกอนลิกนินเนื่องจาก CaO ที่เป็นองค์ประกอบสำคัญของเถ้าไม้ขาว ส่วนกรณีเถ้าไม้ดำ การหาปริมาณเถ้าไม้ที่เหมาะสมทำโดยคำนวณจากสมการไอโซเทอร์มของการดูดติดผิว ทั้งแบบแลงมัวร์เชิงเส้นและแบบฟรุนดิช พฤติกรรมการดูดติดผิวของสีและลิกนินของเถ้าไม้ดำพบว่ามีแนวโน้มเป็นแบบกายภาพ ผลการวิจัยบ่งชี้ได้ว่า เถ้าไม้ขาวมีความเหมาะสมในการนำไปใช้บำบัดน้ำเสียจากโรงงงานเยื่อกระดาษมากกว่าเถ้าไม้ดำ

ศูนย์วิจัยแห่งชาติด้านการจัดการสิ่งแวดล้อมและของเสียอันตราย มหาวิทยาลัยขอนแก่น/ภาควิชาวิศวกรรมสิ่งแวดล้อม คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่น อำเภอเมือง จังหวัดขอนแก่น 40002

Pulp and paper mill is a large industrial enterprise that generates a significant amount of wastewater containing high concentration of lignin causing brown color and COD (Environmental Technology Office, 2000). Lignin is difficult to degrade by microorganisms. Therefore, the effluent from the wastewater treatment system, which is a biological process, still contains a high content of color, lignin and COD. Moreover, the derivative of lignin is hazardous to aquatic animals/plants (Borisutpetch, 2002 and Sreekrishnan, 2001). To treat color in wastewater requires costly advanced technologies. Therefore, an alternative method is being sought. Meanwhile, the factory also produces wood ash which are solid waste generated from the wood used as fuel energy in the boiler. There are two types of wood ash resulting from different raw materials and different burning temperature: the white wood ash contains mostly CaO and black wood ash contains mostly SiO_2

(Sakolchai, 2003). It is well known that Ca^{2+} can precipitate lignin which has negative charge, and the molecule of SiO_2 is a web crystal structure that is the character of adsorbent. It is thus possible to use wood ash to remove color, COD and lignin in the pulp and paper wastewater. This would be of benefit not only to the mill in terms of minimizing cost of color and lignin treatment but also to minimize the impact on the environment.

Materials and Methods

Two types of wood ash, white wood ash from the multi-fuel boiler (or bark boiler) and black wood ash from dust fired boiler, were used as the media (precipitating agent and/or adsorbent) to remove color, lignin and COD of wastewater from pulp and paper mill. Wastewater sample used was collected from the wastewater treatment plant effluent (activated sludge system) of a pulp and paper mill. The studied parameters included pH, color, COD and lignin for which the analyses followed the standard methods. Instruments and methods used are pH meter, Space Unit (SU) using UV-Visible Spectrophotometer (400-700 nm), Standard Method Dichromate Digestion-Close Reflux and Standard Method 5550 using UV-Visible Spectrophotometer for pH, color, COD and lignin respectively. Batch tests were set for every experiments and performed in the laboratory at room temperature. The steps of the experiments were described below:

1. Equilibrium time: The optimum mixing speed and time were determined based on comparing the removal efficiency of color at various mixing speeds and times. Experiments were firstly performed to determine the optimum mixing speed, including 30, 50, 100 and 200 rpm, and secondly the optimum mixing time including 2, 4, 6, 8, 10, 15, 20, 25, 30 minutes. The amounts of white and black wood ash used obtained from initial test were 15 and 50 g per 500 ml of wastewater, respectively.

2. Optimum pH: pH plays an important role in the precipitation and adsorption mechanisms. Therefore, the pH in wastewater that should be adjusted before treated with wood ash was experimented. The experiments were performed by varying pH level of the samples wastewater ranging from 2 to 10 before adding wood ash. The amount of wood ash used was 30 g/L and 100 g/L for white and black wood ash, respectively. The mixing speed and time used were obtained from the optimum values received from previous experiments. Optimum pH was considered base on the maximum color removal.

3. Optimum dosage of wood ash: The experiments were individually set for each wood ash. For each 500 ml of wastewater sample, the amounts of wood ash used were 2, 4, 6, 8 and 10 g of the white wood ash, and 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 g of the black wood ash. The optimum conditions for mixing speed, time and pH were obtained from the two sets of experiment described above. The optimum dosage of white wood ash was determined based on the removal efficiency. The result for the black wood ash employed the adsorption, isotherms based on Langmuir and Freundlich equations.

Results and Discussion

1. Equilibrium time: The experimental results for white and black wood ash are demonstrated in Figures 1 and 2 respectively. For the white wood ash, at the beginning of the mixing (0-2 minutes) the high mixing speed, 100 and 200 rpm had greater impact on color removal (i.e. 70%) compared to the lower speeds of 30 and 50 rpm where the removal efficiency was only 30%. After the first 2 minutes, the higher mixing speeds showed the likely constant of about 70% removal, whereas the lower mixing speeds showed significant increase of removal efficiency with increasing time up to 25 minutes at which the removal was about 75 %. As a result, for the white wood ash, the two-steps mixing were used for further experiments. The mixing steps were at first applying the high mixing speed (150 rpm) for two minutes and then reducing the speed to 30 rpm (low speed) for another 10 minutes. For the black wood ash, a

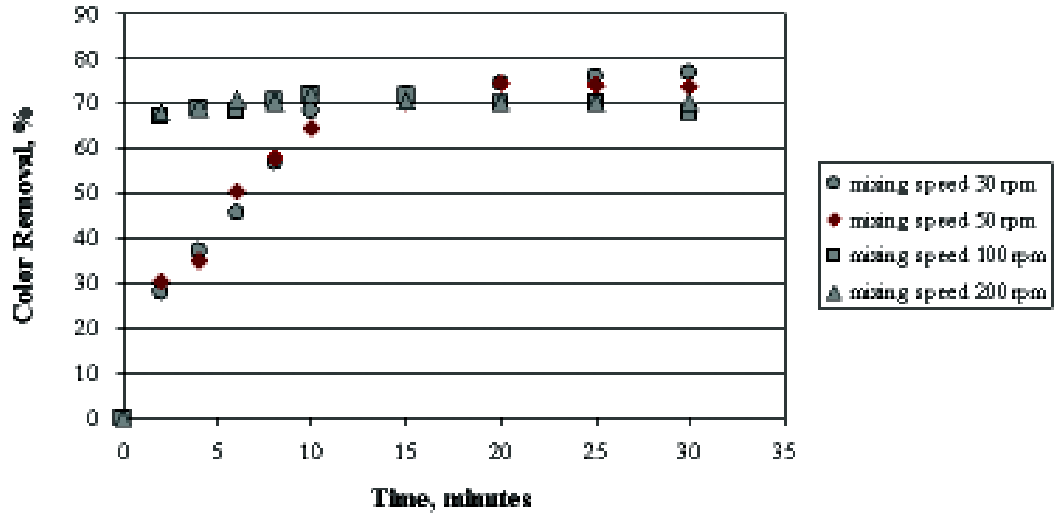


Figure 1. Plot between percent removal and time for white wood ash

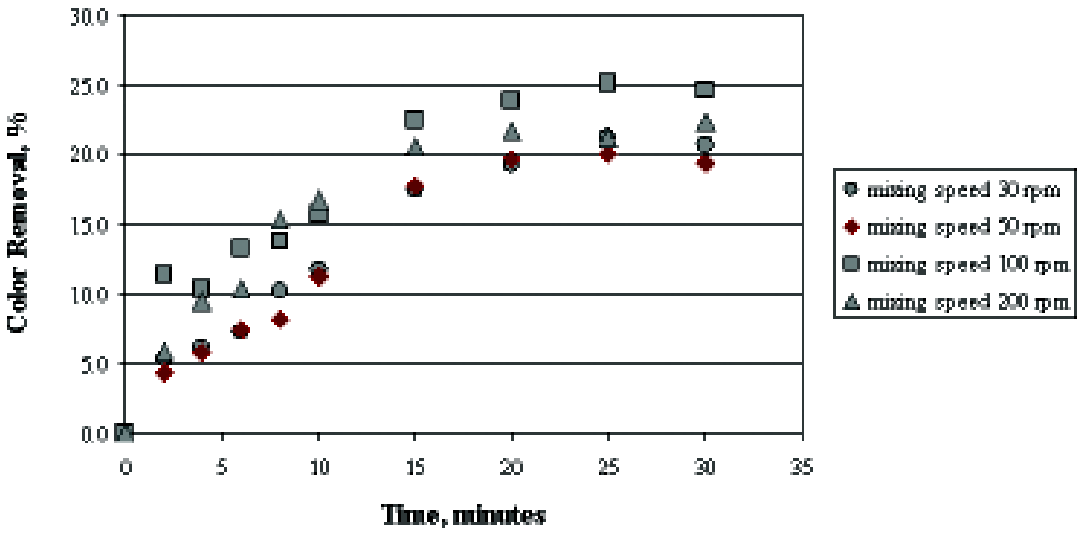


Figure 2. Plot between percent removal and time for black wood ash

similar result was found, thus, a two-steps mixing was also applied, but with a high mixing speed (150 rpm) for two minutes and low speed (30 rpm) for 30 minutes.

2. Optimum pH. Since pH play important role in removal efficiency, optimum pH for chemical precipitation and adsorption were investigated for white wood ash and black wood ash, respectively. For the white wood ash, variation of the adjusted pH to values of 2, 4, 6, 8, and 10 before adding the wood ash has no significant effect on the removal efficiency of color, COD and lignin as indicated by 89-93%, 78- 82% and 66-70%, respectively (Figure 3). It was noted that after adding the white wood ash to the wastewater samples that had different initial pH, the final pH of all precipitating

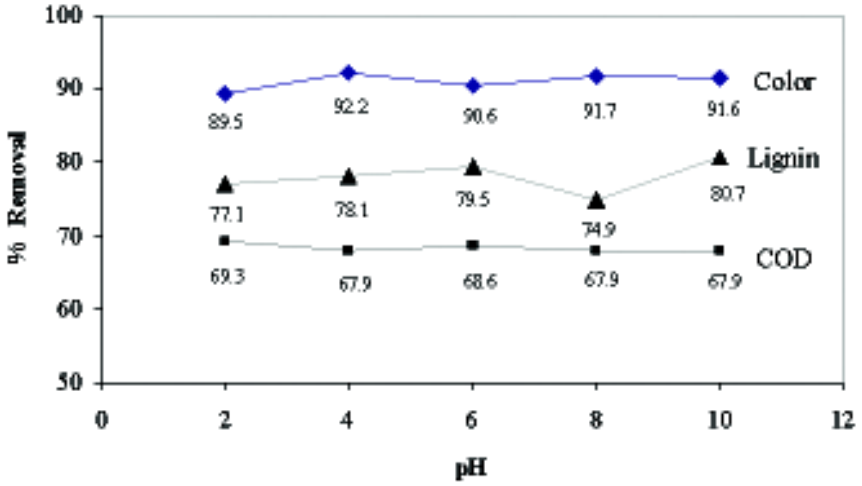


Figure 3. Plot between percent removal and pH for white wood ash

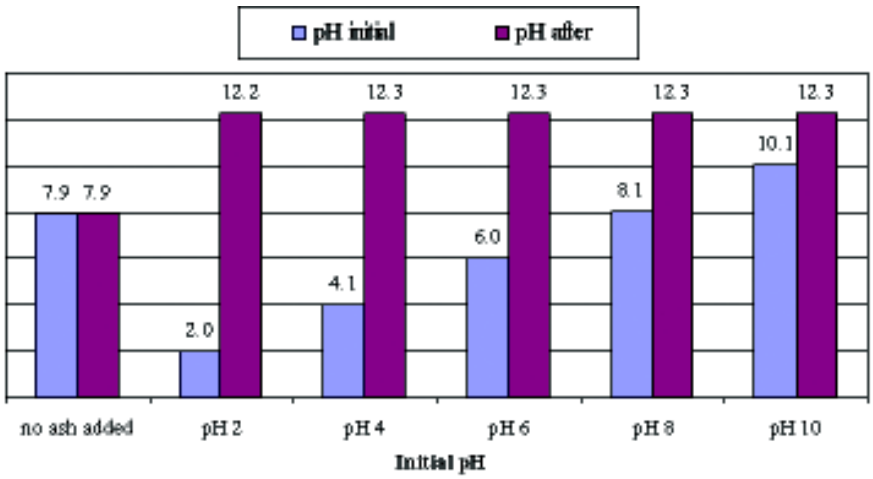


Figure 4. pH of wastewater before and after treated with white wood ash

samples was in the range of 11-12 (Figure 4). This may be a result of precipitating reaction of Ca^{2+} (major component of the white wood ash) with any negative charge ions of lignin derivative (Sundin, 2000). As $CaCO_3$ is highly alkaline and can make pH up to 11-12, within this range the precipitation of lignin can be taken place. Therefore, pH adjustment of the wastewater before adding the white wood ash is not necessary.

For the black wood ash, variation of pH (pH 2, 4, 6, 8, 10) has an influence on the removal efficiency of color, COD and lignin (Figure 5). The lower the pH yields better removal efficiency. At pH 2, the color removal efficiency was highest as 42.2%, which then decreased to 24.7%, 12.6%, 11.8% and 9.7% at pH 4, 6, 8 and 10, respectively. After adding the black wood ash to wastewater that had different initial pH, the final pH of wastewater increased to the range from 7-10 (Figure 6). Lignin and COD showed the same pattern of removal, decreasing when pH is increase. The removal efficiency of lignin was 31.1%, at pH 2

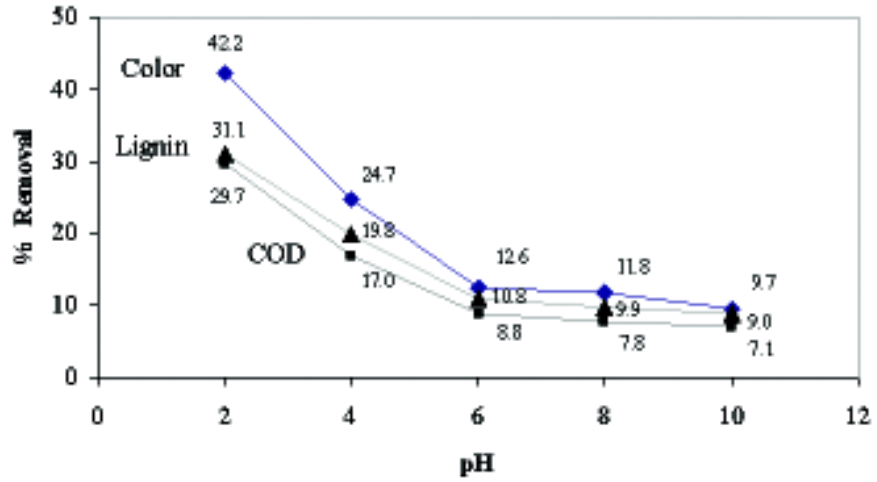


Figure 5. Plot between percent removal and pH for black wood ash

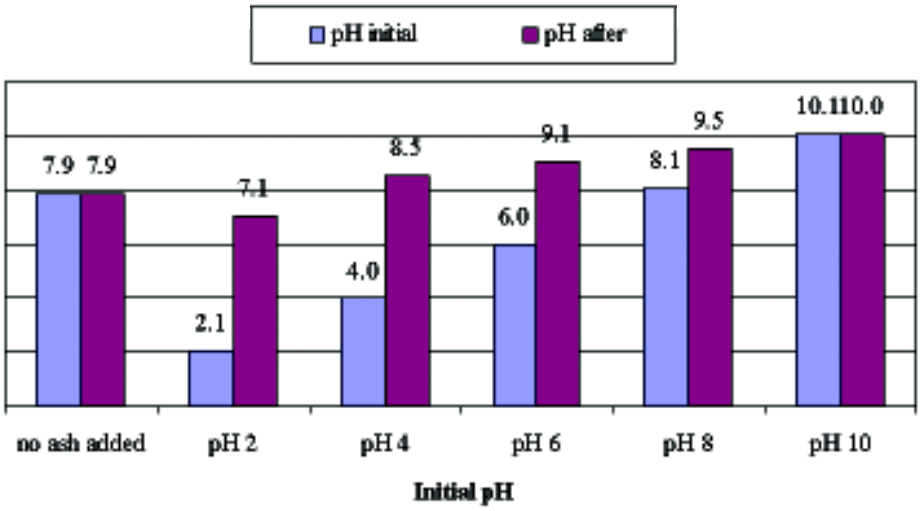


Figure 6. pH of wastewater before and after treated with black wood ash

decreasing to 19.8%, 10.9%, 9.9% and 9.0% , and COD from 29.7% to 17.0%, 8.8%, 7.85 and 7.0%, at the respective to increasing value of pH. The structure of the black wood ash, which is composed of 45% SiO_2 (Sakolchai, 2003), is a network of covalent bonds of Si and O_2. At the lower pH, which was adjusted with H_2SO_4, the surface of the wood ash may accumulate positive charges that can adsorb negative charges of lignin onto its surface. (Mohan and Karthikeyan, 1997) At higher pH, that was adjusted with NaOH, the competition between OH^- of NaOH and lignin would occur, and thus the adsorption would be less. Most of the final pH after adding the black wood ash to wastewater was in the range of 7 to 9 (complying with the Thai government effluent standard) except when the initial pH was 8 or 10,in which cause a pH of about 10 was obtained. This makes the treatment of wastewater with black wood ash in the treatment plant possible to apply. However,

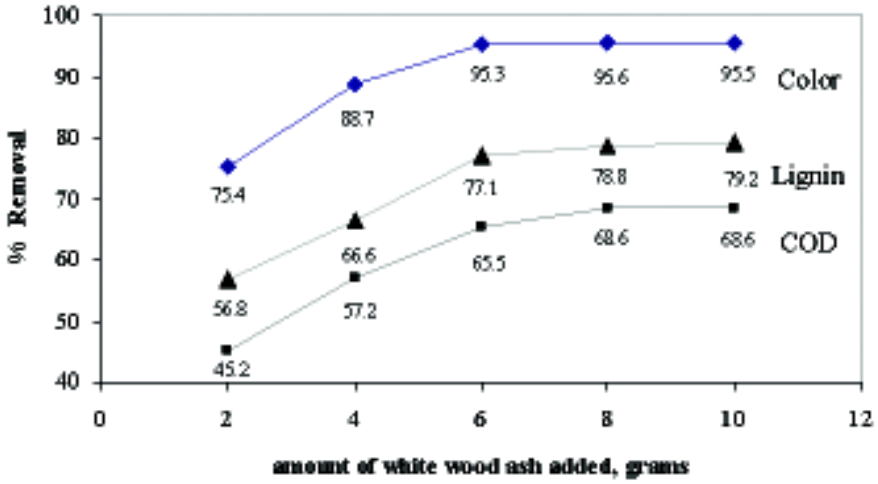


Figure 7. Plot between percent removal and amount of white wood ash added

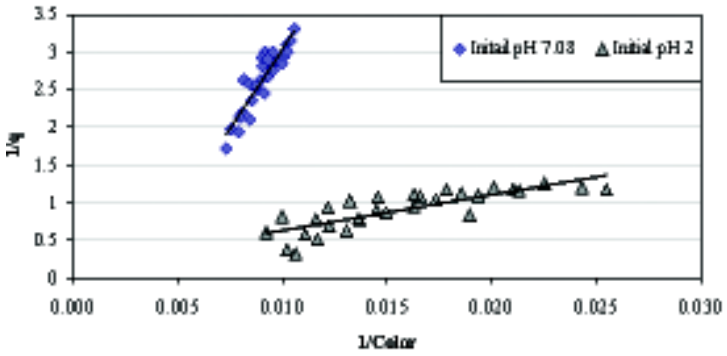
the removal efficiency by the black wood ash was substantially lower than that by the white wood ash.

3. Optimum dosage of wood ash: For white wood ash, the results show that the amount of ash required to remove color, COD and lignin were quite low, about 10 g per 500 ml of wastewater as shown in Figure 7, which yielded the maximum removal efficiency of 95% of color, 80% of lignin and 69% of COD. The removal efficiency of color was higher than that of lignin and COD, which is because color is formed from large molecular weight compounds such as lignin, tannin, humic and fulvic. These compounds, with molecular weight higher than 1,000 , can be precipitated by Ca^{2+} at a pH ranging from 11 to 13 (Sundin, 2000). As the composition of white wood ash is 74% CaO (Sakolchai, 2003), that would yield a relatively high amount of Ca^{2+} when dissolved in water. As a result, lignin with a molecular weight higher than 1,000 can be precipitated by white wood ash. However the lower molecular weight lignin cannot be precipitated and remains in the water, thus the removal of lignin is not as high as that of color. The COD is generated from various complex organic compounds which could not be all precipitated with Ca^{2+}. So that the removal of COD was lower than that of color and lignin. The optimum dosage of white wood ash for color, lignin and COD was 20 g/l of wastewater. During the experiment, it was observed that there is only small amount of solid phase occurred from the precipitation. This might be because most of the white wood ash is dissolved as the water and wastewater used in this study has low concentration of suspended and dissolved solids. Therefore, the application of this method would benefit in terms of reducing cost of disposal sludge from the process.

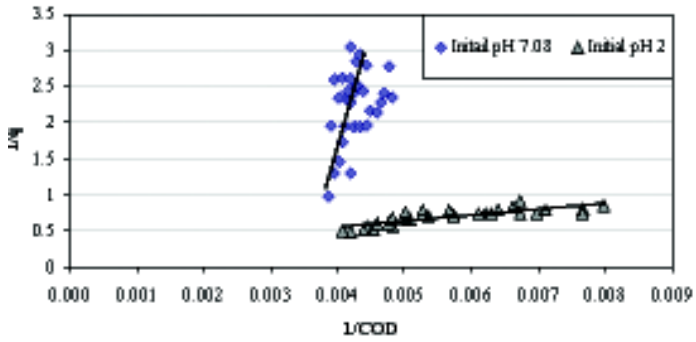
For black wood ash, the results show that the amount of ash required to remove color, COD and lignin were quite low, about 10 g per 500 ml of wastewater. As shown in Figure 2, the amount above yielded the maximum removal efficiency as 42.2% of color, 31.1% of lignin and 29.7% of COD. As the main component of the black wood ash is SiO_2, the removal mechanism tends to be adsorption. The optimum quantity of the black wood ash was determined by employing Langmuir and Freundlich equations. Since the highest removal efficiency of the black wood ash was reached at pH 2, the experiments were carried out under two conditions, one without adjusting pH and another one with initial pH adjusted to 2.

1) Langmuir adsorption isotherm

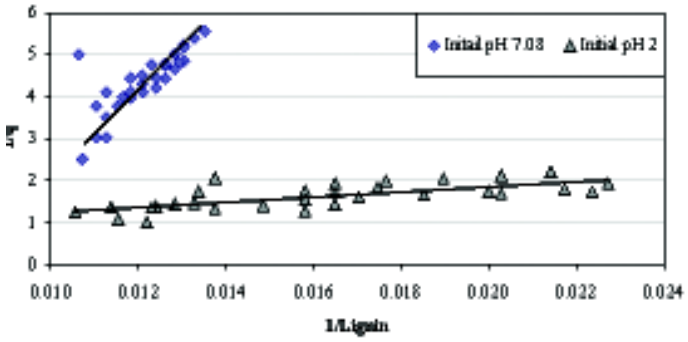
The experimental results plotted against the Langmuir adsorption isotherm (equation 1) are



(a) Color



(b) COD



(c)

Figure 8. Langmuir Isotherm Plot for (a) Color, (b) COD and (c) Lignin

demonstrated in Figure 8. The constants are determined as shown in Table 1.

$$1/q = (1/C)(1/K_A * q_m)+(1/q_m) \quad \ldots\ldots\ldots \quad (1)$$

where C is the equilibrium concentration (mg/L)

q is the amount of chemical adsorbed per unit weight of the adsorbent at equilibrium concentration (mg/g)

q_m is the maximum adsorption at monolayer coverage (mg/g)

K_A is the adsorption equilibrium constant (L/mg)

Figure 8 shows the linear plot of Langmuir isotherm model with the correlation coefficient (R^2) for all experiments ranging from 0.8 to 0.9.

Table 1. Langmuir adsorption isotherm

Color Adsorption Isotherm and Constants					
Wastewater	$1/q = (1/C)(1/K_A*q_m)+(1/q_m)$	Slope	q_m	K_A	R^2
Without pH adjusted	1/q = 601.66(1/C) - 2.73	601.66	-0.37	-0.00454	0.903
With pH adjusted	1/q = 55.37(1/C) + 0.0487	55.37	20.53	0.00088	0.814
COD Adsorption Isotherm and Constants					
Wastewater	$1/q = (1/C)(1/K_A*q_m)+(1/q_m)$	Slope	q_m	K_A	R^2
Without pH adjusted	1/q = 3156.1(1/C) - 11.081	3156.10	-0.09	-0.00351	0.855
With pH adjusted	1/q = 137.44(1/C) - 0.061	137.44	-16.39	-0.00044	0.906
Lignin Adsorption Isotherm and Constants					
Wastewater	$1/q = (1/C)(1/K_A*q_m)+(1/q_m)$	Slope	q_m	K_A	R^2
Without pH adjusted	1/q =1047.1(1/C) - 8.4784	1047.10	-0.12	-0.00810	0.964
With pH adjusted	1/q = 61.036(1/C) + 0.5643	61.04	0.177	0.00925	0.816

In accordance with the Langmuir adsorption isotherm, the adsorption behavior is a physical adsorption with monolayer coverage. Even though, the isotherm plots of COD (both with and without pH adjustment), color and lignin color for the case of without pH adjustment seems to fit the Langmuir, the constants and maximum adsorption were negative values. It is likely indicated that adsorption of COD, color and lignin are not able to be explain by the monolayer coverage theory.

However, the adsorption of lignin at initial pH equal to 2 provides a good fitting with Langmuir Isotherm. When comparing K_A (optimum at initial pH 2 =0.00925 L/mg) and q_m (0.177 mg/g)) of the black wood ash (Table 1) with K and q_m of activated charcoal for lignin removal which are 0.068 L/mg and 0.42 mg/g, respectively (Mohan and Karthikeyan,1997), the adsorption pattern of both materials are similar but activated charcoal is better than that of the black wood ash. This is due to that black wood ash having a lower specific surface area (0.128 m^2/g) than activated charcoal (200-1000 m^2/g).

2) Freundlich adsorption isotherm

The adsorption isotherm following the Freundlich equation (equation 2) for color, COD and lignin are plotted in Figure 9 and the calculated constants are shown Table 2.

$$q = K_F C^{1/n} \quad \text{..... (2)}$$

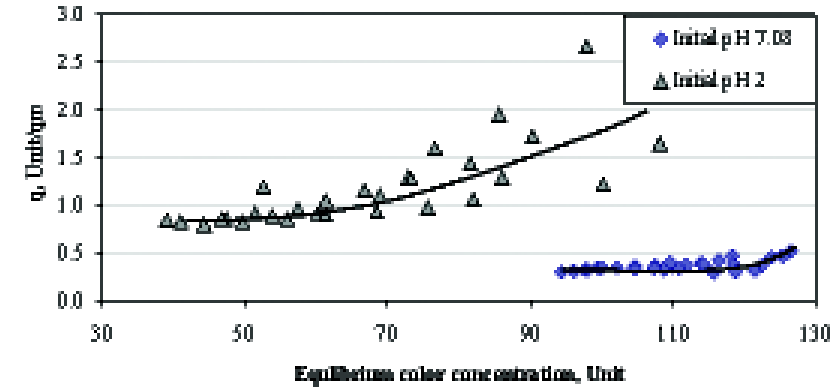
where C is the equilibrium concentration (mg/L)
q is the amount adsorbed per unit weight of the adsorbent at equilibrium concentration (mg/g)
K_F is the adsorption equilibrium constant (L/mg)

This linear plot implied the Freundlich isotherm model with R^2 for all experiments ranging from 0.78 to 0.92.

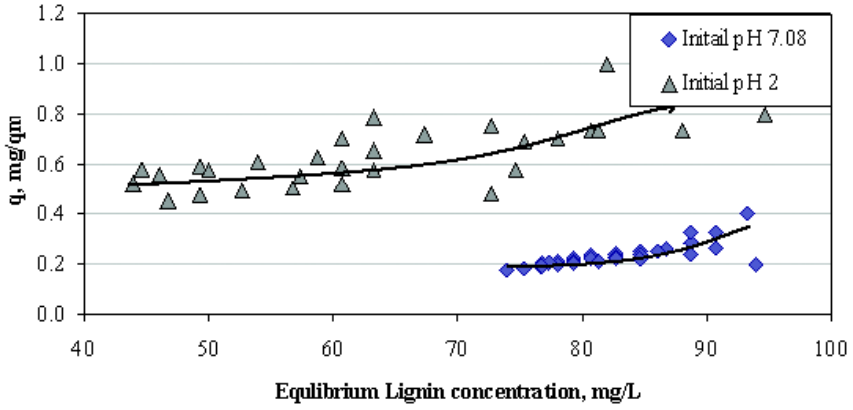
Conclusions

The conclusions are drawn as follows.

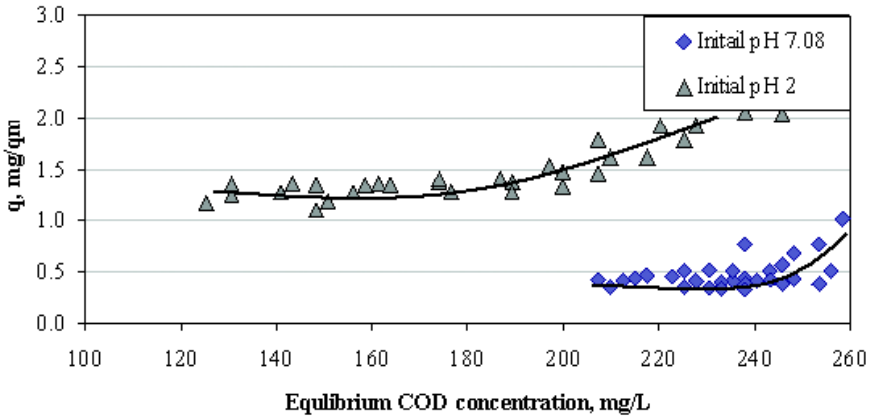
1. The optimum mixing speed and time followed a two steps schedule, beginning with a



(a) Color



(b) COD



(c)

Figure 9. Fundlitch Isotherm Plot for (a) Color, (b) COD and (c) Lignin

Table 2. Fundlitch adsorption isotherm

Color Adsorption Isotherm and Constants					
Wood ash	$q = K_F C^{1/n}$	Slope	n	K_F	R^2
Raw wastewater	$q = 0.316\ C^{0.0079}$	0.0079	126.58	0.3162	0.921
pH adjusted wastewater	$q = 0.937\ C^{0.0177}$	0.0177	56.50	0.9367	0.776
COD Adsorption Isotherm and Constants					
Wood ash	$q = K_F C^{1/n}$	Slope	n	K_F	R^2
Raw wastewater	$q = 0.0001\ C^{0.0196}$	0.0196	51.02	0.0001	0.813
pH adjusted wastewater	$q = 0.583\ C^{0.0093}$	0.0093	107.53	0.5830	0.905
Lignin Adsorption Isotherm and Constants					
Wood ash	$q = K_F C^{1/n}$	Slope	n	K_F	R^2
Raw wastewater	$q = 0.322\ C^{0.0089}$	0.0089	112.36	0.3220	0.892
pH adjusted wastewater	$q = 1.470\ C^{0.0077}$	0.0077	129.87	1.4696	0.820

rapid mixing at speed of 150 rpm for 2 minutes and slow mixing at speed of 30 rpm for another 10 minutes for the white wood ash, and a rapid mixing at speed of 150 rpm for 2 minutes and slow mixing at speed of 30 rpm for another 30 minutes for the black wood ash.

2. Variation of the initial pH (before adding wood ash) had no effect on the removal efficiency for the white wood ash, but it did for the black wood ash. pH adjustment for the white wood ash was not necessary. If the black wood ash is used, pH 2 adjustment is recommended.

3. The optimum amount of white wood ash for removal of such studied parameters was 20 g/L, giving removals of 95% color, 80% lignin and 69% COD. The removal mechanism for the white wood ash was likely to be precipitation.

4. As the removal of the black wood ash tended to be adsorption, the adsorption isotherm was determined by both Langmuir and Freundlich equations. The adsorption mechanism of black wood ash is physical with monolayer coverage. The amount of the black wood ash can be calculated from the adsorption isotherms.

5. The white wood ash presented a higher removal ability compare to that the black wood ash by using a batch mixing (Jar test) system.

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