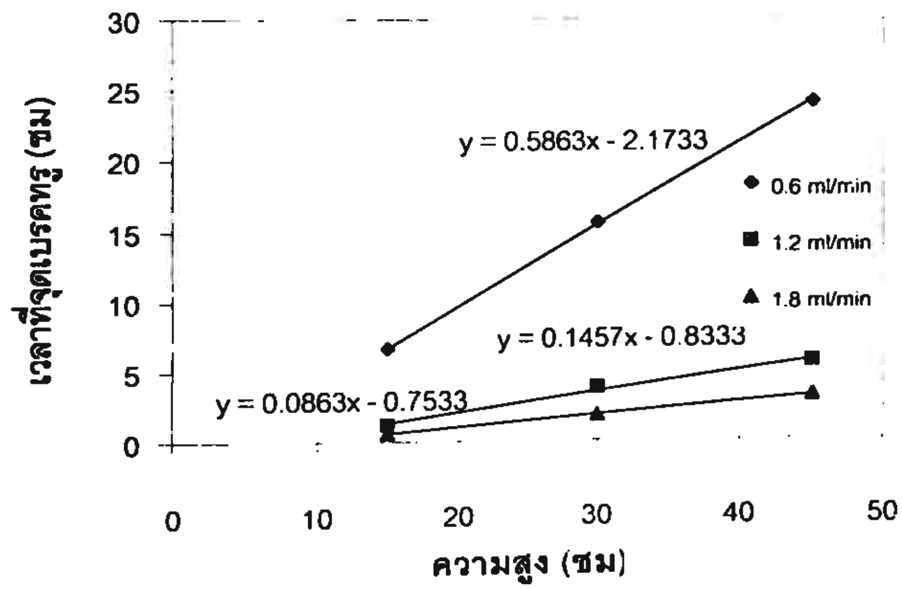
จากผลการทดลองปริมาตรน้ำที่บำบัดได้ที่ 90% เบรคทรู ($V_B$), เวลาที่จุดเบรคทรู ($T_B$) และความสามารถในการดูดซับ ($q_e$) ลดลงเมื่ออัตราการไหลเพิ่มขึ้น ทั้งนี้เป็นเพราะเวลาสัมผัสระหว่างสีรีแอคทีฟกับหญ้าแขมลดลง ดังนั้นเบรคทรูจึงเกิดขึ้นก่อนที่อัตราการไหลสูงๆ

**การใช้ Bed Depth Service Time Model ในการวิเคราะห์ผลของอัตราการไหล**

จากข้อมูลในตารางที่ 7 สามารถนำมาเขียนกราฟแสดงความสัมพันธ์ระหว่างความสูงกับเวลาที่จุดเบรคทรูที่อัตราการไหลต่างๆ ได้ โดยแสดงดังรูปที่ 14 จากรูปนี้จะเห็นว่าสมการที่ได้เป็นสมการเส้นตรง ซึ่งแสดงว่า BDST model เหมาะสมสำหรับการทำนายการดูดซับสีรีแอคทีฟโดยหญ้าแขม ซึ่งสอดคล้องกับค่าสัมประสิทธิ์ correlation ($R^2$) ที่ได้รับจากกราฟ ซึ่งพบว่ามีค่ามากกว่า 0.99 ทั้ง 3 อัตราการไหล นอกจากนี้จากกราฟจะเห็นว่าเวลาที่จุดเบรคทรูลดลงเมื่ออัตราการไหลเพิ่มขึ้นที่ความสูงเดียวกัน และความชันของกราฟจะลดลงเมื่ออัตราการไหลเพิ่มขึ้น สำหรับค่าพารามิเตอร์ที่คำนวณได้จากกราฟจะแสดงในตารางที่ 8




**รูปที่ 14** BDST model สำหรับการดูดซับสีรีแอคทีฟโดยหญ้าแขมที่อัตราการไหลต่างๆ

**ตารางที่ 8** ค่าพารามิเตอร์ของ BDST model สำหรับการดูดซับสีรีแอคทีฟโดยหญ้าแขมที่อัตราการไหลต่างๆ

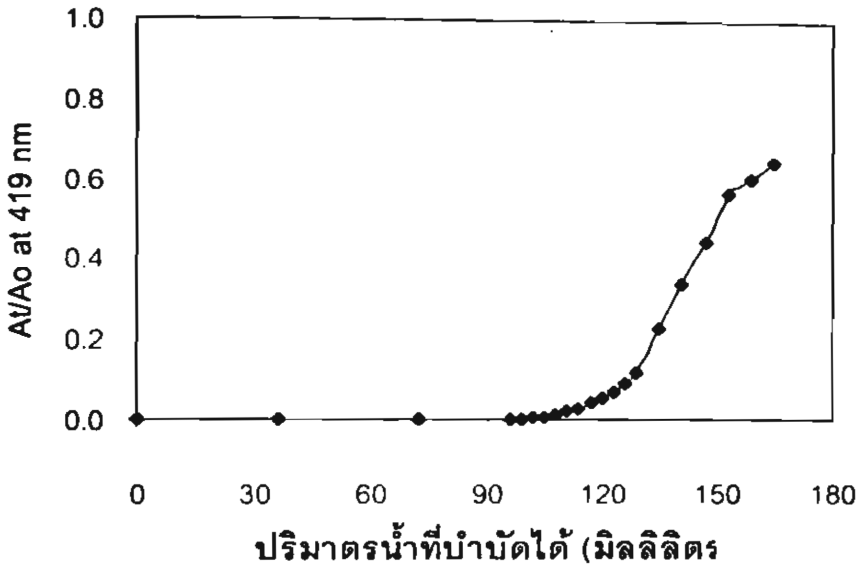
| Flow rate (ml/min) | Linear flow rate ($v$) (cm/hr) | $D_o$ (cm) | $N_o$ (mg/cm$^3$) | K (L/mg.hr) | $N_o$ (mg/g) | $R^2$ |
|---|---|---|---|---|---|---|
| 0.6 | 7.3 | 3.71 | 0.128 | 0.034 | 0.98 | 0.9999 |
| 1.2 | 14.7 | 5.72 | 0.064 | 0.088 | 0.49 | 0.9947 |
| 1.8 | 22.0 | 8.73 | 0.057 | 0.097 | 0.44 | 0.9974 |

จากตารางที่ 8 จะเห็นว่าความสูงวิกฤต ($D_o$) ซึ่งเป็นความสูงของตัวดูดซับที่เพียงพอที่จะป้องกันไม่ให้ความเข้มข้นของตัวที่ถูกดูดซับมีค่าเกินความเข้มข้นที่จุดเบรคทรู และค่าคงที่ (K) ลดลงเมื่ออัตราการไหลลดลง โดยความสูงวิกฤต ($D_o$) ลดลง 58% และค่าคงที่ (K) ลดลง 65% เมื่ออัตราการไหลลดลง 3 เท่า ทั้งนี้เป็นเพราะในการกำจัดสีรีแอคทีฟที่อัตราการไหลสูงๆ ต้องการความยาวของบริเวณที่มีการดูดซับ ($L_m$) มากขึ้น จากการทดลองค่าความสามารถในการดูดซับ ($N_o$) ลดลงเมื่ออัตราการไหลเพิ่มขึ้น โดยความสามารถในการดูดซับลดลง 55% เมื่อเมื่ออัตราการไหลเพิ่มขึ้น 3 เท่า ทั้งนี้เป็นเพราะการเพิ่มอัตราการไหลจะเป็นการลดเวลาสัมผัสระหว่างสีรีแอคทีฟกับหญ้าแขม เมื่อเปรียบค่าความสามารถในการดูดซับระหว่างระบบกะกับระบบคอลัมน์ พบว่า ความสามารถในการดูดซับในระบบกะมีค่า 4.42 มิลลิกรัมต่อกรัม ในขณะที่ในระบบคอลัมน์มีค่าความสามารถในการดูดซับ 0.98 มิลลิกรัมต่อกรัม จะเห็นว่าในระบบกะมีค่าความสามารถในการดูดซับมากกว่าในระบบคอลัมน์ ทั้งนี้เป็นเพราะการศึกษาในคอลัมน์ไม่ได้เป็นการศึกษาที่สมดุลหรือเวลาสัมผัสอาจจะไม่เพียงพอที่อัตราการไหลในช่วงที่ทำการศึกษา จากการทดลองทั้งหมดจะเห็นว่าที่ความสูง 45 ซม.และอัตราการไหล 0.6 มิลลิลิตรต่อนาที จะมีปริมาตรน้ำที่บำบัดได้ที่ 90% เบรคทรู ($V_B$) และความสามารถในการดูดซับสูงสุดเมื่อเทียบกับสภาวะอื่น ดังนั้นสภาวะนี้จึงถูกเลือกเพื่อใช้ในการทดลองต่อไป

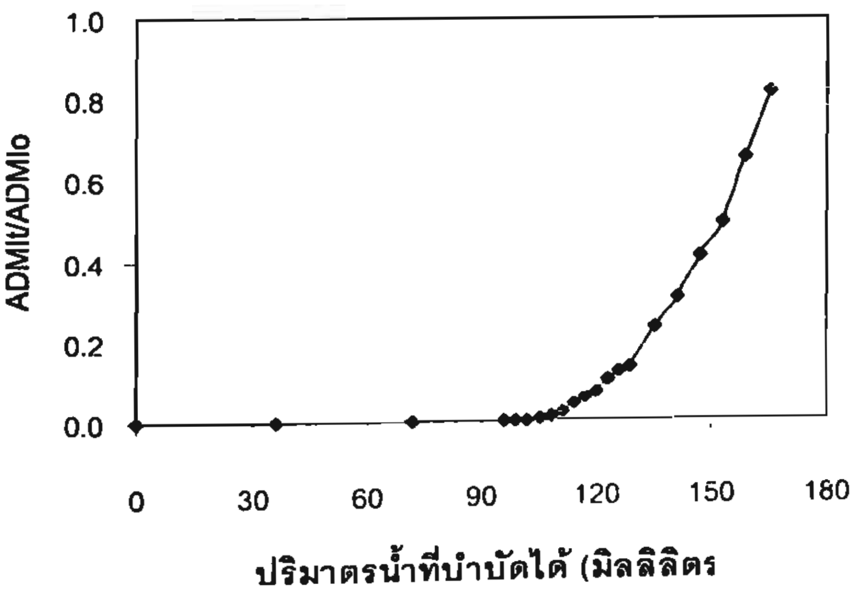
## 2.5 การศึกษาโดยใช้น้ำเสียจริง

### 2.5.1 น้ำเสียจากโรงงานย้อมผ้า

เนื่องจากลักษณะน้ำเสียจากโรงงานย้อมผ้ามีความเข้มข้นของสีมาก ดังนั้นจึงทำการทดลองโดยใช้คอลัมน์ที่บรรจุหญ้าแขมสูง 45 ซม.ต่อกัน 10 คอลัมน์ โดยใช้อัตราการไหล 0.6 มิลลิลิตรต่อนาที การวัดความเข้มข้นของสีจะวัดที่ความยาวคลื่น 419 นาโนเมตร และวัดความเข้มข้นของสีที่ความยาวคลื่นระหว่าง 400-700 นาโนเมตร ในหน่วย ADMI กราฟเบรคทรูของการวัดสีทั้ง 2 วิธีดังแสดงในรูปที่ 15 และ 16 ตามลำดับ




รูปที่ 15 กราฟเบรคทรูของโรงงานย้อมผ้าที่ความเข้มข้นของสีวัดที่ความยาวคลื่น 419 นาโนเมตร




รูปที่ 16 กราฟเบรคทรูของโรงงานย้อมผ้าที่ความเข้มข้นของสีวัดในหน่วย ADMI

ลักษณะสมบัติของน้ำเสียจากโรงงานย้อมผ้าก่อนและหลังการดูดซับด้วยหญ้าแขมในคอลัมน์แสดงในตารางที่ 9

**ตารางที่ 9** ลักษณะสมบัติของน้ำเสียจากโรงงานย้อมผ้าก่อนและหลังการดูดซับด้วยหญ้าแขมในคอลัมน์

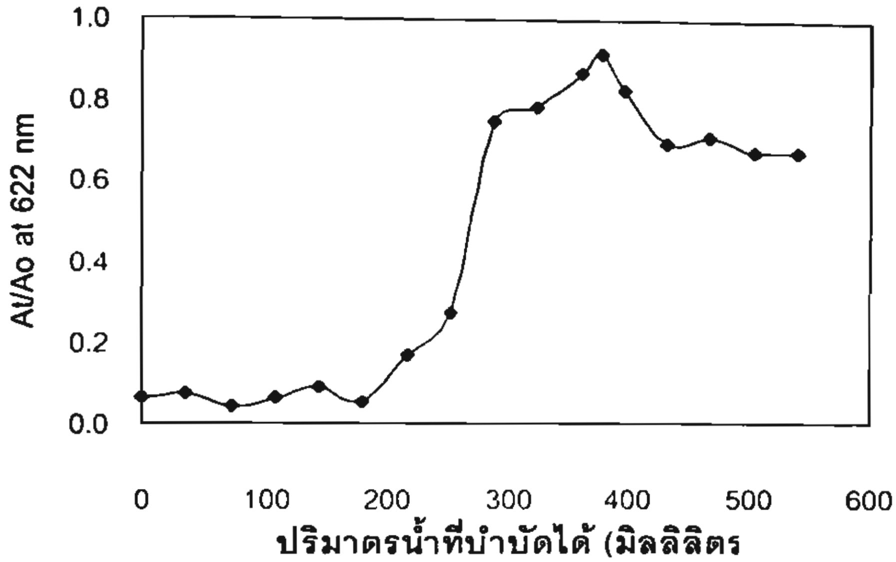
| พารามิเตอร์ | ก่อนการดูดซับ | หลังการดูดซับ | % การกำจัด | มาตรฐานน้ำทิ้ง* |
|---|---|---|---|---|
| pH | 11.80 | 3.07 | - | 5.5-9 |
| SS (mg/L) | 1,296 | 8 | 99 | 50 |
| COD (mg/L) | 38.4 | 57.6 | - | 400 |
| Color (ADMI Unit) | 1,715,000 | 191 | 99 | - |
| Absorbance (419 nm) | 567 | 0.052 | 99 | - |

* ที่มา: กระทรวงวิทยาศาสตร์ เทคโนโลยี และสิ่งแวดล้อม (2536)

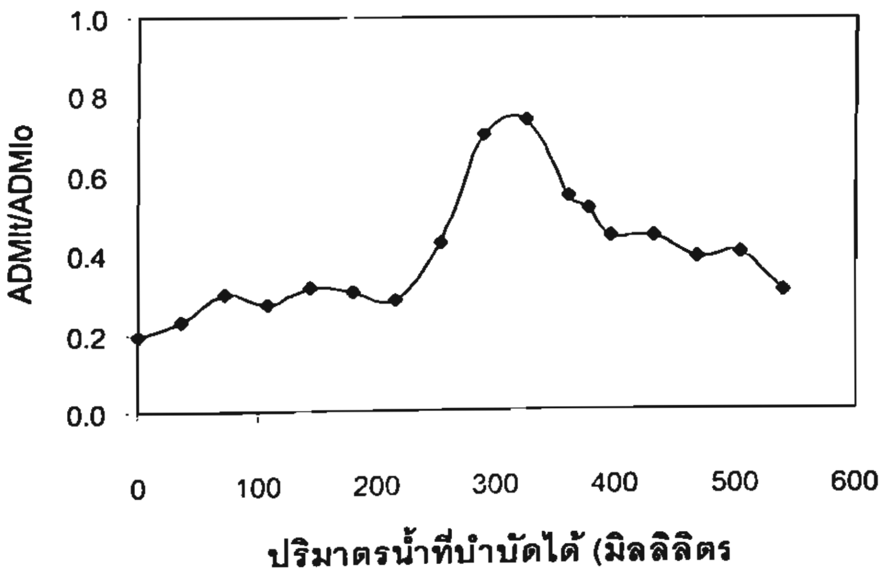
จากตารางที่ 9 จะเห็นว่าความเข้มข้นของสีที่วัดในหน่วย ADMI, ความเข้มข้นของสีที่วัดที่ความยาวคลื่น 419 นาโนเมตร และปริมาณสารแขวนลอยลดลง 99% โดยที่ความเข้มข้นของสีที่วัดในหน่วย ADMI ลดลงจาก 1,715,000 ADMI เป็น 191 ADMI ค่าการดูดกลืนแสงที่วัดที่ความยาวคลื่น 419 นาโนเมตร ลดลงจาก 567 เป็น 0.052 และปริมาณสารแขวนลอยลดลงจาก 1,296 เป็น 8 มิลลิกรัมต่อลิตร ในขณะที่ pH หลังการดูดซับจะลดลงอย่างมากจาก 11.80 เป็น 3.07 ทั้งนี้เป็นเพราะหญ้าแขมมีประจุบวกที่พื้นผิวเนื่องจากถูกล้างด้วยกรดซัลฟูริค เมื่อน้ำเสียไหลผ่านชั้นของหญ้าแขมในคอลัมน์จะชะเอากรดออกมาทำให้น้ำที่ออกจากคอลัมน์มี pH ลดลง เมื่อพิจารณาค่า COD พบว่า หลังการดูดซับมี COD เพิ่มขึ้นจาก 38.4 เป็น 57.6 มิลลิกรัมต่อลิตร การที่น้ำเสียหลังการดูดซับมีค่า COD เพิ่มขึ้นเป็นผลมาจากการที่มีสีของหญ้าแขมปนเปื้อนมากับน้ำเสียหลังออกจากคอลัมน์ จากผลการทดลองวัด COD ของหญ้าแขม พบว่าหญ้าแขมมี COD ประมาณ 240 มิลลิกรัมต่อลิตร อย่างไรก็ดี ค่า COD ที่เพิ่มขึ้นนี้ก็ยังอยู่ในมาตรฐานที่กำหนด จากค่าพารามิเตอร์ต่างๆ ที่ทำการตรวจวัดทั้งหมด พบว่า ค่า pH หลังจากดูดซับมีค่าต่ำกว่ามาตรฐานที่กระทรวงวิทยาศาสตร์ เทคโนโลยี และสิ่งแวดล้อมกำหนดไว้ ดังนั้นจึงจำเป็นต้องบำบัดก่อนปล่อยลงสู่แหล่งน้ำสาธารณะ วิธีหนึ่งที่แก้ปัญหาได้ คือ นำน้ำทิ้งที่ออกจากคอลัมน์ไปรวมกับน้ำทิ้งในส่วนอื่นๆ ที่มี pH สูง

### 2.5.2 น้ำเสียจากโรงงานพิมพ์ผ้า

กราฟเบรคทรูของน้ำเสียจากโรงงานพิมพ์ผ้าที่ทำการศึกษาที่ความสูงของหญ้าแขมในคอลัมน์ 45 เซนติเมตร และอัตราการไหลของน้ำที่เข้าสู่คอลัมน์ 0.6 มิลลิลิตรต่อนาที ซึ่งความเข้มข้นของสีวัดที่ความยาวคลื่น 622 นาโนเมตร และวัดความเข้มข้นของสีที่ความยาวคลื่นระหว่าง 400-700 นาโนเมตร ในหน่วย ADMI แสดงในรูปที่ 17 และ 18 ตามลำดับ




รูปที่ 17 กราฟเบรคทรูของโรงงานพิมพ์ผ้าที่ความเข้มข้นของสีวัดที่ความยาวคลื่น 622 นาโนเมตร




รูปที่ 18 กราฟเบรคทรูของโรงงานพิมพ์ผ้าที่ความเข้มข้นของสีวัดในหน่วย ADMI

ลักษณะสมบัติของน้ำเสียจากโรงงานพิมพ์ผ้าก่อนและหลังการดูดซับด้วยหญ้าแขมในคอลัมน์แสดงในตารางที่ 10

**ตารางที่ 10** ลักษณะสมบัติของน้ำเสียจากโรงงานพิมพ์ผ้าก่อนและหลังการดูดซับด้วยหญ้าแขมในคอลัมน์

| พารามิเตอร์ | ก่อนการดูดซับ | หลังการดูดซับ | % การกำจัด | มาตรฐานน้ำทิ้ง* |
|---|---|---|---|---|
| pH | 8.69 | 3.30 | - | 5.5-9 |
| SS (mg/L) | 84 | 74 | 12 | 50 |
| COD (mg/L) | 336 | 576 | - | 400 |
| Color (ADMI Unit) | 3800 | 840 | 78 | - |
| Absorbance (419 nm) | 0.306 | 0.067 | 78 | - |

* ที่มา: กระทรวงวิทยาศาสตร์ เทคโนโลยี และสิ่งแวดล้อม (2536)

จากตารางที่ 10 จะเห็นว่าความเข้มข้นของสีที่วัดในหน่วย ADMI, ความเข้มข้นของสีที่วัดที่ความยาวคลื่น 622 นาโนเมตรลดลง 78% และปริมาณสารแขวนลอยลดลง 12% โดยที่ความเข้มข้นของสีที่วัดในหน่วย ADMI ลดลงจาก 3,800 ADMI เป็น 840 ADMI ค่าการดูดกลืนแสงที่วัดที่ความยาวคลื่น 622 นาโนเมตรลดลงจาก 0.306 เป็น 0.067 และปริมาณสารแขวนลอยลดลงจาก 84 เป็น 74 มิลลิกรัมต่อลิตร ในขณะที่ pH หลังการดูดซับจะลดลงอย่างมากจาก 8.69 เป็น 3.30 ทั้งนี้เป็นเพราะหญ้าแขมมีประจุบวกที่พื้นผิวเนื่องจากถูกล้างด้วยกรดซัลฟูริก เมื่อน้ำเสียไหลผ่านชั้นของหญ้าแขมในคอลัมน์จะชะเอากรดออกมาทำให้น้ำที่ออกจากคอลัมน์มี pH ลดลง เมื่อพิจารณาค่า COD พบว่า หลังการดูดซับมี COD เพิ่มขึ้นจาก 336 เป็น 576 มิลลิกรัมต่อลิตร การที่น้ำเสียหลังการดูดซับมีค่า COD เพิ่มขึ้นเป็นผลมาจากการที่มีสีของหญ้าแขมปนเปื้อนมากับน้ำเสียหลังออกจากคอลัมน์ จากผลการทดลองวัด COD ของหญ้าแขม พบว่าหญ้าแขมมี COD ประมาณ 240 มิลลิกรัมต่อลิตร จากค่าพารามิเตอร์ต่างๆ ที่ทำการตรวจวัดทั้งหมด พบว่าค่า pH มีค่าต่ำกว่ามาตรฐาน ในขณะที่ค่า SS และ COD หลังจากดูดซับมีค่าเกินมาตรฐานที่กระทรวงวิทยาศาสตร์ เทคโนโลยีและสิ่งแวดล้อมกำหนดไว้ ดังนั้นจึงจำเป็นต้องบำบัดก่อนปล่อยลงสู่แหล่งน้ำสาธารณะ

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**สรุปผลการศึกษา**

1. โครงสร้างหลักของหญ้าแขมและธูปฤาษีประกอบด้วยเซลลูโลสและลิกนิน ซึ่งเป็นโครงสร้างที่มี binding site ที่เหมาะสำหรับแลกเปลี่ยนประจุกับสีรีแอคทีฟอยู่มาก
2. การปรับสภาพวัชพืชด้วยสารละลายฟอร์มัลดีไฮด์ 37% และกรดซัลฟุริก 0.2 N เป็นวิธีที่เหมาะสมที่สุดเนื่องจากให้ประสิทธิภาพในการกำจัดสีสูงสุดและยังเป็นสารป้องกันการเน่าเสีย สามารถยืดอายุวัชพืชสำหรับการนำมาประยุกต์ใช้งานในอนาคต
3. ผลจากการวิเคราะห์ประจุโดยรวมที่ผิวของวัชพืชยืนยันว่าวัชพืชที่ปรับสภาพด้วยวิธีฟอร์มัลดีไฮด์จะทำให้มีประจุบวกที่ผิวเพิ่มขึ้น ดังนั้นวัชพืชที่ปรับสภาพฟอร์มัลดีไฮด์จึงเหมาะสมสำหรับนำมาใช้ในการดูดซับสีที่มีประจุลบอย่างสีรีแอคทีฟ
4. จากการดูดซับสีที่ pH ต่างๆ พบว่าที่ pH ต่ำประสิทธิภาพการดูดซับสีโดยหญ้าแขมปรับสภาพจะสูงกว่าที่ pH สูง และจากการเปรียบเทียบประสิทธิภาพของหญ้าแขมปรับสภาพในการดูดซับสีที่มีขนาดโมเลกุลต่างกันที่ pH ต่างกัน ชี้ให้เห็นว่าการดูดซับสีที่ pH ต่ำ เกิดจากการดูดซับทางเคมีเป็นหลัก ในขณะที่ที่ pH สูง การดูดซับสีโดยการดูดซับทางเคมีเกิดขึ้นได้ยาก สีที่มีมวลโมเลกุลต่ำสามารถถูกดูดซับได้ง่ายกว่าสีที่มีมวลโมเลกุลสูงโดยการดูดซับทางกายภาพ
5. จากการใช้ผงหญ้าแขมปรับสภาพขนาดต่างกัน 2 ขนาดคือ เล็กกว่า 0.420 มิลลิเมตร และขนาดตั้งแต่ 0.420-1.190 มิลลิเมตรมาดูดซับสี พบว่าประสิทธิภาพการดูดซับสีของหญ้าแขมทั้ง 2 ขนาดไม่ต่างกัน ดังนั้นในการนำหญ้าแขมไปใช้งานจริงอาจไม่จำเป็นต้องสิ้นเปลืองพลังงานและเวลาในการบดให้หญ้าแขมมีขนาดเล็กที่สุดก่อนนำไปใช้งาน
6. จากกราฟ adsorption isotherm ที่อุณหภูมิต่างๆ แสดงให้เห็นว่าการดูดซับสีของหญ้าแขมปรับสภาพเป็นการดูดซับทางเคมีแบบดูดความร้อน
7. ผลจากการชะกากหญ้าแขมและธูปฤาษีหลังผ่านการดูดซับสีแสดงให้เห็นว่าการดูดซับสีของหญ้าแขมปรับสภาพเกิดเนื่องจากการดูดซับทางเคมีเป็นหลัก และเกิดจากการดูดซับทางกายภาพเป็นส่วนน้อย
8. ถึงแม้ว่าหญ้าแขมและธูปฤาษีปรับสภาพฟอร์มัลดีไฮด์จะมีความจุในการดูดซับสีค่อนข้างต่ำ แต่โดยทั่วไปแล้วหญ้าแขมเป็นวัสดุที่ไม่ได้นำมาใช้ประโยชน์ในประเทศไทยและใช้ค่าใช้จ่ายต่ำในการจัดหา จึงมีความเป็นไปได้ที่จะเป็นทางเลือกใหม่ในการประยุกต์ใช้วัสดุชนิดนี้เป็นวัสดุดูดซับสีสำหรับบำบัดน้ำเสียจากโรงงานในอนาคต
9. จากผลการศึกษาเบื้องต้นในการประยุกต์ใช้ในคอลัมน์ชั้นตรึงพบว่า ปริมาตรน้ำที่บำบัดได้จะเพิ่มขึ้นเมื่อขนาดของอนุภาคของหญ้าแขมลดลง ที่ความเข้มข้นของสีที่ใช้ 10 มิลลิกรัมต่อลิตร ที่ความสูงของคอลัมน์ 45 เซนติเมตร โดยมีอัตราการไหลของน้ำเข้าสู่คอลัมน์ 0.6 มิลลิลิตรต่อนาที เมื่อนำมาศึกษาในน้ำเสียจริงจากโรงงานอุตสาหกรรมฟอกย้อม พบว่าสามารถลดความ

เข้มข้นของสีลงได้ 99% ลดของแขวนลอย (SS) ได้ 99% จึงมีความเป็นไปได้ที่จะนำมาประยุกต์ใช้จริงในโรงงานฟอกย้อมขนาดเล็ก

**ข้อเสนอแนะ**

1. ควรมีการศึกษาการดูดซับสีโดยใช้ผงหญ้าแขมและธูปฤาษีปรับสภาพขนาดใหญ่กว่านี้และดูดซับสีที่อุณหภูมิของระบบสูงกว่านี้ เพื่อให้เหมาะสมสำหรับนำไปใช้งานจริง
2. ควรศึกษาการใช้หญ้าแขมและธูปฤาษีปรับสภาพฟอร์มัลดีไฮด์ดูดซับสีในถังปฏิกิริยา (reactor) แบบกะเพื่อการประยุกต์ใช้งานในอนาคต
3. ควรมีการวิเคราะห์โครงสร้างที่ซับซ้อนของกากหญ้าแขมและธูปฤาษีปรับสภาพที่ผ่านการดูดซับสีแล้วโดยใช้เครื่อง Nuclear Magnetic Resonance (NMR) mass spectrophotometer เพื่อยืนยันถึงกลไกการดูดซับที่เกิดขึ้น
4. ควรมีการศึกษาคุณภาพของน้ำทิ้งหลังผ่านการดูดซับสีโดยหญ้าแขมและธูปฤาษีแล้วกากหญ้าแขมและธูปฤาษีหลังผ่านการดูดซับสีแล้วอาจกำจัดโดยการเผาซึ่งควรมีการศึกษาต่อไป

**Out put ที่ได้จากโครงการ**

**1. ผลงานวิจัยที่ตีพิมพ์ในวารสารวิชาการระดับนานาชาติ (อาจมีการเปลี่ยนแปลงชื่อเรื่องหรือวารสาร)**

1. Decolorization of basic, direct and reactive dyes by pre-treated narrow leaved cattail (*Typha angustifolia*) I (Bioresource Technology ได้แก้ไขครั้งที่ 1 ส่งไปเรียบร้อยแล้ว **(เอกสารแนบ ในภาคผนวก G ).**
2. Textile wastewater treatment by using treated flute reed in a fix-bed column (Submitted to Water Science Technology) **(เอกสารแนบในภาคผนวก H)**
3. Decolorization of reactive dyes by pre-treated flute reed (*Phragmites karka* (Retz.) I (In preparation). Environmental. Technology หรือเทียบเท่า
4. Decolorization of reactive dyes by pre-treated flute reed (*Phragmites karka* (Retz.) II (In preparation). Environmental Technology หรือเทียบเท่า
5. Decolorization of basic, direct and reactive dyes by pre-treated narrow leaved cattail (*Typha angustifolia*) II (In preparation) คาดว่าจะส่งไปที่ Bioresource Tecnology เมื่อเรื่องที่ 1 ได้รับการตอบรับแล้ว

**2. กิจกรรมอื่นๆที่เกี่ยวข้อง ได้แก่**

**การไปเสนอผลงานวิจัยทั้งในและต่างประเทศ**

1. ไปเสนอผลงานวิชาการ (poater presentation) เรื่อง Decolorization of reactive dyes by pre-treated Flute Reed (*Phragmites karka* (Retz) ..ในการประชุม 34th Mid-Atlantic Industrial & Hazardous Waste Conference ที่ Cook College, Rutgers University, New Brunswick, NJ ณ ประเทศสหรัฐอเมริกา ระหว่างวันที่ 20-21 กันยายน 2545 (ดังรายละเอียดแนบในภาคผนวก I)

2. จะนำเสนอผลงานวิจัยนี้ใน ASIAN WATERQUAL2003- IWA Asia-Pacific Regional Conference, The Imperial Queen's Park Hotel, Bangkok, Thailand วันที่ 22 ตุลาคม 2546. 2 เรื่องคือ

   2.1 Decolorization of basic, direct and reactive dyes by pre-treated Narrow-leaved cattail (*Typha angustifolia Lin.)* (Poster presentation ) abstract code number is P-N-261

   2.2 Textile wastewater treatment by using treated Flute reed in a fixed-bed column (Oral Presentation) Code: N-N-193 Authors: K. TIPPRASERTSIN, D. INTHORN, P. THIRAVETYAN, E. KHAN. Session: F, Industrial wastewater treatment and management. Presentation Date: October 22, 2003 Time: 14.10 – 14.30 p.m. Room: Queen's Park 1, The Imperial Queen's Park Hotel, Bangkok, Thailand (เอกสารแนบในภาคผนวก H )

   หมายเหตุ เรื่องที่ได้รับคัดเลือกจะได้ลงตีพิมพ์ในวารสาร Water Science Technology

**การเชื่อมโยงทางวิชาการกับนักวิชาการอื่นๆทั้งในและต่างประเทศ**

มีการร่วมงานวิจัยกับนักวิจัยในประเทศมากขึ้น เริ่มจากการขอความอนุเคราะห์และความร่วมมือในการใช้เครื่องมือต่างๆ และสร้างเครือข่ายการวิจัยในอนาคตร่วมกัน และจากการไปนำเสนอผลงานทางวิชาการที่ประเทศสหรัฐอเมริกาทำให้ได้รู้จักนักวิจัยในสาขาที่สนใจร่วมกันในต่างประเทศมากขึ้น ซึ่งเป็นโอกาสอันดียิ่งในการการสร้างเครือข่ายการวิจัยทั้งในต่างประเทศ

# ภาคผนวก A

## TAPPI standard method

**Ash content** : To analyze ash content in wood, pulp, paper and paperboard by combustion at 525°C. A test specimen is ignited in a muffle furnace at 525°C. A separate test specimen is analyzed for the percentage moisture. The resulting weights of ash and moisture level in the sample are used to calculate the percentage ash present at 525°C on a moisture free sample basis (TAPPI standards T211).

**1% NaOH solubility** : To analyze one percent sodium hydroxide solubility of wood and pulp. Wood or pulp is extracted with hot 1% sodium hydroxide solution for hour. The loss in weight is determined and calculated as percent solubility (TAPPI standards T212).

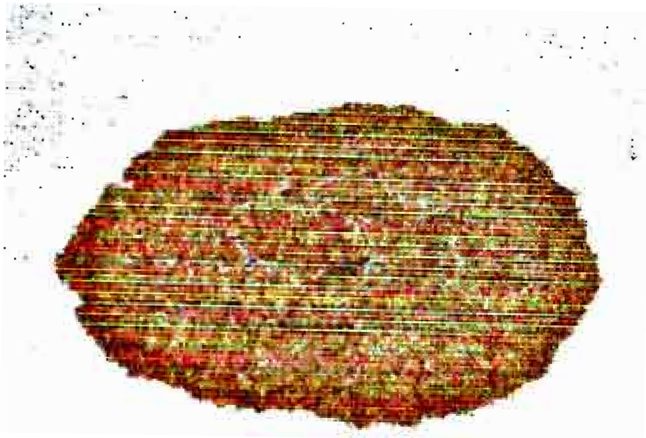
**Hot water solubility** : To analyze water solubility of wood and pulp. For the determination of hot water solubility, wood or pulp is extracted with water under reflux in a boiling water bath for 3 hours (TAPPI standards T207).

**Alcohol-benzene solubility** : To analyze solvent extractives of wood and pulp. For determination of solvent-soluble and non-volatile material, wood or pulp is extracted with ethanol-benzene or ethanol-toluene in the soxhlet extraction flask (TAPPI standards T204).

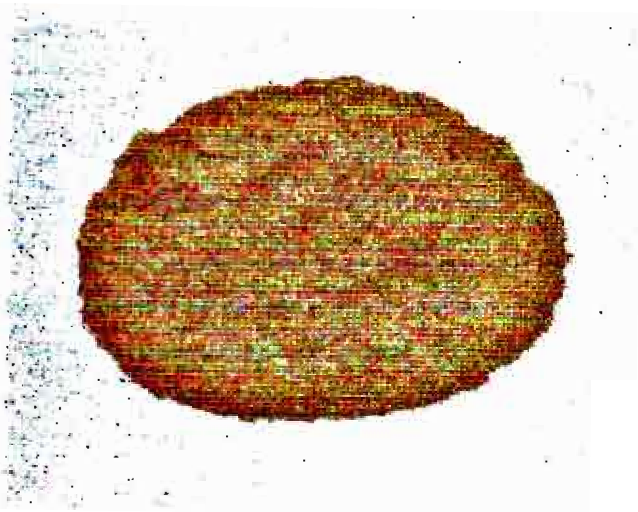
**Holocellulose** : To analyze alpha-, beta- and gamma-cellulose in pulp. Pulp is extracted consecutively with 17.5% and 9.45% sodium hydroxide solutions at 25°C. The soluble fraction, consisting of beta- and gamma-celluloses, is determined volumetrically by oxidation with potassium dichromate, and the alpha-cellulose, as an insoluble fraction, is derived by difference (TAPPI standards T203).

**Lignin** : To analyze acid-insoluble lignin in wood and pulp. The carbohydrates in wood and pulp are hydrolyzed and solubilized by sulfuric acid; the acid-insoluble lignin is filtered off, dried, and weighed (TAPPI standards T222).

# ภาคผนวก B



A. ผงหญ้าแขมหลังปรับสภาพฟอร์มัลดีไฮด์ร่วมกับกรด



B. ธูปฤาษีหลังปรับสภาพฟอร์มัลดีไฮด์ร่วมกับกรด

**รูปที่ 1** วัชพืชหลังจากนำมาตากแห้ง ปั่นให้เป็นผง ปรับสภาพฟอร์มัลดีไฮด์ร่วมกับกรดและตากแห้ง

# ภาคผนวก C

**รูปที่ 2** การกำจัดสีรีแอคทีฟ M-5B โดยใช้หญ้าแขมปรับสภาพฟอร์มัลดีไฮด์ร่วมกับกรดที่ พีเอชต่างๆ เมื่อทำการดูดซับเป็นเวลา 18 ชั่วโมง

**รูปที่ 3** การกำจัดสีเบสิก โดยใช้ฐูปฤาษีปรับสภาพฟอร์มัลดีไฮด์ร่วมกับกรด ที่ พีเอชต่างๆ เมื่อทำการดูดซับเป็นเวลา 18 ชั่วโมง

# ภาคผนวก D

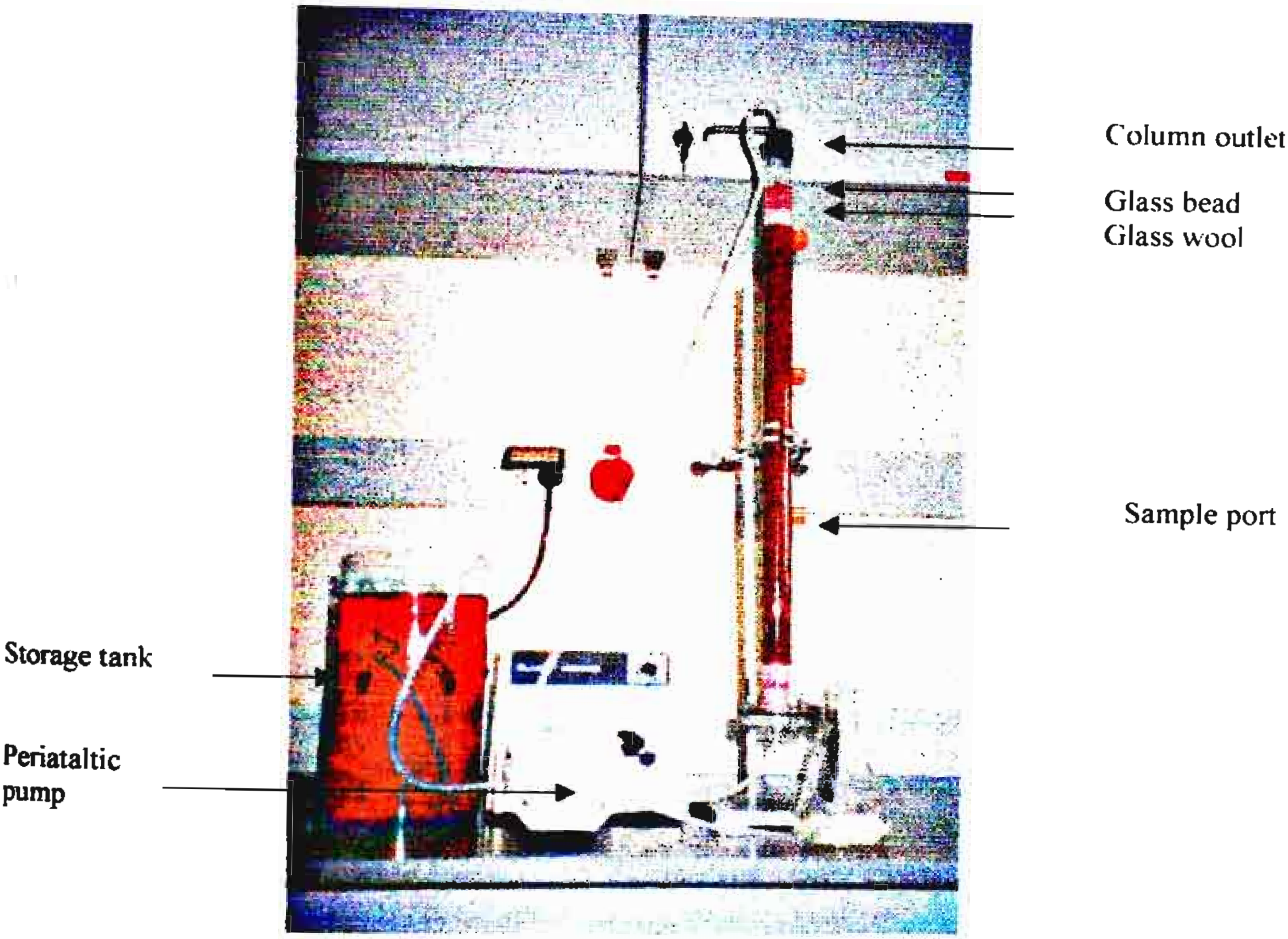
**รูปที่ 4** การกำจัดสีไดเรกต์ โดยใช้ธูปฤาษีปรับสภาพฟอร์มัลดีไฮด์ร่วมกับกรด ที่ พีเอชต่างๆ เมื่อทำการดูดซับเป็นเวลา 18 ชั่วโมง

A. Ch-บ่อรวม

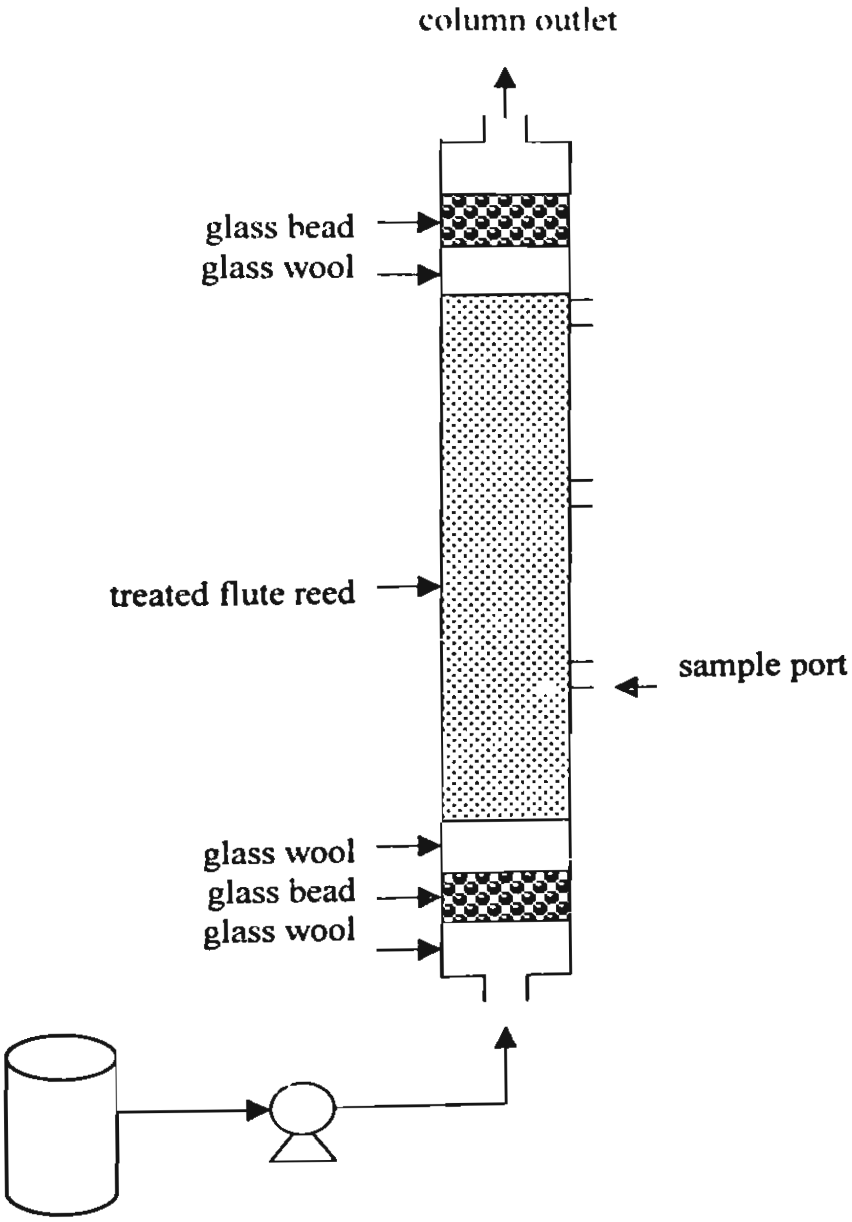
B.Ch-บ่อตกตะกอน

**รูปที่ 5** การบำบัดน้ำเสียโรงพิมพ์ผ้าด้วยหญ้าแขมปรับสภาพฟอร์มัลดีไฮด์ร่วมกับกรด เมื่อทำการดูดซับเป็นเวลา 18 ชั่วโมง

# ภาคผนวก E

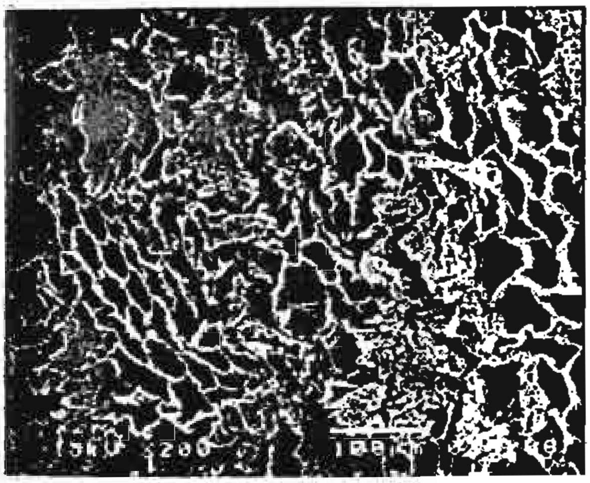



**รูปที่ 6** **A.** แสดงการใช้คอลัมน์ชั้นตรึง (fixed bed column) ในการกำจัดสีรีแอคทีฟโดยใช้หญ้าแขม ปรับสภาพฟอร์มัลดีไฮด์ร่วมกับกรด




**รูปที่ 6 B** แสดง sheme diagram ของคอลัมน์ชั้นตรึง

## ภาคผนวก F



A. ภาพถ่ายตัดขวาง (cross-section)

ที่กำลังขยาย 1 x 200

B. ภาพถ่ายตัดตามยาว (long-section)

ที่กำลังขยาย 1x1,500

**รูปที่ 7** SEM microphotographs ของหญ้าแขมปรับสภาพฟอร์มัลดีไฮด์ร่วมกับกรด

# ภาคผนวก G

**ผลงานวิจัยที่กำลังจะตีพิมพ์**

**Decolorization of basic, direct and reactive dyes by pre-treated narrow leaved cattail (*Typha angustifolia*) I (Bioresource Technology ได้แก้ไขครั้งที่ 1 ส่งไปเรียบร้อยแล้ว (เอกสารแนบ ในภาคผนวก G ).**

# BIORESOURCE TECHNOLOGY

* bioenergy * biowastes * conversion technologies * biotransformations * production technologies * agriculture * food

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Jan.. 8, 2003

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Bangkok 10400, Thailand

Dear Dr. Inthorn,

I am writing to inform you that your manuscript entitled "Decolorization of basic, direct and reactive dyes by pre-treated narrow-leaved cattail (*Typha angustifolia* Linn.)" which was assigned reference number **BRT 02-24** has received a mixed response by the reviewers with all reviewers suggesting revisions. Therefore, the manuscript must be revised and submitted for a second review. Please use this **BRT** number for all correspondence regarding this manuscript. I have enclosed the reviewer comments. The primary concern expressed by all reviewers was the need to extensively revise the manuscript, particularly of the results section. The authors must carefully rewrite and add statements that succinctly focus on the issues raised by all reviewers. Other concerns included the need for the authors to reformat the references (remove reference numbers and alphabetize by author) to follow the appropriate format for Bioresource Technology. In addition, there was considerable concern regarding the need for variation estimates of the data and presentation of standard errors and standard error bars in the respective tables and figures. To address this concern the authors must conduct and add a statistical analyses methodology subsection (computer package used for statistical analyses, analysis of variance, probability values used to establish statistically significant differences and experimental design and number of replicates) in the materials and methods section. I concur with all of these concerns. If you choose to revise the manuscript you must return **all original materials**, three copies of the revised version and three copies of the itemized list stating your disposition to all revisions suggested by the reviewers (each point, as identified by the respective reviewer) to me at the address given above. I will then submit your manuscript for a second review. If I have not received your manuscript within **six months** of the date on this letter I will consider it withdrawn. Thank you for submitting your work to this journal.

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# Decolorization of basic, direct and reactive dyes by pre-treated narrow-leaved cattail (*Typha angustifolia* Linn.)

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**Abstract**

The efficiency of basic, direct and reactive dye removal from water by narrow-leaved cattail (NLC) powder treated with distilled water (DW-NLC), 37% formaldehyde + 0.2 N sulfuric acid (FH-NLC), or 0.1 N sodium hydroxide (NaOH-NLC) at various pH levels (3, 5, 7 and 9) was tested. Desorption of the adsorbed dyes was also investigated. The type of NLC treatment and pH of the dye solution had little effect on removal of basic dyes, and efficiencies ranged from 97% to 99% over the range of pH used. Over a wide range of pH, all types of treated cattail powder had negative charges and probably attracted the basic dyes that had positive charges. Efficiency of removal by the three NLC treatments ranged from 37% to 42% for direct dyes and from 22% to 54% for direct dyes at pH 7. The pH of the dye solution had strong effects on the efficiency of removal in direct and reactive dyes. Dye removal was highest at pH 3, with 99% for a direct dye (Sirius Red Violet RL) and 96% for a reactive dye (Basilen Red M-5B). There was mutual attraction between negatively charged direct dye molecules and positively charged molecules on the surface of the FH-treated cattail. In tests of desorption of dyes from cattail in distilled water, the desorption percentage for FH-NLC after adsorbing basic, direct and reactive dyes was 6%, 10% and 35%, respectively, which indicated a chemisorption mechanism for basic and direct dyes and some physisorption for reactive dyes.

*Keywords* : Narrow-leaved cattail; Adsorption; Desorption; Dye removal

## 1. Introduction

The textile industry in Thailand now consists mostly of large factories which have expanded swiftly during the last decade. These factories have created several environmental problems. They use a high volume of water in each step of process; cleaning, scouring, bleaching and dyeing (Grau, 1991). Textile factories use various types of dye depending on production orders. Thus, the characteristics of textile wastewater are different for each factory. This wastewater contains a variety of organic compounds and toxic substances, which are harmful to fishes and other aquatic organisms (Ramakrishna and Viraraghavan, 1997). Moreover, some are even considered to be carcinogenic (Digiano et al., 1992). Dying wastewater discharged to natural receiving waters may make them unacceptable for public consumption. Dye can interfere with photosynthesis of aquatic plants and phytoplankton, which are major sources of food in ecosystems, by reflecting or absorbing sunlight. Thus, it is desirable to eliminate dyes from textile wastewater.

There are many color removal methods for textile wastewater including membrane filtration (Buckley, 1992), ozone treatment (Churchley, 1994), chemical coagulation (Kuo, 1992), and ion exchange (Koprivanac et al., 1993). Although these methods have high efficiencies, most are difficult to operate and have high costs. Thus, they are not considered suitable for Thailand's economy in its present situation. Methods of dye removal by low-cost adsorbents are of great interest; these may include rice straw (Meyer et al., 1992), silica (Ahmed and Kam, 1994), bagasse (McKay et al., 1987), and corncob (El-Geundi, 1991). Most of these adsorbents have high efficiency. Furthermore, weed biomass is a natural material of interest because it has low cost, is easily available, and its major component is cellulose which is known to adsorb dye effectively (Techasoponmanee, 1987).

Narrow-leaved cattail (NLC), or *Typha angustifolia* Linn., is an abundant weed in agricultural areas throughout the lowlands. In this study, it was tested as an adsorbent for removal of basic, direct and reactive dyes at various pH levels. In addition, we also studied the desorption of dyes from treated NLC.

## 2. Material and methods

### *2.1 Dyes*

Two basic, two direct, and three reactive dyes were used in this study. The descriptions (name, color, and molecular weight) of the dyes and their chemical structures are shown in Fig. 1.

### *2.2 Treatment of cattail leaves*

Narrow-leaved cattail (NLC) was collected from Mahidol University, Salaya campus, Nakhon Nayok Province, Thailand and sliced into pieces smaller than 1 cm. The sliced material was dried by exposure to the sunlight for 3 days and then at 80°C for 12 hours in a hot air oven (Memmert U30). The dried material was milled into a powder (Disk mill, FFC-15) and was passed through a 0.42 mm opening size sieve (U.S. standard sieve No 40). The sieved powder was then divided up and given one of three different treatments: distilled water (DW-NLC); 37% formaldehyde + 0.2 N sulfuric acid at 1:20 ratio (FH-NLC); and 0.1 N sodium hydroxide (NaOH-NLC). After that, the samples were filtered and rinsed with distilled water until pH remained constant at 6–8. The treated material was dried again at 80°C for 12 hours, sealed in plastic bags, and stored in a desiccator (Sanplatec Corp. D-box).

### *2.3 Preparation of dye solutions and standard curve*

Three groups of dyes, basic dyes, direct dyes and reactive dyes, were dried at 103–105°C for 3 hours before being dissolved in distilled water. For each dye type, a solution of 30 mg/l was scanned in the range of visible wavelengths (400–800 nm) using a spectrophotometer (UV-160, Shimadzu). The wavelength that provided maximum absorbance (optimum wavelength) for each dye solution was obtained from the scans. The

30-mg/l dye solutions were then diluted to 25, 20, 15, 10 and 5 mg/l with distilled water and were scanned at the optimum wavelengths. The absorbances at the optimum wavelength were plotted against corresponding concentrations of each dye to generate a standard curve for use in the analysis of dye.

*2.4 Decolorization of basic, direct, and reactive dye solutions*

The three types of treated NLC were each used to adsorb basic, direct, and reactive dyes. For each type of treated NLC and each dye tested, four flasks were used: three contained treated NLC and 150 ml of dye solution at 30mg/l of dye, and the fourth was a control which contained only dye solution. The pH of the NLC-containing flasks was adjusted to the pH of the control flask. All flasks were shaken at 140 rpm on a shaker at room temperature. Six milliliters of dye solution were collected from each flask for assay with a 10-ml syringe at 0, 1, 2, 3, and 4 hours for basic dyes and 0, 2, 4, 6, 8, 10 and 12 hours for direct and reactive dyes. All samples were centrifuged at 5,000 rpm for 10 minutes (D-7200, Hettich Universal II) and their absorbances were measured.

The experimental protocol was as follows. Three dyes of different classes, Astrazon Brilliant Red 4G (basic), Sirius Red Violet RL (direct), and Basilen Red M5B (reactive), were each tested with the three types of treated narrow-leaved cattail. The cattail treatment, which had the highest removal efficiency, was selected for testing with other basic, direct and reactive dyes. Then, the dye with the highest removal efficiency within each class of dyes was selected for testing of the efficiency of dye removal in relation to pH. The pH of the test solutions was adjusted to 3, 5, 7, and 9 (Index ID1001) with usually less than 1 ml of 0.2 N $H_2SO_4$ or less than 1 ml of 0.1 N NaOH. Sampling times were 0, 3, and 18 hours for basic dyes, 0, 18, and 21 hours for direct dye, and 0, 18, 42 and 48 hours for reactive dye.

*2.5 Desorption of treated narrow-leaved cattail*

Treated cattail powder that had adsorbed basic, direct, and reactive dyes was used for experiments on color desorption. The dyed cattail powder was shaken with distilled water at a ratio of 1 g per 50 ml water, and filtered and transferred into 50 ml of new distilled water every hour until the samples showed no further dye leaching. All flasks were shaken at 140 rpm at room temperature for 1 hour. Afterwards, all flasks were heated in a water bath (Type W350: Memmert Co. Ltd.) to 80°C every hour until samples showed no further leaching. Samples were collected from the flasks and centrifuged for measurement of absorbance. All experiments had performed in 3 replications.

*2.6 Data analyses*

Using the Microsoft Excel, three statistical analyses were performed on the adsorption data: average, standard deviation, and student *t*-test. Average and standard deviation were used to represent the data resulting from triplication. Student *t*-test was applied to determine whether the differences in dye removal provided by different conditions (type of NLC treatment, adsorption time, and pH) are statistically significant.

**3. Results and discussion**

*3.1 Decolorization of basic dye solutions*

All three treatments removed nearly all the dye after only 1 hour (Fig.2). The sampling time did not significantly affect the dye removal using a significance level criterion of 0.05 ($p > 0.05$) indicating that the equilibrium was reached at $\leq$ 1 hour. The FH-NLC provided the highest average efficiency of approximately 99% whereas DW-NLC and NaOH-NLC removed about 98% of the dye. This is likely because the positive charges on the basic dye molecules were attracted to the negative charges on the treated NLC surfaces. The results were very precise that the standard deviation of the removal was less than 0.4% for all me and treatments, and was not visible when plotting it as an error bar in Fig. 2. Although quantitatively the three types of NLC treatment had a very slight effect on Astrazon Brilliant Red 4G dye removal, the removal given by FH-NLC was statistically higher than those provided by the other two treatments ($p < 0.02$). FH-NLC was therefore selected for the next experiments on Astrazon Red 6B.

As shown in Fig. 3, FH-NLC adsorbed Astrazon Red 6B dye and Astrazon Brilliant Red 4G dye with statistically the same average efficiency of about 99% ($p > 0.20$). Similar to Fig.2, error bars cannot be clearly seen because very low standard deviation (< 0.6%). Astrazon Red 6B dye was selected for examining the effect of pH on basic dye removal because it has a more complex structure than Astrazon Brilliant Red 4G dye and was of greater interest for that reason.

FH-NLC was tested for its ability to adsorb Astrazon Red 6B dye at various pH levels (Fig. 4). Dye removal was nearly complete at all pH levels. There was no statistical difference between the two adsorption times ($t$-test, $p > 0.16$) and among pH 3, 5, and 7 ($p > 0.05$ in 4 out of 6 comparisons) on the dye removal. At pH 9, the removal efficiencies were significantly lower than those at the other three pHs ($p < 0.02$). Therefore, pH between 3 and 7 had an insignificant effect on Astrazon Red 6B dye removal. This may be because basic dyes have positive charges over a wide range of pH. These results agree with previous studies by Low et al. (1994 and 1995). They reported that sorption of methylene blue by water hyacinth roots was unaffected by pH in the range of 5–12 (Low et al., 1995), and that within the pH range of 4–12 there was very little variation in the uptake of methylene blue and basic blue dyes by *Hydrilla verticilata* (Low et al., 1994).

*3.2 Decolorization of direct dye solutions*

Only at10 and 12 hours that the Sirius Red Violet RL removal efficiencies were not significantly different ($p > 0.20$). FH-NLC had the highest average efficiency of 42% on adsorbing the dye, while DW-NLC and NaOH-NLC removed 41% and 37%, respectively, at 12 hours (Fig. 5). The negative charges on Sirius Red Violet RL dye molecules were attracted to the positive charges on the surface of FH-NLC. This result is similar to findings of other researchers (McKay et al., 1986, Gang and Xiangjing, 1997). Although the differences in dye removal provided by FH-NLC and DW-NLC at 12 hours were not statistically significant ($p = 0.11$), FH-NLC was selected for further experiments on direct dyes because of its highest average adsorption efficiency.

FH-NLC was tested against Sirius Red F3B and the results were compared with Sirius Red Violet RL removal (Fig. 6). FH-NLC adsorbed 42% of Sirius Red Violet RL, but only 1% of Sirius Red F3B after the equilibrium was attained at 10 hours. Hence, Sirius Red Violet RL dye was selected for further experimentation with pH variation. Sirius Red Violet RL was adsorbed more effectively than Sirius Red F3B probably because it has a less complex molecular structure as well as much lower molecular weight.

The adsorption of Sirius Red Violet RL dye by FH-NLC was strongly affected by pH (Fig. 7). Adsorption averaged highest (98%) at pH 3, and declined sharply between pH 3 and 5 and eventually to about 5% at pH 9. The percent removal of dye did not significantly change between and 18 and 21 hours ($p > 0.05$). Needless to analyze the data statistically, it is evident that pH > 3, especially between 5 and 9, was not suitable for the adsorption of Sirius Red Violet RL. The negative charges on the Sirius Red Violet RL dye molecules were attracted by the positive charge on surface of FH-NLC, which was increased by $H^+$ ions in the dye solution. These results suggest that direct dye adsorption might be via a chemisorption mechanism, similar to the results of other researchers (Lee et al., 1996, Ramakrishna and Viraraghavan, 1997). Lee et al. (1996) indicated that anionic dye (Acid Blue 29) removal by chrome sludge decreased from nearly 90% at pH 2 to about 20% at pH 10. Ramakrishna and Viraraghavan (1997) reported maximum removal of the anionic dye Acid Blue 29 with bentonite clay, peat, and steel plant slag at pH 2.

*3.3 Decolorization of reactive dye solutions*

At 8 and 10 hours, differences in Basilen Red M5B removal efficiencies were insignificant ($p > 0.18$); highest average adsorption efficiency of the dye of approximately 54% was achieved by FH-NLC while removal by DW-NLC and NaOH-NLC averaged only around 24% and 22%, respectively (Fig. 8). The negative charges on Basilen Red M5B dye molecules were attracted to the positive charge on surface of FH-NLC.

FH-NLC was tested for its ability to adsorb the two other reactive dyes, Basilen Red E-B and Procion Red H-E7B. As presented in Fig. 9, the average removal efficiency at equilibrium (8 or10 hours) for these dyes was 51% and 41%, respectively, statistically less than 54% for Basilen Red M5B dye ($p < 0.003$). Thus, Basilen Red M5B dye was selected for tests on the effect of pH on removal of reactive dyes. These results confirm that dyes with less complex molecular structures and lower molecular weights can be removed more effectively since the complexity and molecular weight of the dyes tested is in the following order: Basilen Red M5B < Basilen Red EB < Procion Red HE7B.

At pH 3, about 96% of Basilen Red M5B was adsorbed by FH-NLC, and the removal efficiency declined dramatically with increasing pH (Fig. 10). This observation is similar to the adsorption of the direct dye, Sirius Red Violet RL (Fig. 7). The negative charges on Basilen Red M5B dye molecules were attracted to the positive charge on the surface of FH-NLC, which was increased by $H^+$ ions in the dye solution. These results indicate reactive dye adsorption by a chemisorption mechanism. These results also agree with those reported by

Lee et al. (1996) that anionic dye (Reactive Blue 2) removal by chrome sludge decreased from 100% at pH 2 to below 70% at pH 10.

*3.4 Desorption of treated narrow-leaved cattail*

The desorption of color from FN-NLC samples adsorbed with one basic dye (Astrazon Red 6B), one direct dye (Sirius Red Violet RL), and one reactive dye (Basilen Red M-5B) was tested in distilled water at ambient temperature, and after the temperature was raised to 80°C. The results (Table 1) indicate that for the basic and direct dyes, there was little desorption and no effect of increasing temperature. Desorption of the direct dye Basilen Red M-5B increased from 8.65% at normal temperature to 26.17% at 80°C, for a total desorption of 34.82%. This effect indicates that dye absorption was partly by a physical mechanism.

**4. Conclusions**

The type of NLC treatment and the pH of the solution had a slight effect on the removal of basic dyes. All three treated NLCs removed a basic dye efficiently at the unadjusted pH of the dye solution while. Therefore, it is possible for NLC treated only with tap water to adsorb basic dye from wastewater. Direct and reactive dyes, however, were removed more effectively from solution by the FH-NLC treatment at low pH ($\leq$ 3). Furthermore, the desorption of basic and direct dyes demonstrated the existence of a chemisorption mechanism, while the desorption of reactive dye demonstrated the partial presence of a physisorption mechanism. Increases in direct and reactive dye removal efficiencies observed with lower molecular weight and less complex structure dyes indicating physisorption as a probable main removal mechanism.

For all seven dyes tested, FH-NLC provided the highest removal efficiency. In addition, and the FH treatment also preserves and protects NLC from fermentation and decomposition (Low et al., 1994). Therefore, it is suggested that FH-NLC should be used for adsorbing basic dyes at any pH, and for absorbing direct and reactive dyes at low pH. A future study on the adsorption capacity of NLC, the detailed adsorption mechanism, and the effect of varying temperature on the mechanism should be conducted.

**Acknowledgments**

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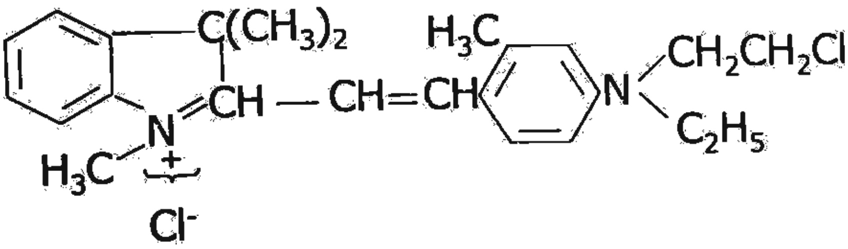

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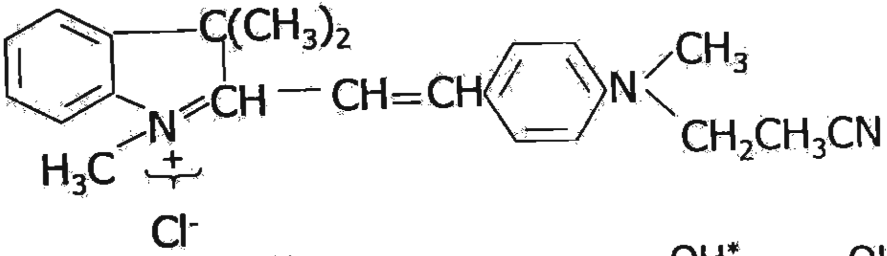

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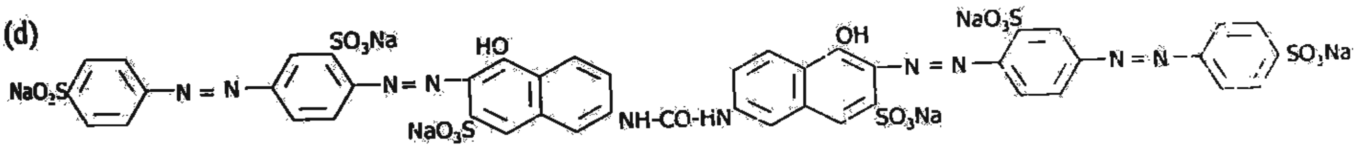

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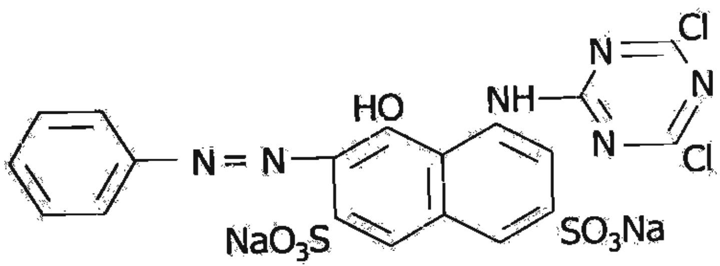

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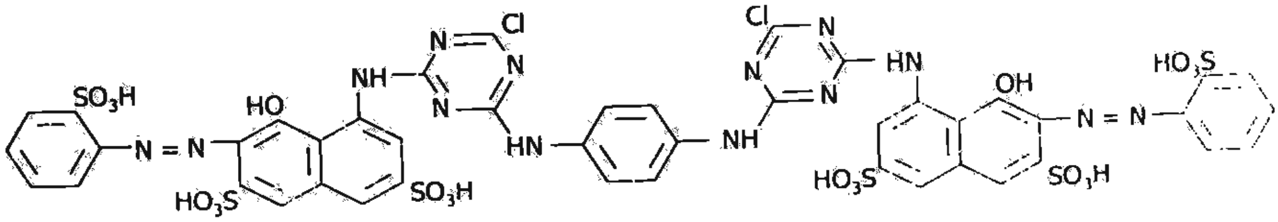

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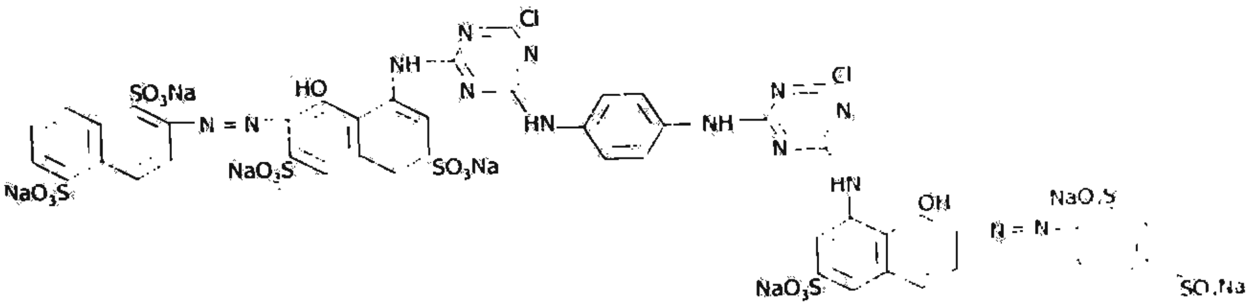
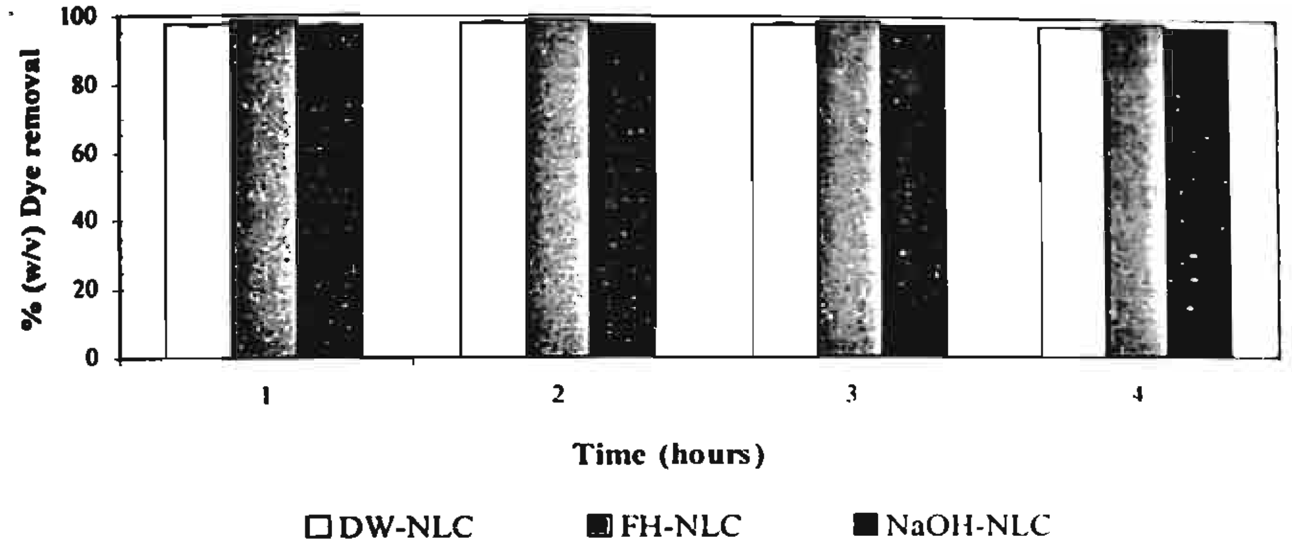
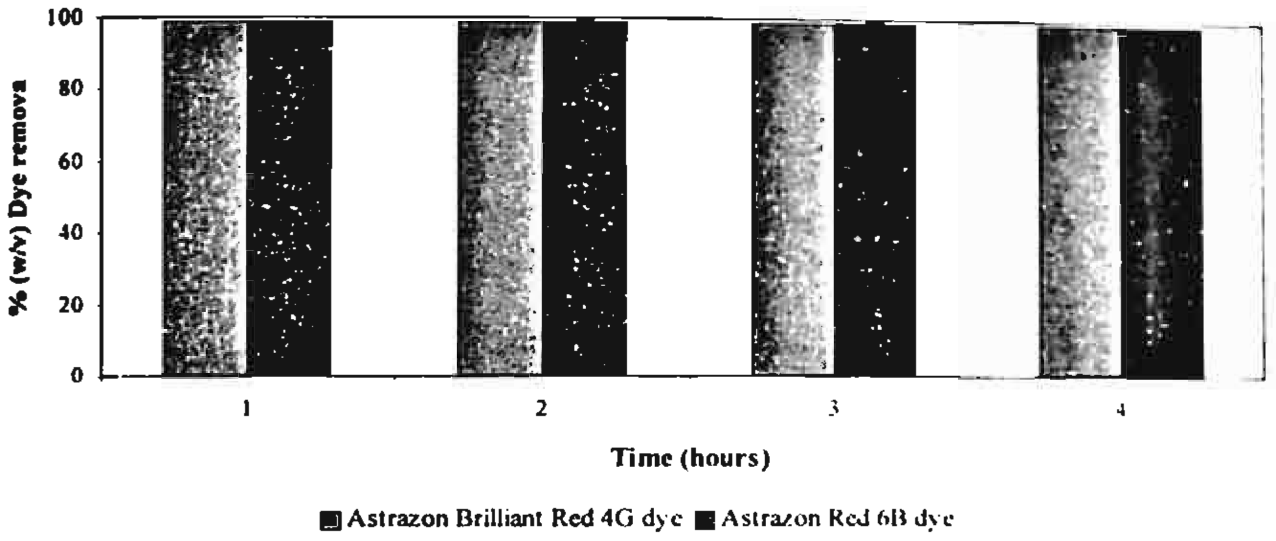
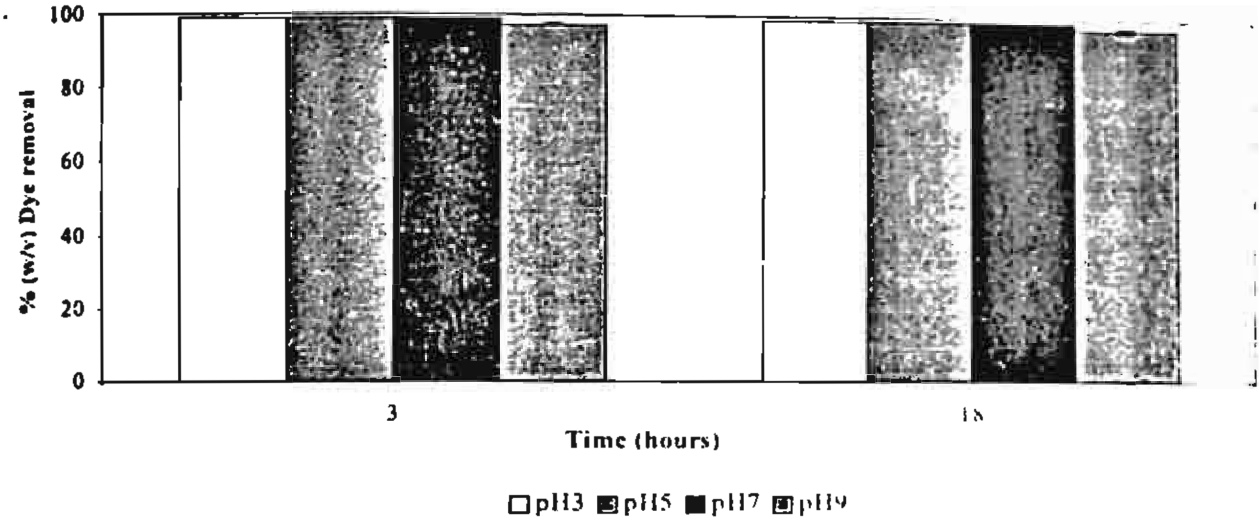


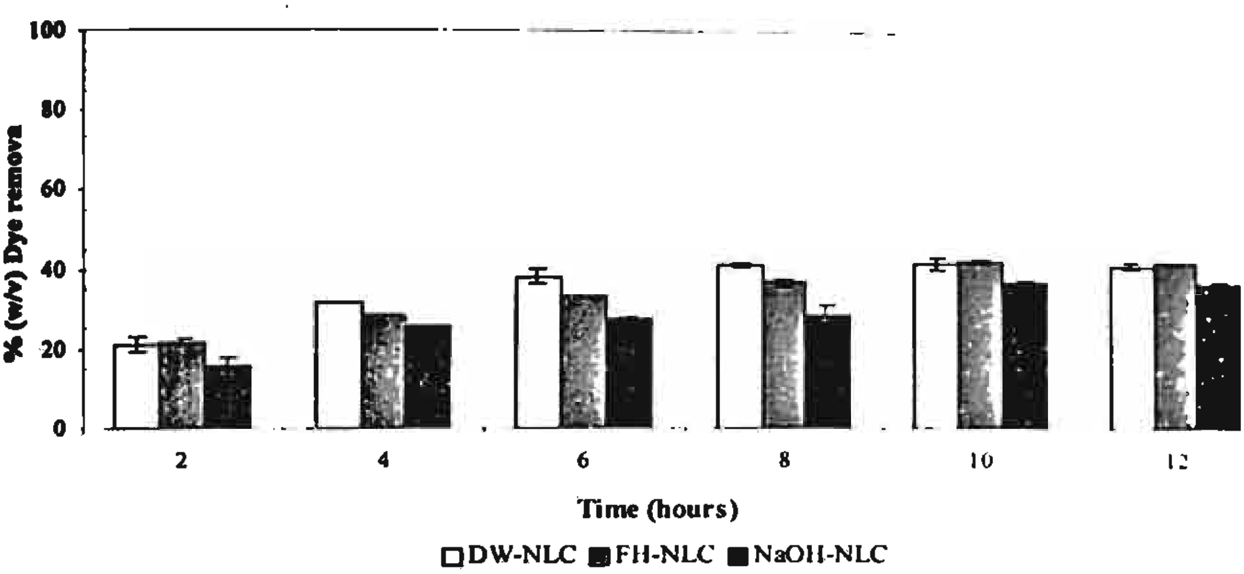

% (w/v) Dye removal
100
80
60
40
20
0
1
2
3
4
Time (hours)
DW-NLC
FH-NLC
NaOH-NLC



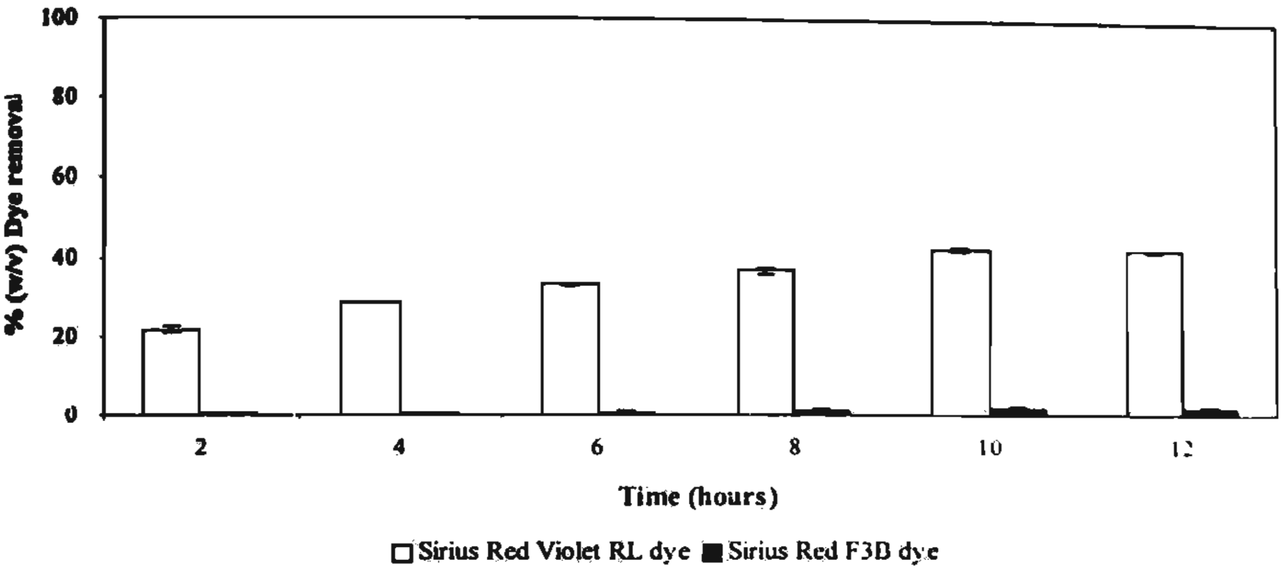
100
80
60
40
20
0
% (w/v) Dye remova
1
2
3
4
Time (hours)
Astrazon Brilliant Red 4G dye
Astrazon Red 6B dye

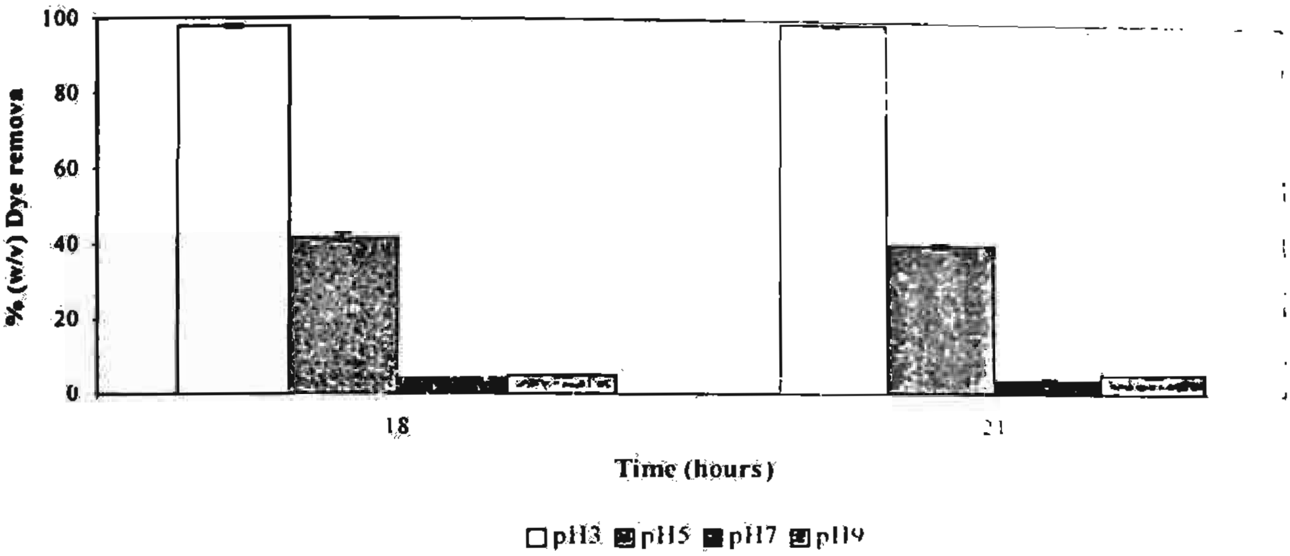


100
80
60
40
20
0
% (w/v) Dye removal
3
18
Time (hours)
pH3 pH5 pH7 pH9



100
80
60
40
20
0
% (w/v) Dye remova
2
4
6
8
10
12
Time (hours)
DW-NLC FH-NLC NaOH-NLC


100
80
60
40
20
0
% (w/v) Dye removal
2
4
6
8
10
12
Time (hours)
Sirius Red Violet RL dye
Sirius Red F3B dye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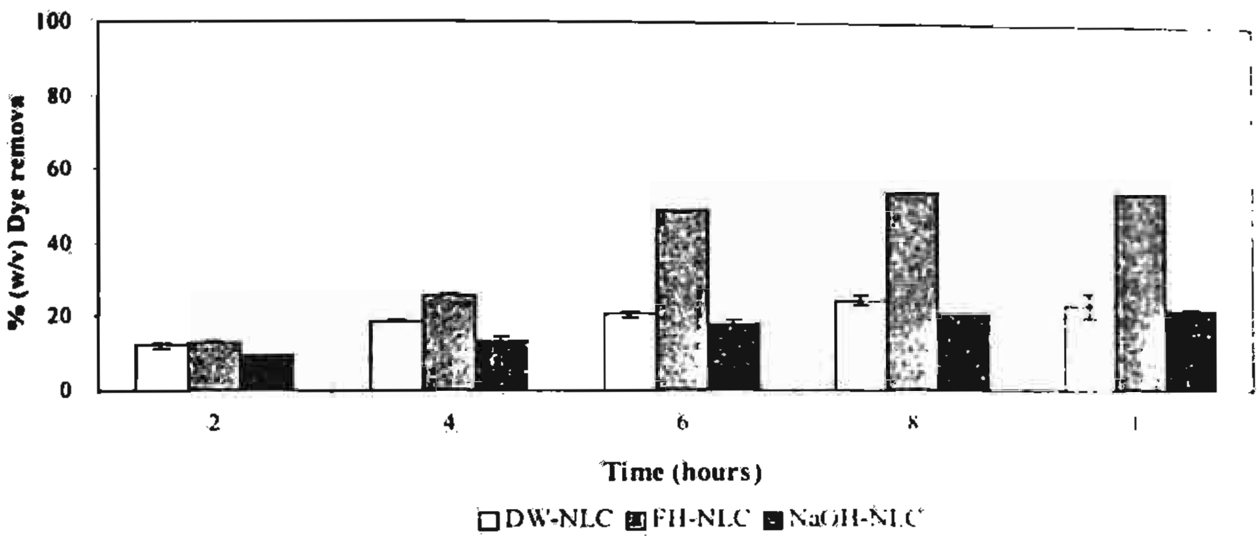
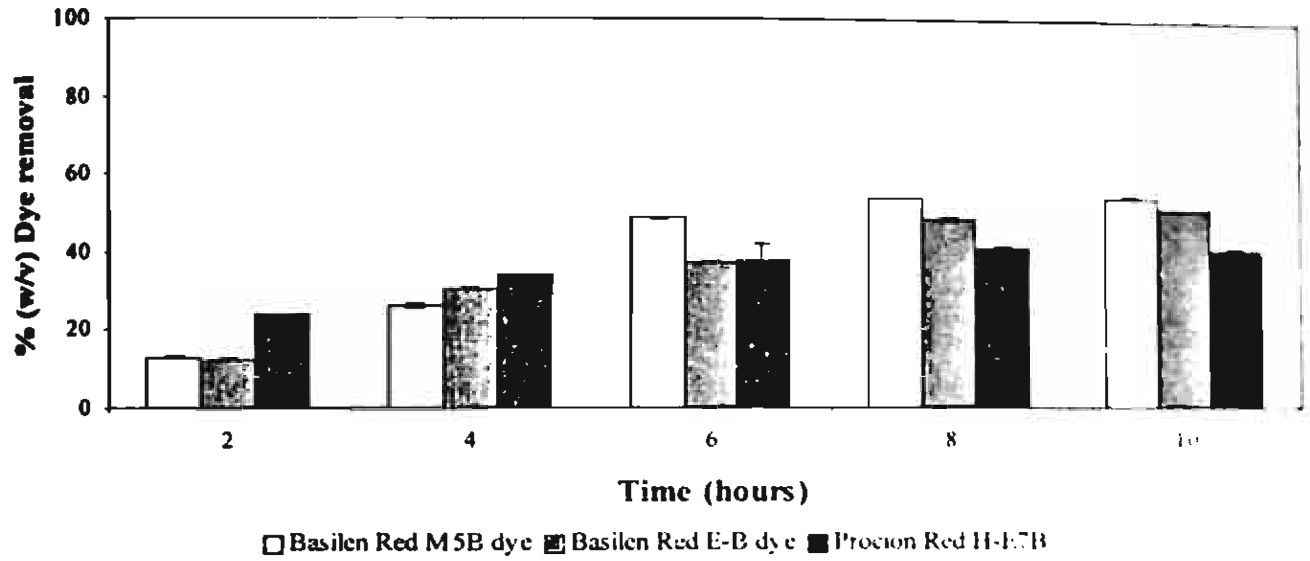
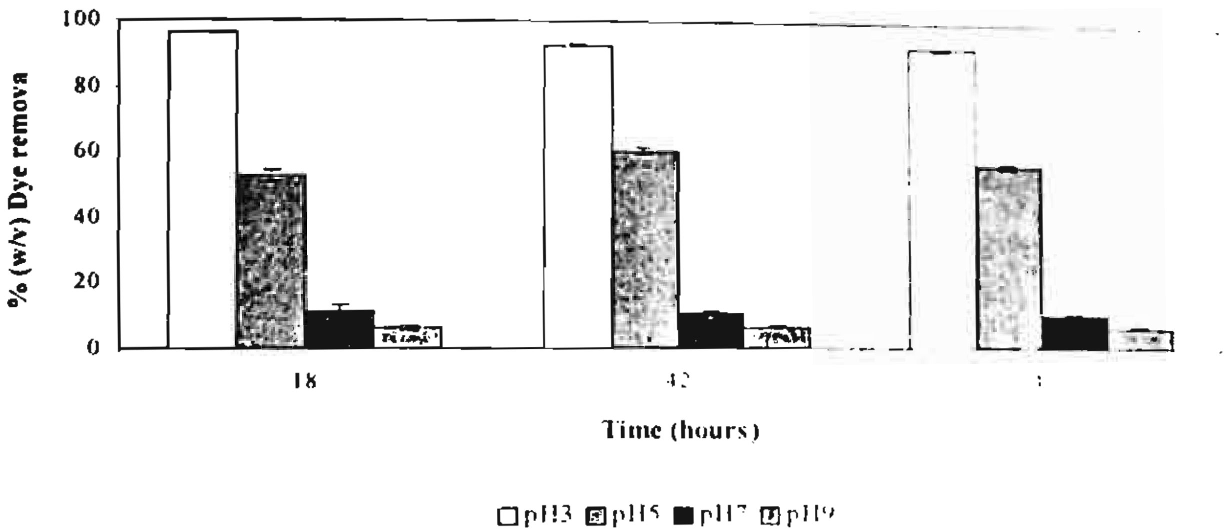
% (w/v) Dye remova
18
21
Time (hours)
pH3 pH5 pH7 pH9



100
80
60
40
20
0
% (w/v) Dye remova
2
4
6
8
1
Time (hours)
DW-NLC
FH-NLC
NaOH-NLC



100
80
60
40
20
0
% (w/v) Dye removal
2
4
6
8
Time (hours)
Basilen Red M 5B dye
Basilen Red E-B dye



100
80
60
40
20
0
% (w/v) Dye remova
18
42
Time (hours)

**Table 1**
**The desorption of treated narrow-leaved cattail containing adsorbed basic, direct, and reactive dye**

| Type of dye | Type of solution | Desorption percentage (%) |
|---|---|---|
| Astrazon Red 6B | Distilled water | 2.73 ± 0.00 |
| | Distilled water at 80°C | 3.39 ± 0.00 |
| | Total | 6.12 ± 0.00 |
| Sirius Red Violet RL | Distilled water | 6.23 ± 0.00 |
| | Distilled water at 80°C | 3.96 ± 0.00 |
| | Total | 10.19 ± 0.00 |
| Basilen Red M-5B | Distilled water | 8.65 ± 0.00 |
| | Distilled water at 80°C | 26.17 ± 0.00 |
| | Total | 34.82 ± 0.00 |

**List of figures**

# ภาคผนวก H

## ผลงานวิจัยที่กำลังจะตีพิมพ์

1. Textile wastewater treatment by using treated flute reed in a fix-bed column (Submitted to Water Science Technology (Oral presentation) )
2. Poster presentation

(เอกสารแนบในภาคผนวก H)

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# TEXTILE WASTEWATER TREATMENT BY USING TREATED FLUTE REED IN A FIXED BED COLUMN

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## ABSTRACT

This study investigated the ability of treated flute reed to adsorb synthetic reactive dye and textile wastewater in a fixed bed column with a diameter of 2.5 cm and length of 60 cm. The effects of particle size, initial reactive dye concentration, bed depth and flow rate were also investigated. The results showed that the volume treated increased with decreasing particle size, influent reactive dye concentration and flow rate, and with increasing bed depth. A BDST model was used to analyze the experimental data and evaluate the bed performance. From this model, the critical bed depths were 3.71, 5.72 and 8.73 cm at flow rates of 0.6, 1.2 and 1.8 ml/min, respectively. The capacity of column adsorption decreased from 0.98 to 0.44 mg/g with a threefold increase in the flow rate. As a bed depth of 45 cm and a flow rate of 0.6 ml/min resulted in a maximum adsorption capacity, this condition was selected for dyeing and printing textile wastewater treatment. In dyeing textile wastewater, treated flute reed could reduce SS from 1,296 to 8 mg/L, color from 1,715,000 to 191 ADMI, but the COD increased from 2,688 to 4,032 mg/L. The effluent pH decreased from 11.80 to 3.07. Similar results were obtained with the printing textile wastewater; SS and color decreased from 84 to 74 mg/L and from 3,800 to 840 ADMI, respectively, whereas the COD increased from 1,680 to 2,880 mg/L. The effluent pH decreased from 8.69 to 3.30. The COD increase may have resulted from the leaching of organic matter from the treated flute reed. As a result, the pH values of dyeing and printing textile wastewater after treatment were lower than the Industrial Effluent Standards so treatment would be necessary before discharge to receiving waters.

## KEYWORDS

**Adsorption; BDST model; breakthrough curve; fixed bed; treated flute reed**

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## NOMENCLATURE

| | | |
|---|---|---|
| $C_o$ | = | initial concentration of dye (mg/L) |
| $C_t$ | = | effluent concentration of dye at time t (mg/L) |
| $V_B$ | = | volume treated at breakpoint (ml) |
| $T_B$ | = | time required for the effluent liquid to reach the breakthrough concentration or service time (hours) |
| $V_S$ | = | volume treated at exhaustion point (ml) |
| $T_S$ | = | time to complete saturation for the entire bed (hours) |
| EBCT | = | empty bed contact time (min) |
| $L_m$ | = | the length of the mass transfer zone (cm) |
| W | = | weight of treated flute reed in the column (g) |
| $v$ | = | linear velocity through the bed (cm/min) |
| $D_o$ | = | minimum bed depth sufficient to prevent the effluent solute concentration to exceed the desired breakthrough concentration at zero time (cm) |
| $N_o$ | = | adsorption capacity (mg/cm$^3$) |
| $K$ | = | rate constant in BDST model (l/mg.hr) |

## INTRODUCTION

The textile industry produces large volumes of wastewater, especially from dyeing and finishing processes. The wastewater from textile factories differs in quality and quantity depending on the type of textile industry, dyestuff and finishing method (Choi and Cho, 1996). The textile wastewater generally contains biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), heat, pH, color and other soluble substances (Kuo, 1992). However, the major treatment problem of textile wastewater is color.

There are several methods used to decolorize textile wastewater such as ion exchange (Lin and Chen, 1997), membrane filtration (Ciardelli *et al*, 2000), coagulation (Chu, 2001), ozonation (Radetski *et al*, 2002) and activated carbon adsorption (Walker and Weatherley, 1999). These methods are costly and require skillful operation and high maintenance. Nowadays, adsorption processes using agricultural residues are very attractive alternative methods for the decoloration of textile wastewater. A variety of adsorbents for this purpose have been reported in literature such as water hyacinth roots (Low *et al.*, 1995), sunflower stalks (Sun and Xu, 1997), eucalyptus bark (Morais *et al.*, 1999), coir pith (Namasivayam *et al.*, 2001), orange peel (Sivaraj *et al.*, 2001) and narrow-leaved cattail (Singhtho, 2001).

The aim of this research is to study the use of treated flute reed as an adsorbent for color removal. Flute reed (*Phragmites karka* (Retz.) Trin. Ex Steud) is one of the abundant weed types in Thailand. Singhakant (2001) demonstrated the possibility of treated flute reed for reactive dye removal in a batch system. This research investigated the ability of treated flute reed to adsorb synthetic reactive dye and textile wastewater in a column system. The effects of particle size, initial reactive dye concentration, bed depth and flow rate were also studied. Finally, the color removal from actual dyeing and printing textile wastewater was studied using the optimum conditions obtained from the synthetic reactive dye experiments.

## MATERIALS AND METHODS

### Preparation of treated flute reed

Flute reed was collected from Mahidol University (Salaya), Thailand. It was sliced into pieces of less than 1 inch, sun dried for 3 days and ground in a disk mill. After grinding, the flute reed was treated by soaking with 0.2 N $H_2SO_4$ for 1 hour, the solution being replaced every hour until color was no longer leaching from the weed. After that, it was dried in a hot air oven at 80°C for 12 hours and then sieved through U.S. standard sieves into three different particle size ranges of 420-1190, 1190-2000 and 2000-2800 μm.

### Preparation of synthetic reactive dye solution

The reactive dye used in this study was Procion Red H-E7B (C.I. Reactive Red 141). A stock solution of 30 mg/L was prepared by mixing 0.03 g of dried dye with 1000 $cm^3$ distilled water. The desired initial concentration was obtained from diluting this stock solution.

### Column experiments

The adsorption experiments were carried out in an acrylic column with an internal diameter (i.d.) of 2.5 cm and a length of approximately 60 cm. The treated flute reed was packed in the column between glass wool and glass beads to prevent the wash out of the treated flute reed particles from the column (Fig. 1). Prior to the packing, the treated flute reed was wetted for 24 hours in distilled water to avoid the formation of air pockets in the column.

In order to study the effect of particle size on the color removal, each particle size range of treated flute reed was packed separately and then replaced by the next range in the column which was filled with water to 15 cm bed depth. Using a peristaltic pump, 30 mg/L synthetic reactive dye solution, without pH adjustment, was fed through the column in an upflow mode at a constant flow rate of 0.6 ml/min. The effluent samples were collected at regular time intervals at septa ports by using a syringe and needle capable of taking a sample from the center of the bed. The sample dye concentrations were analyzed using a spectrophotometer at a wavelength 543 nm. The operation of the column was terminated when the effluent dye concentration approached the influent dye concentration. In this study, the breakthrough and exhaustion concentrations were set at 0.1 $C_o$ or 3 mg/L and 0.9 $C_o$ or 27 mg/L, respectively.

The effect of initial reactive dye concentration varies at 10, 20 and 30 mg/L by using the optimum particle size. To study the effect of bed depth and flow rate, the treated flute reed was packed to a bed depth of 45 cm. Three flow rates of 0.6, 1.2 and 1.8 ml/min were tested. The samples were collected at regular time intervals at bed depths of 15, 30 and 45 cm.

### Actual textile wastewater adsorption in a fixed bed column

In this study, dyeing textile wastewater was collected from the wash water of a dyeing process which was separated from the non-color wastewater. Its color was dark brown because it

contained very high concentrations of various reactive dyes. Therefore, ten columns of 45 cm bed depth were operated in series at a constant flow rate of 0.6 ml/min.
Printing textile wastewater was collected from the sedimentation tank after the coagulation process. It was dark green in color and consisted of various reactive dyes and other wastewater contaminants. In this experiment, one column was used. Samples were collected at regular time intervals and analyzed for color intensity in the visible wavelengths of 400 to 700 nm by a spectrophotometer and reported as ADMI (American Dye Manufacturers Institute) units. Parameters such as pH, COD and SS in the influent and effluent were also monitored.

## RESULTS AND DISCUSSION

### Effect of particle size

The breakthrough curves of three different particle size ranges of treated flute reed on the adsorption of 30 mg/L synthetic reactive dye solution at a bed depth of 15 cm and flow rate of 0.6 ml/min are shown in Fig. 2. The column parameters are displayed in Table 1. The slope of the breakthrough curves of all particle sizes was not different suggesting that the adsorption rate of the three different particle size ranges was similar. However, the length of the mass transfer zone ($L_m$) of the smallest particle size range was the shortest compared to those of the other particle size ranges (Table 1). From the breakthrough curve theory, a shorter length of mass transfer zone shows a higher rate of adsorption (Snoeyink and Summers, 1999). Therefore, the smallest particle size had the highest rate of adsorption. The reason for this phenomenon is that the smaller particles reduced the film mass transfer resistance and the intraparticle diffusion path, resulting in the reduction of the length of the mass transfer zone (Yu and Kaewsarn, 1999).

As shown in Table 1, the volume treated at 90% breakpoint ($V_B$) and exhaustion point ($V_S$), breakthrough time at 90% breakpoint ($T_B$) and exhaustion point ($T_S$) increased as the particle size decreased. This means that the breakthrough concentration of the larger particle size was saturated quicker than the smaller particle size. This is due to the smaller particle size having a specific surface area greater than the larger particle size (Walker and Weatherley, 1997). Therefore, it could adsorb more synthetic reactive dye solution than the larger particle size.

### Effect of initial reactive dye concentration

Fig. 3 shows the breakthrough profile for different initial reactive dye concentrations. It is clear that the $V_B$ slightly increased with decreasing initial reactive dye concentration. It increased from 242 to 287 ml while the initial reactive dye concentration decreased from 30 to 10 mg/L. This is because the range of the initial reactive dye concentration used in this study was narrow. Increasing the initial reactive dye concentration to higher than 30 mg/L might cause a greater difference in $V_B$ value.

Increasing the influent concentration resulted in decreasing $V_B$, $V_S$, $T_B$ and $T_S$ (Table 1). This is due to the treated flute reed being quickly saturated at higher initial reactive dye concentrations (Walker and Weatherley, 1997). Thus, the $V_B$, $V_S$, $T_B$ and $T_S$ values for higher influent concentrations were reached earlier than for the lower influent concentrations. In addition, the $L_m$ increased with decreasing initial reactive dye concentration. This is because the intraparticle diffusivity varies with the liquid concentration. Increasing influent concentration caused an intraparticle diffusivity increase and resulted in a decreasing mass transfer zone (Noll *et al.*, 1992).

**Effect of bed depth**

The breakthrough curve of various bed depths at constant flow rates of 0.6, 1.2 and 1.8 ml/min are shown in Figs. 4-6, respectively. From these figures, the breakpoint of the shorter bed depth was earlier than of the longer bed depth. The slopes of the breakthrough curves at all flow rates were similar indicating that the rate of adsorption of the three different bed depths was not different. Pressure drop and clogging in the column did not occur at bed depths of 15-45 cm. This suggested that the particle size range of treated flute reed and the range of bed depth used in this study were suitable. Thus, the column that contains the treated flute reed particle size range of 420-1190 μm at bed depth of 45 cm could be used in series to increase the color removal efficiency. An increase in bed depth at the same flow rate resulted in increasing the EBCT between the synthetic reactive dye solution and the treated flute reed. Therefore, the $V_B$, $V_S$, $T_B$ and $T_S$ increased as the bed depth increased (Table 2).

In this study, the length of the mass transfer zone ($L_m$) calculated from the breakthrough curve increased as the bed depth increased. However, it was shorter than the bed depth which indicated that the treated flute reed could remove the synthetic reactive dye solution. This is because when the bed depth of the treated flute reed packed in the column was shorter than the length of the mass transfer zone, the breakthrough occurred immediately (Yu and Kaewsarn, 1999).

**Effect of flow rate**

Figs. 7-9 show the breakthrough profiles of various flow rates at constant bed depths of 15, 30 and 45 cm, respectively. The column parameters for various flow rates are shown in Table 2. The slopes of the breakthrough curves of three different flow rates, 0.6, 1.2 and 1.8 ml/min, at each bed depth were not different. This indicated that the rate of adsorption at the three different flow rates was similar. However, the $L_m$ at the lower flow rate was shorter than at the higher flow rate (Table 2). Snoeyink and Summers (1999) stated that if the adsorption rate is high, the $L_m$ will be short. Therefore, the lower flow rate will have a higher rate of adsorption.

From the breakthrough curve, it can be seen that at all bed depths the $V_B$ of the flow rates of 1.2 and 1.8 ml/min were slightly different, whereas the $V_B$ value for the flow rate of 0.6 ml/min was much higher than for the flow rates of 1.2 and 1.8 ml/min. Thus, the optimum flow rate for this column size was 0.6 ml/min. In addition, increasing flow rate resulted in decreasing $V_B$, $V_S$, $T_B$ and $T_S$ values, whereas the $L_m$ and treated flute reed usage rate increased with increasing flow rate.

**BDST and EBCT with variation of flow rate**

The effect of the flow rate on the column adsorption was described by using the BDST model. The data in Table 2 was used to plot the relationship between bed depth, *D*, against service time, $T_B$, as can be seen in Fig. 10, for three different flow rates of 0.6, 1.2 and 1.8 ml/min. The breakthrough time decreased with increasing flow rate at the same bed depth. The slope of the BDST plot decreased as the flow rate increased suggesting that lower flow rates provided higher rates of adsorption and longer breakthrough times (Rozada *et al*., 2003 and Walker and Weatherley, 1997). The constants in the BDST model for various flow rates are represented in Table 3. The critical bed depth ($D_o$) decreased as the flow rate decreased. The minimum bed depth required for the adsorption of RR-141 dye at flow rates of 0.6, 1.2 and 1.8 ml/min was 3.71, 5.72 and 8.73 cm, respectively. The adsorption capacity ($N_o$) decreased from 0.98 to 0.44 mg/g when increasing the flow rate from 0.6 to 1.8 ml/min. This is due to the increasing flow rate resulting in a decreasing EBCT. However, the rate constant ($A$) decreased from 0.097 to 0.034 l/mg.hr when the flow rate decreased from 1.8 to 0.6 ml/min. Based on the data in Table 2, the relationship between the EBCT and the treated flute reed usage rate is shown in Fig. 11. The treated flute reed usage rate decreased with increasing EBCT. The EBCT used for the column design was taken from the plot base on the lowest treated flute reed usage rate. Therefore, the optimum EBCT was 368 minutes. From this result, a bed depth of 45 cm and a flow rate of 0.6 ml/min were determined as the best conditions. Therefore, these conditions were used in the actual textile wastewater experiments.

**Actual textile wastewater adsorption in a fixed bed column**

The characteristics of dyeing and printing textile wastewater before and after treatment are shown in Table 4 and 5, respectively. In dyeing textile wastewater, the treated flute reed reduced 99% of the color and SS from 1,715,000 to 191 ADMI and 1,296 to 8 mg/L, respectively. However, the COD increased from 2,688 to 4,032 mg/L. This might be because of the leaching of organic matter from the treated flute reed during the experiment. In addition, the pH after treatment decreased extremely from 11.80 to 3.07. This is because the treated flute reed was washed with 0.2 N $H_2SO_4$ which increased the positive charge ($H^+$) on the surface of the treated flute reed. During the column operation, the $H^+$ was removed from the surface by the wastewater flow. Therefore, the effluent had a lower pH when it flowed through the treated flute reed in the fixed bed column. Both the COD and pH of the effluent did not meet the Industrial Effluent Standards of the Ministry of Science, Technology and Environment and therefore need further removal before the effluent can be discharged to receiving waters.

In printing textile wastewater, the color and SS were reduced from 3,800 to 840 ADMI (78%) and 84 to 74 mg/L (12%), respectively, whereas the COD value increased from 1,680 to 2,880 mg/L. A tremendous reduction in pH from 8.69 to 3.30 was observed. The SS of the treated printing textile wastewater slightly decreased when compared to the dyeing textile wastewater. This is due to the dyeing textile wastewater having a dark brown color. Thus, it was treated by ten columns in series, while the printing textile wastewater was treated by only one column because it was dark green in color. Therefore, the filtration of the dyeing textile wastewater was greater than of the printing textile wastewater resulting in a greater decrease of the SS value of the dyeing textile wastewater than of the printing textile wastewater.

## CONCLUSIONS

Treated flute reed can remove synthetic reactive dye solution and textile wastewater in a column system. The volume treated and breakthrough time at 90% breakpoint increased with decreasing particle size, initial reactive dye concentration, flow rate and increasing bed depth. The smallest particle size range (420-1190 μm) had a shorter length of mass transfer zone indicating a higher rate of adsorption. Increasing bed depth and decreasing flow rate resulted in increasing EBCT and decreasing treated flute reed usage rate. For the column diameter used in this study, the optimum bed depth and flow rate were 45 cm and 0.6 ml/min, respectively. The BDST model was suitable for use in predicting the bed performance. The column capacity ($N_o$) obtained from the BDST model decreased with increasing flow rate. In actual textile wastewater experiments, the treated flute reed removed the color and SS from dyeing and printing textile wastewater, but increased the COD value.

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Table 1. Column parameters for various particle size of treated flute reed and initial reactive dye concentration on removal of RR-141 dye solution at bed depth of 15 cm and flow rate of 0.6 ml/min

| **Particle size (μm)** | **$C_o$ (mg/L)** | **$V_B$ (ml)** | **$T_B$ (hours)** | **$V_S$ (ml)** | **$T_S$ (hours)** | **$L_m$ (cm)** | **W (g)** | **Usage rate (g/l)** |
|---|---|---|---|---|---|---|---|---|
| 2000-2800 | 30 | 70 | 1.94 | 340 | 9.44 | 11.92 | 8.03 | 114.71 |
| 1190-2000 | 30 | 161 | 4.47 | 356 | 9.89 | 8.22 | 8.57 | 53.23 |
| 420-1190 | 30 | 242 | 6.72 | 427 | 11.86 | 6.50 | 9.32 | 38.51 |
| 420-1190 | 20 | 269 | 7.47 | 533 | 14.81 | 7.43 | 9.32 | 34.65 |
| 420-1190 | 10 | 287 | 7.97 | 702 | 19.50 | 8.87 | 9.32 | 32.47 |

Table 2. Column parameters for various bed depth and flow rate on removal of RR-141 dye solution at treated flute reed particle size of 420-1190 μm and initial reactive dye concentration of 30 mg/L

| Flow rate (ml/min) | Bed depth (cm) | $V_B$ (ml) | $T_B$ (hours) | $V_S$ (ml) | $T_S$ (hours) | EBCT (min) | $L_m$ (cm) | W (g) | Usage rate (g/l) |
|---|---|---|---|---|---|---|---|---|---|
| 0.6 | 15 | 237 | 6.58 | 420 | 11.67 | 122 | 6.54 | 9.32 | 39.32 |
| | 30 | 558 | 15.50 | 780 | 21.67 | 245 | 8.54 | 18.64 | 33.41 |
| | 45 | 870 | 24.17 | 1176 | 32.67 | 368 | 11.71 | 27.96 | 32.14 |
| 1.2 | 15 | 91 | 1.26 | 252 | 3.50 | 61 | 9.60 | 9.32 | 102.42 |
| | 30 | 268 | 3.72 | 522 | 7.25 | 122 | 14.61 | 18.64 | 69.55 |
| | 45 | 405 | 5.63 | 768 | 10.67 | 184 | 21.26 | 27.96 | 69.04 |
| 1.8 | 15 | 63 | 0.58 | 204 | 1.89 | 40 | 10.40 | 9.32 | 147.94 |
| | 30 | 190 | 1.76 | 408 | 3.78 | 81 | 16.03 | 18.64 | 98.11 |
| | 45 | 342 | 3.17 | 659 | 6.10 | 122 | 21.61 | 27.96 | 81.75 |

Table 3. Constants in BDST model for various flow rates

| **Flow rate (ml/min)** | **Velocity ($v$) (cm/hr)** | **$D_o$ (cm)** | **$N_o$ (mg/cm$^3$)** | **$K$ (l/mg.hr)** | **$N_o$ (mg/g)** | **$R^2$** |
|---|---|---|---|---|---|---|
| 0.6 | 7.3 | 3.71 | 0.128 | 0.034 | 0.98 | 0.9999 |
| 1.2 | 14.7 | 5.72 | 0.064 | 0.088 | 0.49 | 0.9947 |
| 1.8 | 22.0 | 8.73 | 0.057 | 0.097 | 0.44 | 0.9974 |

Table 4. The characteristics of dyeing textile wastewater before and after treatment with treated flute reed through the column adsorption

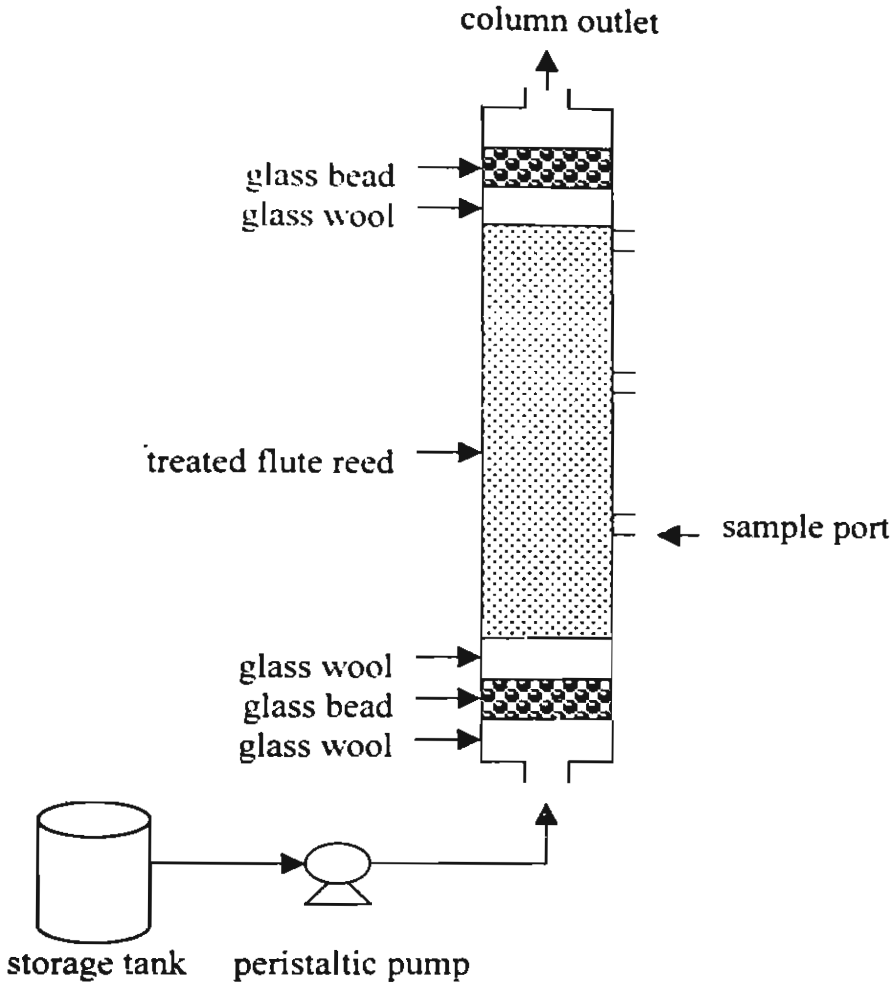
| Parameters | Before treatment | After treatment | % Removal | Industrial Effluent Standard* |
|---|---|---|---|---|
| pH | 11.80 | 3.07 | - | 5.5-9 |
| SS (mg/L) | 1,296 | 8 | 99 | 50 |
| COD (mg/L) | 2,688 | 4,032** | - | 400 |
| Color (ADMI Unit) | 1,715,000 | 191 | 99 | - |
| Apparent color | very dark brown | pale yellow | - | - |

* Source: Ministry of Science, Technology and Environment (1996)
** COD of treated flute reed 960 mg/L

Table 5. The characteristics of printing textile wastewater before and after treatment with treated flute reed through the column adsorption

| **Parameter** | **Before treatment** | **After treatment** | **% removal** | **Industrial Effluent Standard*** |
|---|---|---|---|---|
| pH | 8.69 | 3.30 | - | 5.5-9 |
| SS (mg/L) | 84 | 74 | 12 | 50 |
| COD (mg/L) | 1,680 | 2,880** | - | 400 |
| Color (ADMI Unit) | 3,800 | 840 | 78 | - |
| Apparent color | dark green | pale yellow | - | - |

* Source: Ministry of Science, Technology and Environment (1996)
** COD of treated flute reed 960 mg/L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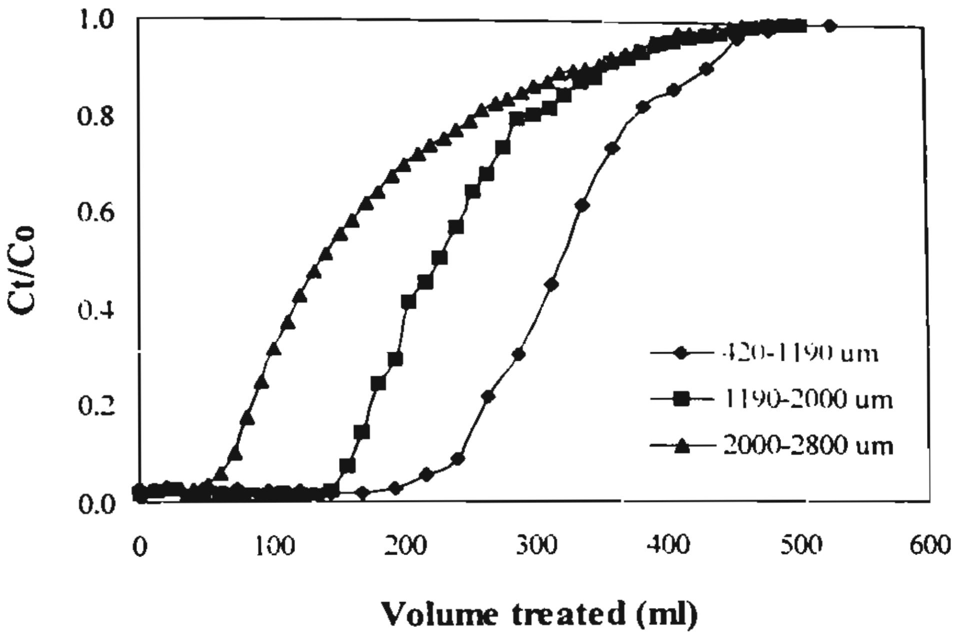
glass bead
glass wool
treated flute reed
sample port
glass wool
glass bead
glass wool
storage tank
peristaltic pump

Figure 1.


1.0
0.8
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Ct/Co
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100
200
300
400
500
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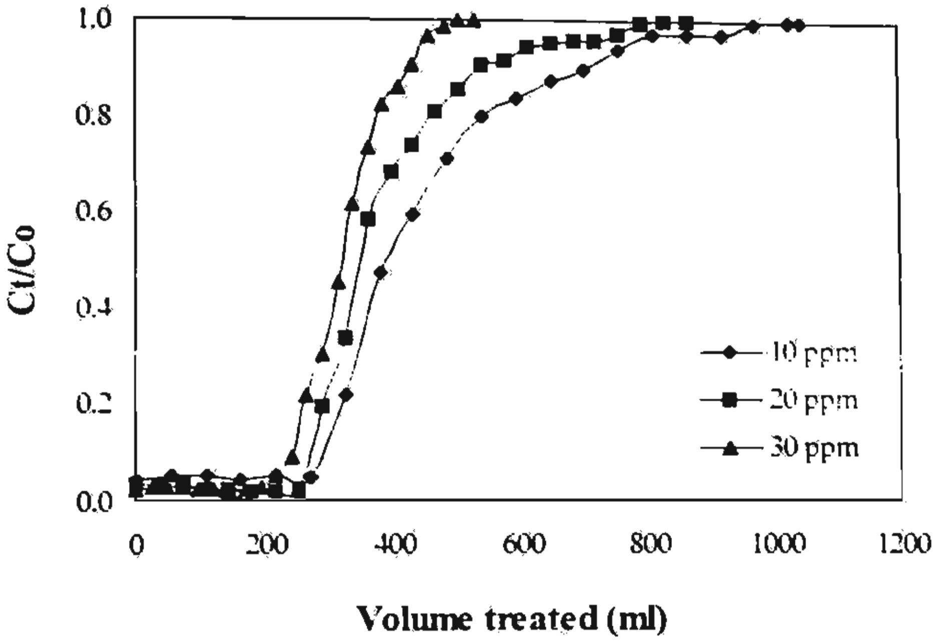
Volume treated (ml)
420-1190 um
1190-2000 um
2000-2800 um

Figure 2.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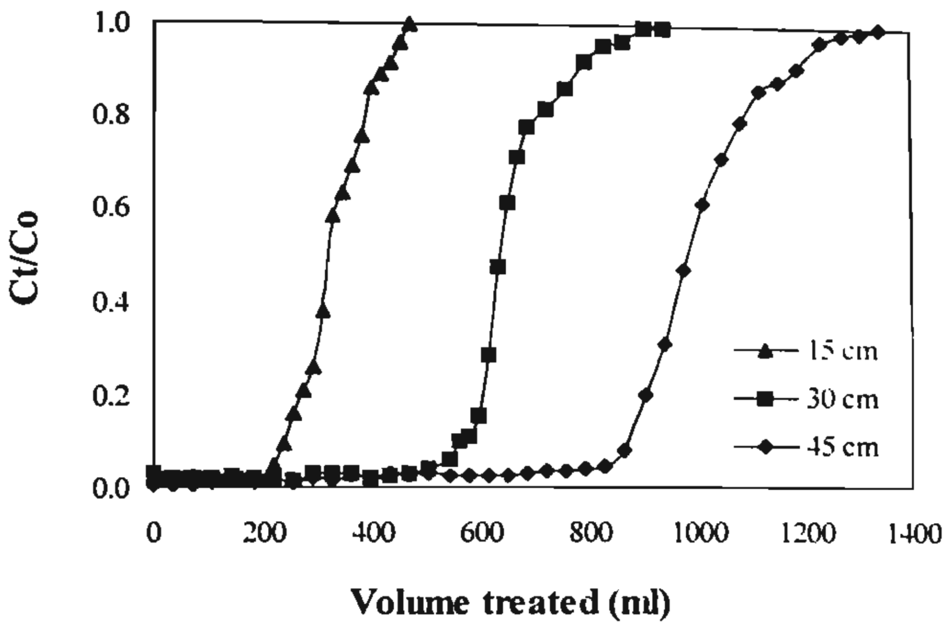
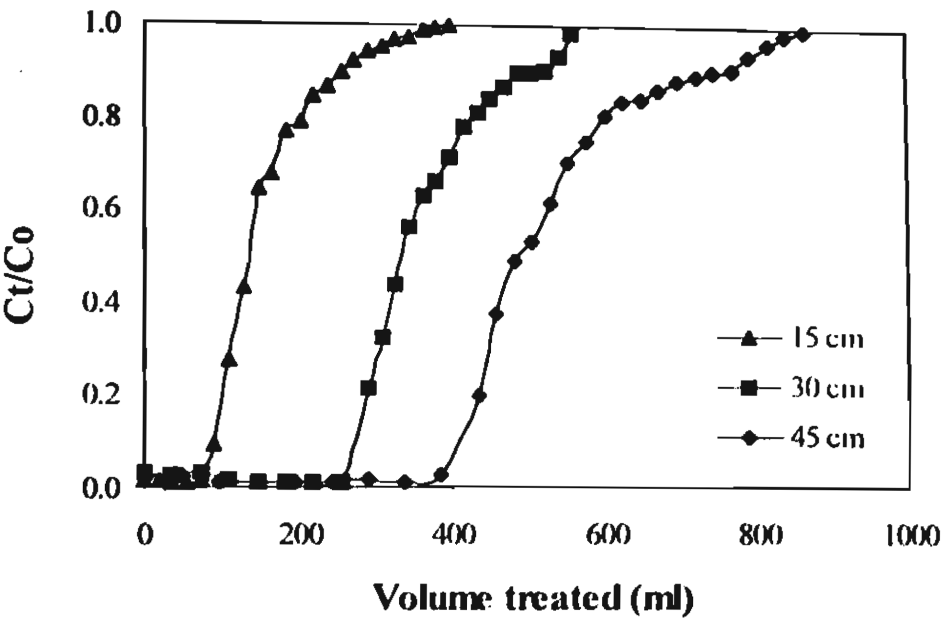
Ct/Co
10 ppm
20 ppm
30 ppm
0
200
400
600
800
1000
1200
Volume treated (ml)

Figure 3.



1.0
0.8
0.6
0.4
0.2
0.0
Ct/Co
0
200
400
600
800
1000
1200
1400
Volume treated (ml)
15 cm
30 cm
45 cm


Figure 4.



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Volume treated (ml)
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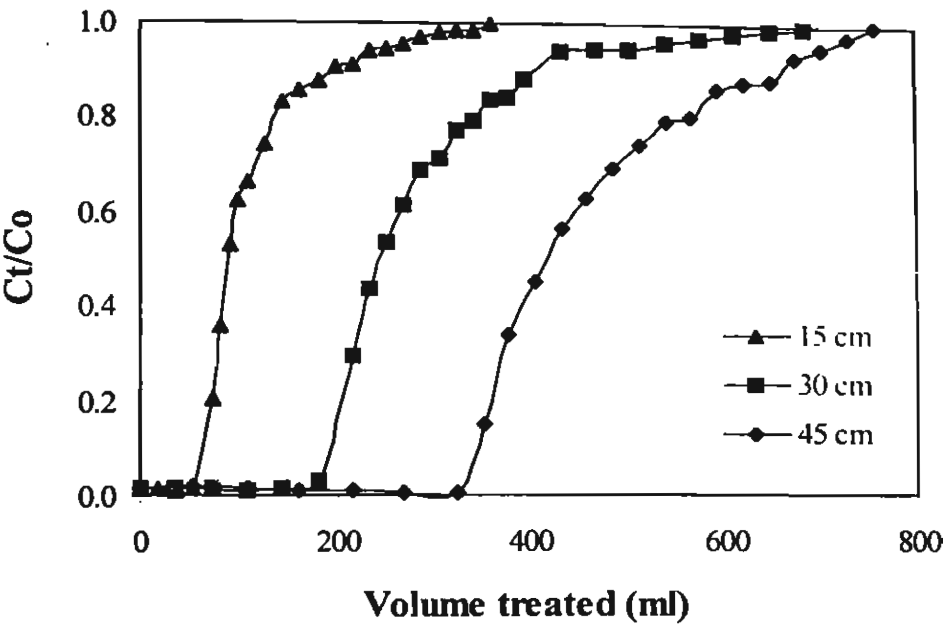
30 cm
45 cm


Figure 5.


Ct/Co
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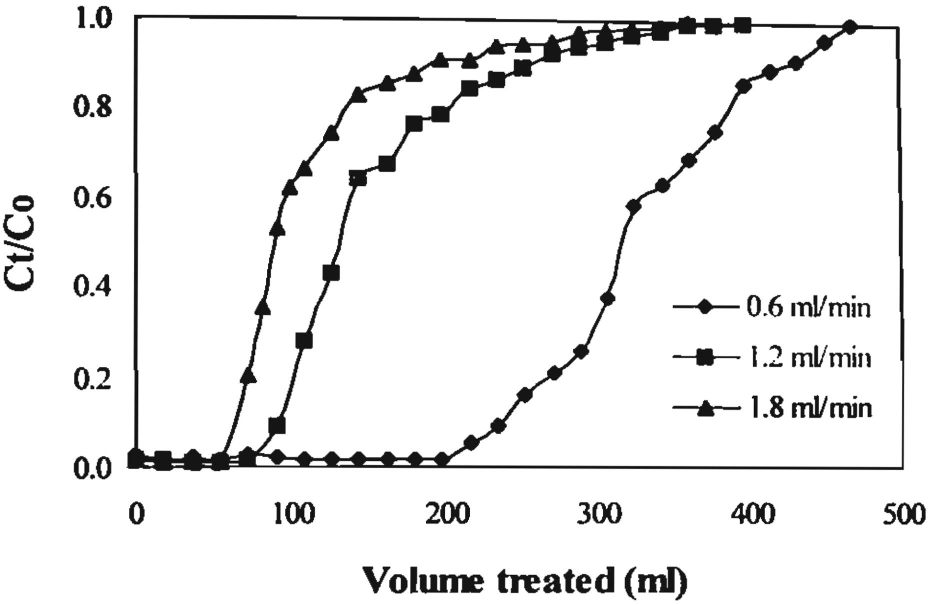
Volume treated (ml)
15 cm
30 cm
45 cm

Figure 6.



1.0
0.8
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Ct/Co
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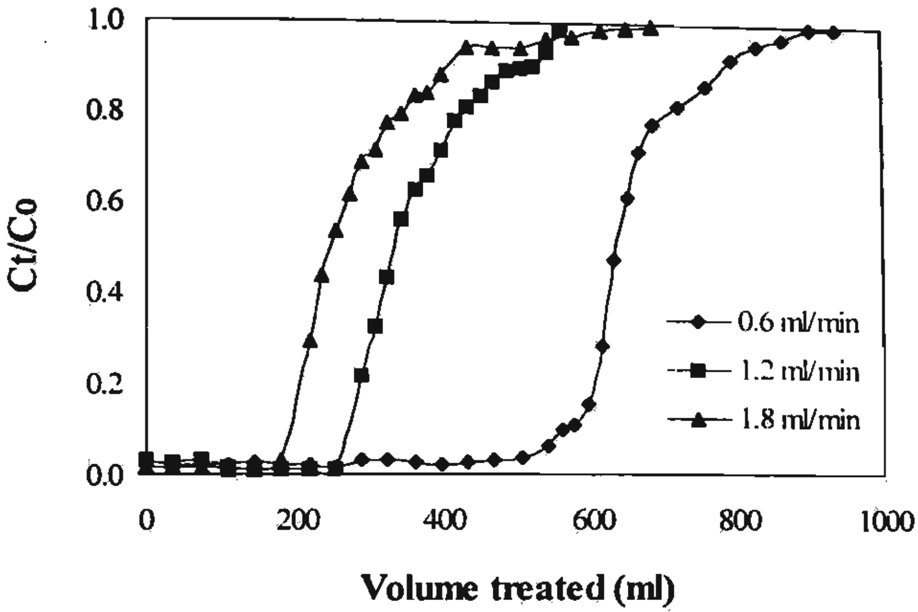
Volume treated (ml)
0.6 ml/min
1.2 ml/min
1.8 ml/min


Figure 7.



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Volume treated (ml)
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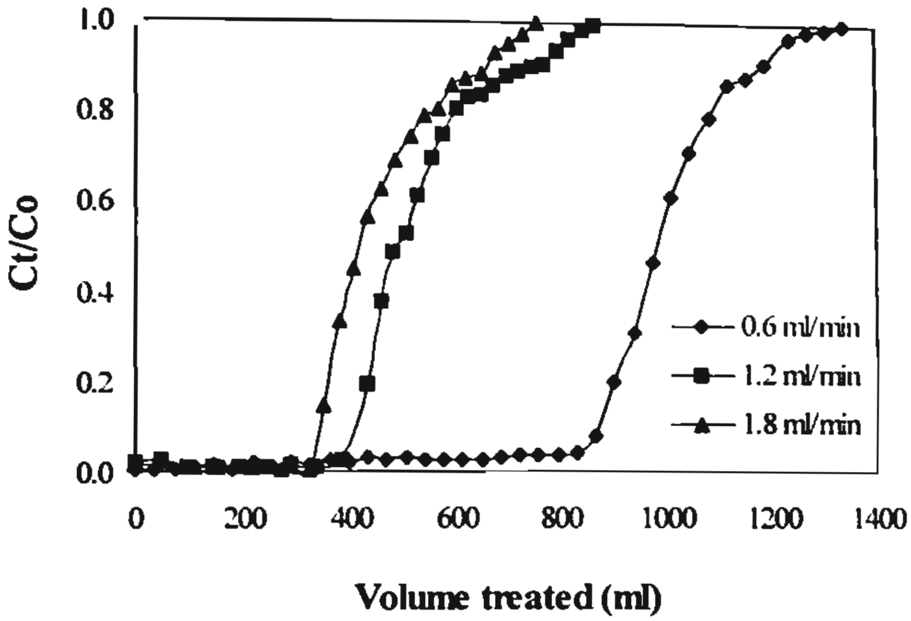
Figure 8.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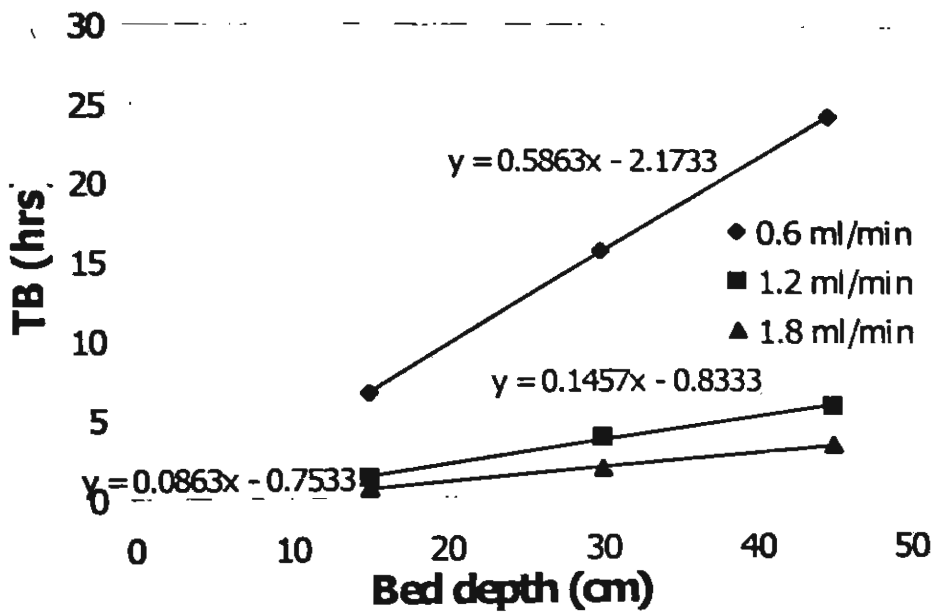
Volume treated (ml)
0.6 ml/min
1.2 ml/min
1.8 ml/min

Figure 9.



30
25
20
15
10
5
0
TB (hrs)
y = 0.5863x - 2.1733
0.6 ml/min
1.2 ml/min
1.8 ml/min
y = 0.1457x - 0.8333
y = 0.0863x - 0.7533
0
10
20
30
40
50
Bed depth (cm)


Figure 10.

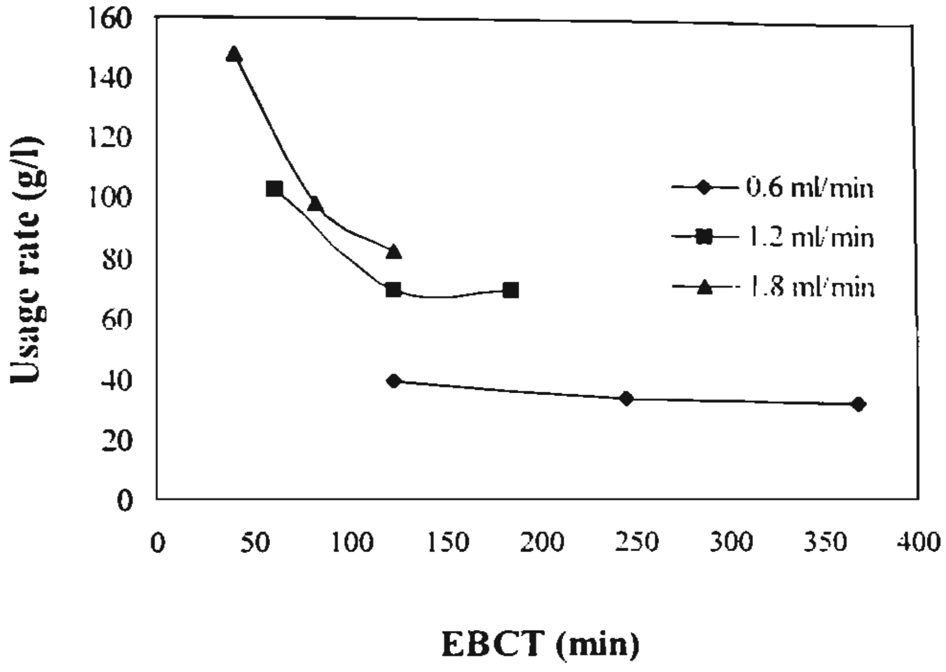

Usage rate (g/l)
160
140
120
100
80
60
40
20
0
0.6 ml/min
1.2 ml/min
1.8 ml/min
0
50
100
150
200
250
300
350
400
EBCT (min)

Figure 11.

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**Correspondence Name:** Asist. Prof. Dr. Duangrat Inthorn

**Poster presentation is inquired**

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# DECOLORIZATION OF BASIC, DIRECT AND REACTIVE DYES BY PRE-TREATED NARROW-LEAVED CATTAIL (*Typha angustifolia Lin.)*

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## ABSTRACT

This study is to compare the efficiency of basic, direct and reactive dye removal by treatment of narrow-leaved cattail with distilled water (DW-NLC), 37% $CH_2O$+0.2 N $H_2SO_4$ (FH-NLC) and 0.1 N NaOH (NaOH-NLC) at various pH (3, 5, 7 and 9). Adsorption isotherm at various temperatures (20°C, 30°C and 40°C ) of dyes was also investigated.

The type of treatment and the various pH levels had little effect on basic dye removal, which was 97% to 99% in 3 types of treatment and 100% to 97% at pH 3 to pH 9. All types of treatment still had a negative charge and the basic dyes still had a positive charge at a wide pH range. For direct and reactive dyes removal, FH-NLC and pH 3 showed the highest efficiency that were at 37% to 42% and 22% to 54% in 3 types of treated narrow-leaved cattail, and 5% to 99% and 7% to 96% at pH 3 to pH 9 of direct and reactive dye removal, respectively. There was a mutual attraction of negatively charged direct dye molecules to some positively charged molecules on the surface of the FH-NLC, which had increased $H^+$. For removal efficiency of the basic dye wastewater and the reactive dye wastewater, before and after treatment, by FH-NLC was 83%, 16% and 17%, respectively. FH-NLC had high efficiency to remove basic dye at various pH levels and treatments, and NaOH in reactive dye wastewater from the dyeing process might compete with the binding with FH-NLC.

Increasing of $q_{max}$, $\triangle$H and *b* constant values from the Langmuir equation and constant values from the Freundlich equation indicated the chemisorption mechanism for basic, direct and reactive dyes. Moreover, l/n constant values from the Freundlich equation were more than 0.1 and less than 1, which indicated favorable adsorption. Furthermore, the desorption percentage of FH-NLC after adsorbing basic, direct and reactive dyes was 6%, 10% and 35%, respectively, which indicated the chemisorption mechanism for basic and direct dye and some physisorption for reactive dye. Furthermore, there should be a study on other treatment types of NLC for increased dye adsorption capacity and NLC should be used to adsorb other adsorbates, such as heavy metal and chemical compounds in wastewater.

# ภาคผนวก I

## การไปเสนอผลงานวิจัยในต่างประเทศ

ไปเสนอผลงานวิชาการ (poater presentation) เรื่อง Decolorization of reactive dyes by pre-treated Flute Reed (*Phragmites karka* (Retz) ..ในการประชุม 34$^{th}$ Mid-Atlantic Industrial & Hazardous Waste Conference ที่ Cook College, Rutgers University, New Brunswick, NJ ณ ประเทศสหรัฐอเมริกา ระหว่างวันที่ 20-21 กันยายน 2545 (ดังรายละเอียดแนบ I)

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# DECOLORIZATION OF REACTIVE DYES BY PRE-TREATED FLUTE REED (*Phragmites karka* Retz.)

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## ABSTRACT

The main components of flute reed are cellulose (62%) and lignin (19.3%), which potentially have a lot of binding sites for ion exchange with reactive dyes. The formaldehyde/sulfuric acid treatment method was most suitable for removal of reactive dyes. The results from Zeta potential analysis confirmed that flute reed had less negative charge after treatment with formaldehyde and sulfuric acid. Thus it was suitable for adsorbing anionic dyes as reactive dyes. Tests of color adsorption at various pH levels showed that color removal efficiency of formaldehyde-treated flute reed was higher at low pH than at high pH. Color adsorption at low pH was mainly by chemisorption, while at high pH, the low molecular weight dye could be adsorbed more easily than high molecular weight dye by physisorption. The adsorption isotherm was described by parameters of Langmuir adsorption equations. At high temperature, color adsorption capacity of formaldehyde treated flute reed was higher than at lower temperature for all three reactive dyes. From adsorption isotherm at various temperature indicated that dye adsorption by formaldehyde treated flute reed was mainly endothermic chemisorption.

## INTRODUCTION

One common weed found in Thailand of potential use is flute reed (*Phragmites karka* (Retz.) Trin. ex Steud). The aim of the present research was to study the feasibility of utilizing flute reed as low-cost, single-use adsorbent for color removal in reactive dye solution. The reactive dyes were used because it is one of the most commonly used dyes in Thai textile industries. This dye is highly soluble that hard to separate from wastewater. It would be economically attractive to use this weed as agriculture waste for color treatment from textile wastewater.

In this study the effect of pretreatment method, temperature and pH on color removal were investigated. The parameters of adsorption isotherm equation were studied at different temperatures. The components of flute reed and total surface charges of flute reed powder were analyzed.

## MATERIALS AND METHODS

Flute reed was collected from Mahidol University, Salaya campus, Thailand. The components were analyzed by TAPPI standards method (Standard methods in wood texture analysis for pulp and paper industry) (1). It was sliced, dried, and ground to a powder and separated into less than 0.420 mm by sieving. The powdered material was treated by three methods for testing. These were pretreatment with distilled water (DW-treatment), with 37% formaldehyde and 0.2 N sulfuric acid (FH-treatment), and with distilled water with pH adjusted to 9 with sodium hydroxide (NH-treatment). Three different treated flute reed were used to adsorb M-5B dye solution (3 g adsorbent per 150 ml dyes solution) for select the best method. The selected treated flute reed was used to adsorb three reactive dyes solution at pH 3, pH 5, pH 7 and pH 9. The total charge of treated and untreated flute reed batches were analyzed by Zeta Sizer 4. The dyes used in all experiments was reactive dye that shown in Table 1.

**Table 1 Molecular weight and maximum wavelength of reactive dyes**

| Type of reactive dyes | Molecular weight | Maximum wavelength |
|---|---|---|
| Basilen Red M-5B (BASF) | 601 | 539 |
| Basilen Red E-B (BASF) | 1338 | 534 |
| Procion Red H-E7B (ICI) | 1774 | 543 |

The concentration of dye solution was determined by a UV-spectrophotometer at the maximum wavelength of each reactive dye.

For adsorption isotherm, FH-treated flute reed was used to adsorb each dye at temperatures 20°C, 30°C and 40°C. The adsorption isotherm was described by Langmuir adsorption equations.

## RESULTS AND DISCUSSION

Components of flute reed were analyzed by TAPPI standards method. The results demonstrated that the main structure of flute reed contained 62.0% holocellulose, 19.3% lignin and 9.0% ash. These components were close to the value of 60% cellulose and 20% lignin in bagasse pith.

From the comparison of color adsorption by the three pretreated flute reed substrates (Fig. 1), formaldehyde-treated flute reed (FH) had the highest efficiency (72% in 8 h.) of adsorbing dye from solution, while the distilled water treatment (DW) and alkaline treatment (NH) absorbed 65% and 64% (in 6 h.), respectively. Therefore, the formaldehyde treatment was selected for further experimentation. FH-flute reed had the highest efficiency for removing reactive dye due to its positive charge. The surface of the cellulose in contact with water is negatively charged (2). As the flute reed is treated with formaldehyde and sulfuric acid, the hydronium ions ($H_2^+$) of sulfuric acid catch anions ($O^-$) at the outer surface of cellulose to form $OH_2^+$. The positively charged interface of $OH_2^+$ associates with $SO_4^{2-}$ ions. The $SO_4^{2-}$ ions are exchanged with dye anions as shown in Fig. 2. The total charge of untreated flute reed and various treated flute reeds were analyzed by Zeta potential analysis as shown in Table 2. The results also confirmed that untreated flute reed had more negative charge while FH-flute reed had less negative charge that increased its ability to adsorb reactive dye.

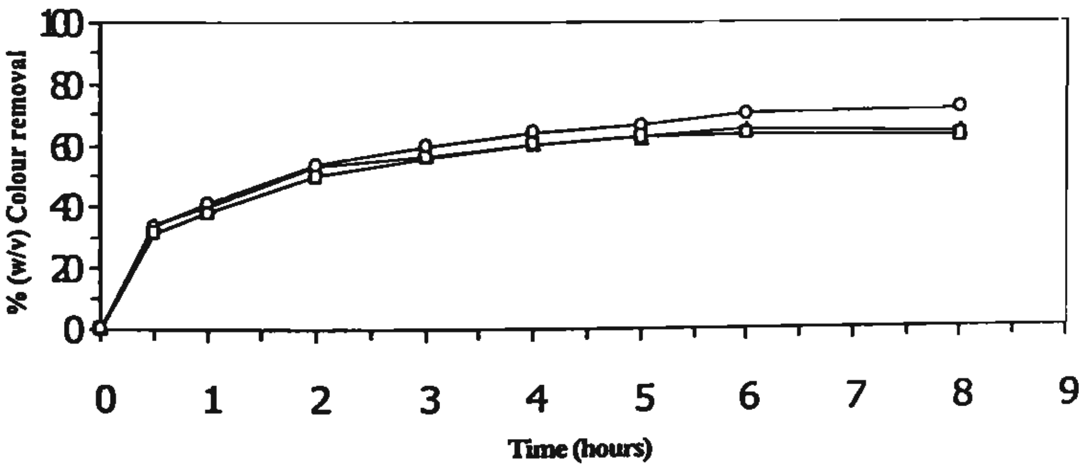


**Fig. 1** **Comparison of M-5B dye solution adsorption by three treated flute reed; Δ Distilled water treated flute reed (DW), ○ Formaldehyde treated flute reed (FH) and □ Alkaline treated flute reed (NH)**

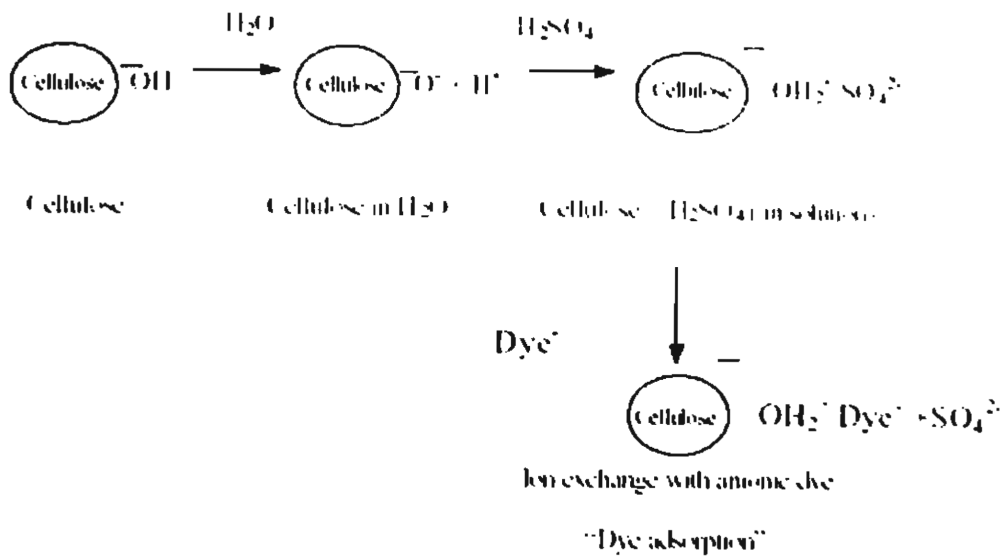

Fig. 2 Anionic dye adsorption of acidic treated flute reed

Distilled water (DW) and alkaline (NH) treated flute reed had the most negative charge. Therefore DW-flute reed and NH-flute reed had lower adsorption capacity than FH-flute reed. Acid pretreatment enhanced the porosity of flute reed and gave it higher physical adsorption capacity. Both formaldehyde and sulfuric can be used as a preservative for flute reed used in wastewater treatment.

Table 2 Zeta potential analysis of flute reed

| Type of flute reed | Zeta potential (mV) | Standard Error |
|---|---|---|
| Untreated flute reed | -14.6 | ±0.5 |
| FH-flute reed | -11.9 | ±2.7 |
| DW-flute reed | -17.3 | ±0.9 |
| NH-flute reed | -19.8 | ±1.1 |

Formaldehyde-treated flute reed was tested for dye-removal capacity for three dye solutions at four different pH levels. From the comparison of color adsorption of all dyes, FH-flute reed had the highest removal efficiency at pH 3 and declined with increasing pH. The color removal reached equilibrium within 18 h. At pH 5 and pH 7 equilibrium was reached in 18-42 h (Figs 3-6). With increasing pH, the adsorbent surface becomes negatively charged and competes with the dye anions, resulting in low adsorption. Moreover, many other reports have demonstrated that dye removal efficiency is higher at lower pH of the dye solution (3, 4, 5, 6). Therefore, pH 3 was selected in this study.

Dye removal by FH-flute reed at equilibrium at different pH levels is shown in Fig. 7. At pH 3 and pH 5, the percentage color removal of three dyes was similar. At pH 7 and pH 9, the percentage color removal of M-5B was higher than for E-B and H-E7B, which implies that the molecular weight (mw) of the dye may affect adsorption. At low pH, removal of all dyes was similar, which suggests that the adsorption was due to a chemical process (chemisorption) in which the molecular size of the dye does not affect its adsorption. At pH 7 and pH 9, however, M-5B (mw = 601) was more easily adsorbed than E-B (mw = 1338) and H-E7B (mw = 1774). At high pH, the positive ions on the flute reed surface decreased, and chemisorption of highly negatively charged dyes hardly occurred. Thus, the adsorption process was mostly due to physisorption. Smaller dye molecules could penetrate into the pores of adsorbent more than larger ones; hence, M-5B was more easily adsorbed than E-B and H-E7B at high pH.

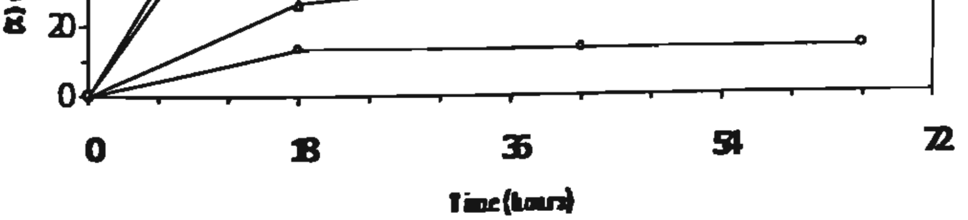


Fig. 3 Effect of pH on M-5B removal by FH-flute reed at various pH of adsorption condition ; ◊ pH 3, □ pH 5, ▵ pH 7 and ○ pH 9

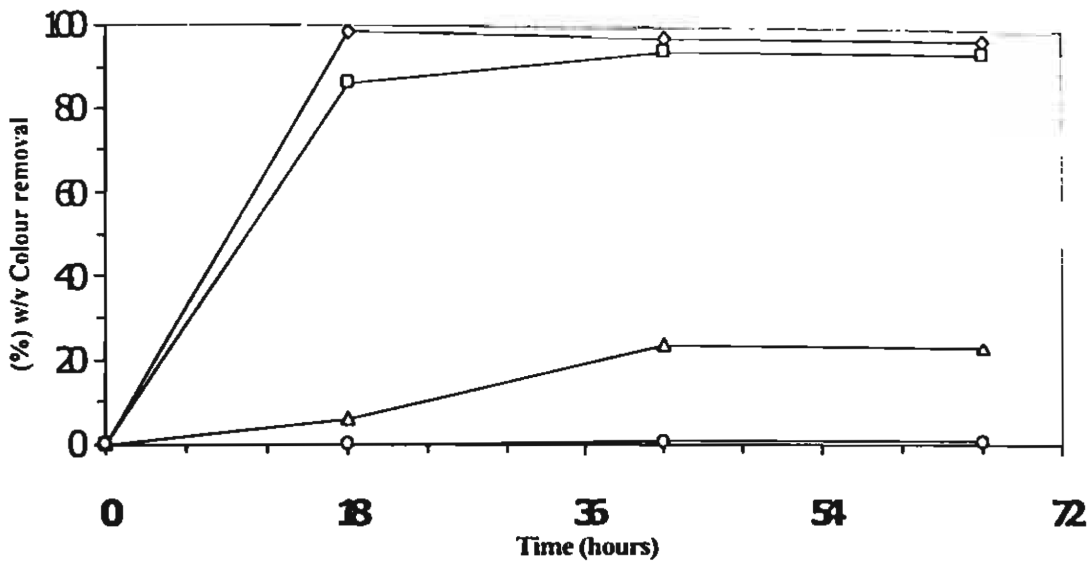


Fig. 4 Effect of pH on E-B removal by FH-flute reed at various pH of adsorption condition;
◊ pH 3, □ pH 5, △ pH 7 and ○ pH 9

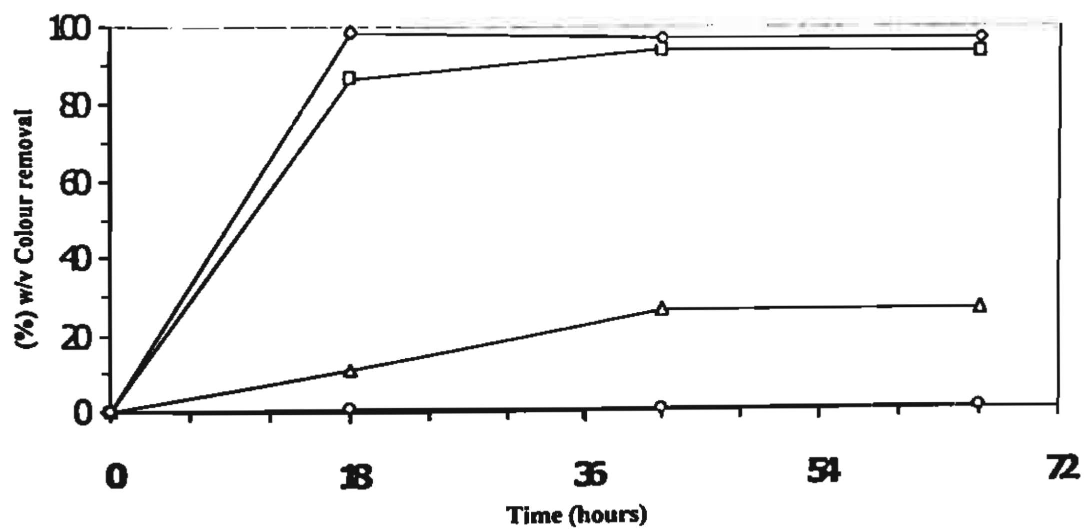


Fig. 5 Effect of pH on H-E7B removal by FH-flute reed at various pH of adsorption condition ;
◊ pH 3, □ pH 5, △ pH 7 and ○ pH 9

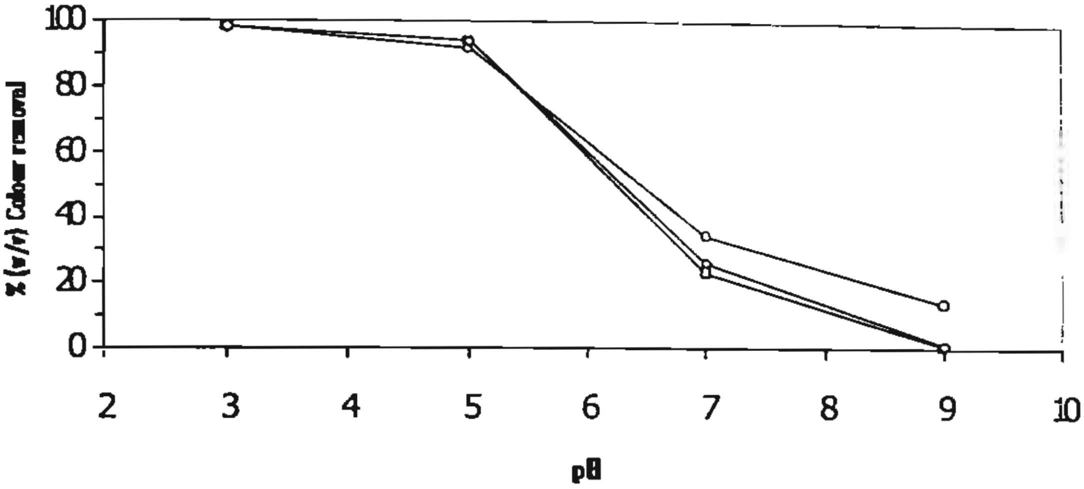


Fig. 6 Comparison of different dye removal at equilibrium by FH-flute reed at various pH of adsorption condition ; O M-5B , □ E-B and ◊ H-E7B

The various concentration of dyes were used to study adsorption isotherm of FH-flute reed at different temperatures. The adsorption phenomena could be described by Langmuir adsorption equation that is given by

$$q_e = \frac{q_{max} b C_e}{1 + b C_e}$$

The Langmuir adsorption equation can be rearranged as

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}}$$

Where $q_e$ is dye adsorbed to FH-flute reed (mg/g dry wt.), $q_{max}$ is maximum adsorption capacity (mg/g dry wt.), b is the constant related to the heat of adsorption (l/mg dye), and $C_e$ is equilibrium concentration of dye solution (mg/l). The Langmuir adsorption isotherm of three reactive dye adsorption were shown in Figs. 8-10.

The adsorption isotherm at 40 °C was higher than 30 °C and 20 °C condition. That demonstrated that FH-flute reed at 40 °C condition accumulated more adsorbate than FH-flute reed at lower temperature under the same condition. From Langmuir adsorption equation, $q_{max}$ at 40 °C of all dyes was higher than at lower temperature. At higher temperature probably brought an increase in kinetic energy and hence mobility of the adsorbate, thus resulting in increasing dye removal. These indicated that the adsorption process was endothermic.

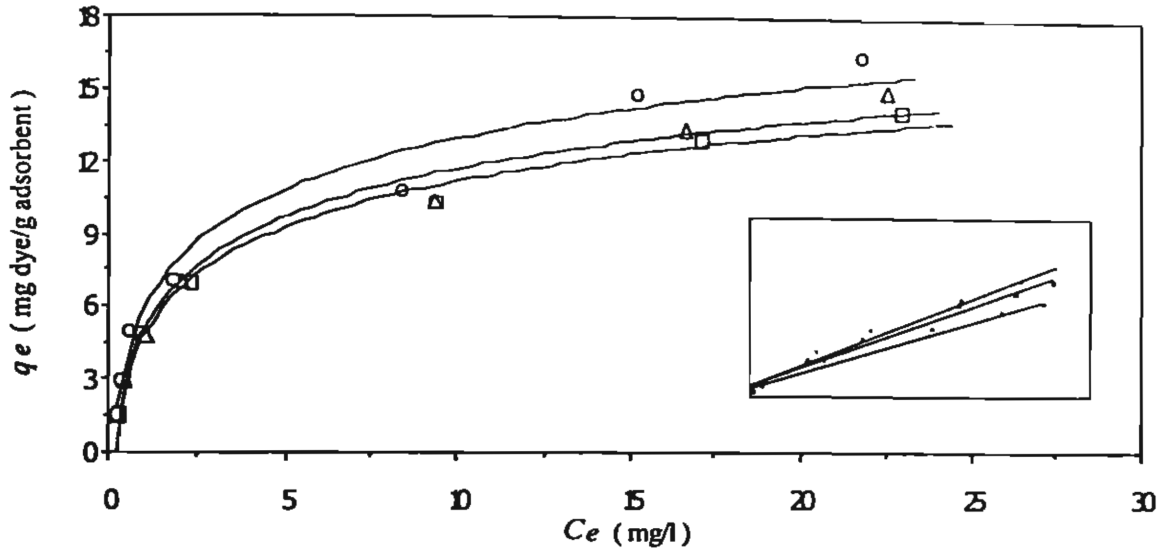


Fig. 7 Langmuir adsorption isotherm of M-5B dye solution by FH-flute reed at various temperatures ; □ 20°C, △ 30°C and ○ 40°C

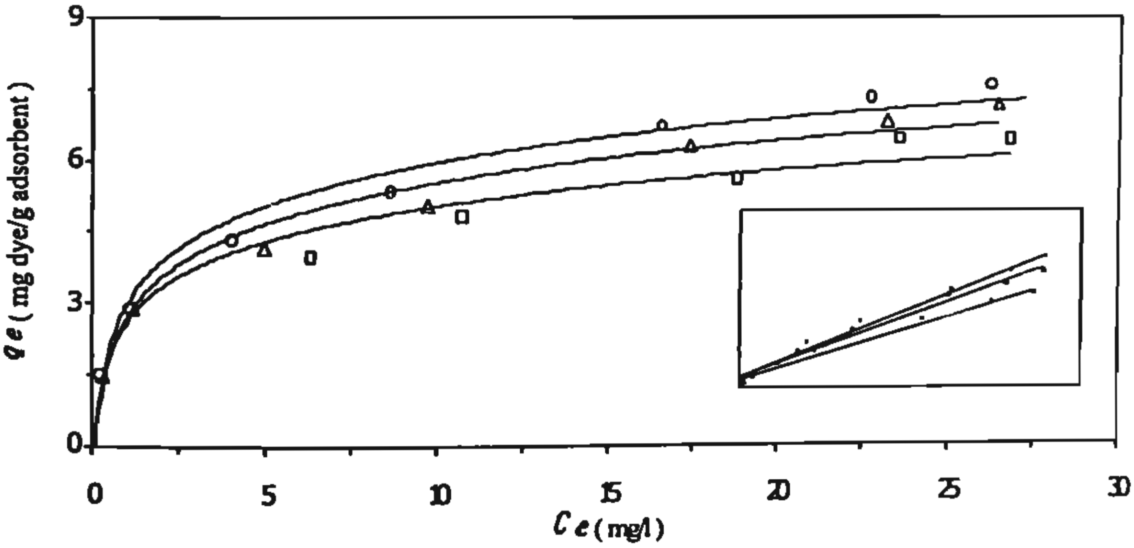


Fig. 8 Langmuir adsorption isotherm of E-B dye solution by FH-flute reed at various temperatures ; □ 20°C, △ 30°C and ○ 40°C

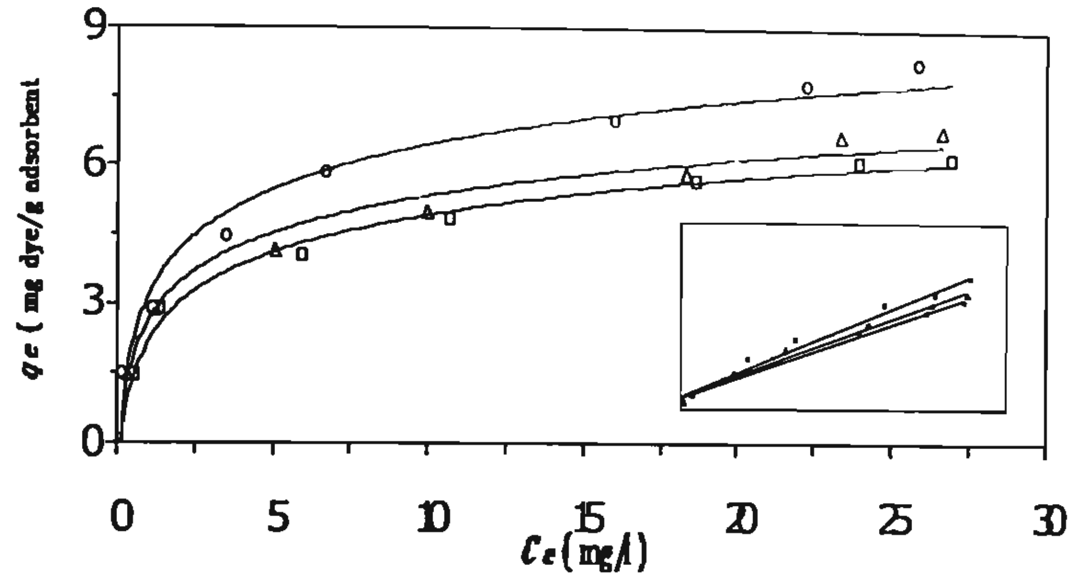


**Fig. 9 Langmuir adsorption isotherm of H-E7B dye solution by FH- flute reed at various temperatures ; □ 20°C, △ 30°C and O 40°C**

The parameters such as $q_{max}$ and b fitted Langmuir adsorption equation were concluded in Table 3. From the present experiment, $q_{max}$ of FH-flute reed from Langmuir adsorption equation for M-5B, E-B and H-E7B at 40°C were 17.51, 8.70 and 8.06 mg dye/g dry wt., respectively. No any reports on reactive dye removal by using flute reed. But there were some reports that showed the higher reactive dye removal by other adsorbent (5, 7). Although the adsorption capacity of FH-flute reed was lower but flute reed had advantage in term of low cost and environmental friendly.

For the b constant could indicated the adsorption affinity between dyes and the binding site of adsorbent. The high b constant indicated high adsorption affinity. From the results, the b constants of all dyes at 40°C were higher than that at lower temperature. Therefore the adsorption affinity at higher temperature was higher than that at lower temperature. That may ensure the adsorption process as endothermic process.

## CONCLUSION

The experimental results showed that flute reed can be used as an adsorbent for removal of reactive dye from wastewater solution. The formaldehyde treatment method of flute reed proved to be the most suitable for removal of reactive dyes.

Table 3 Parameters fitted Langmuir adsorption equation and $\Delta H^c$ of three reactive dyes adsorption by FH-flute reed at various temperatures

| Type of reactive dyes | Temp. (°C) | $q_m$ (mg dye/g flute reed) | b (l/mg dye) | $R^2$ |
|---|---|---|---|---|
| M-5B | 20 | 15.20 | 0.364 | 0.990 |
| | 30 | 15.90 | 0.369 | 0.984 |
| | 40 | 17.51 | 0.383 | 0.978 |
| E-B | 20 | 6.69 | 0.353 | 0.992 |
| | 30 | 7.19 | 0.378 | 0.984 |
| | 40 | 8.70 | 0.394 | 0.989 |
| H-E7B | 20 | 6.84 | 0.364 | 0.979 |
| | 30 | 7.57 | 0.367 | 0.985 |
| | 40 | 8.06 | 0.386 | 0.988 |

The color removal efficiency was highest at low pH of the dye solution. The parameters of Langmuir adsorption equation at various temperatures indicated that dye adsorption by formaldehyde treated flute reed was as endothermic chemisorption. Although dye adsorption capacity of formaldehyde treated flute reed was rather low but it was generally found and low cost.
It might be new approach to use this material as color adsorbent in the future. The color removal at higher temperature and the batch adsorption system in reactor should be studied for future application.

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