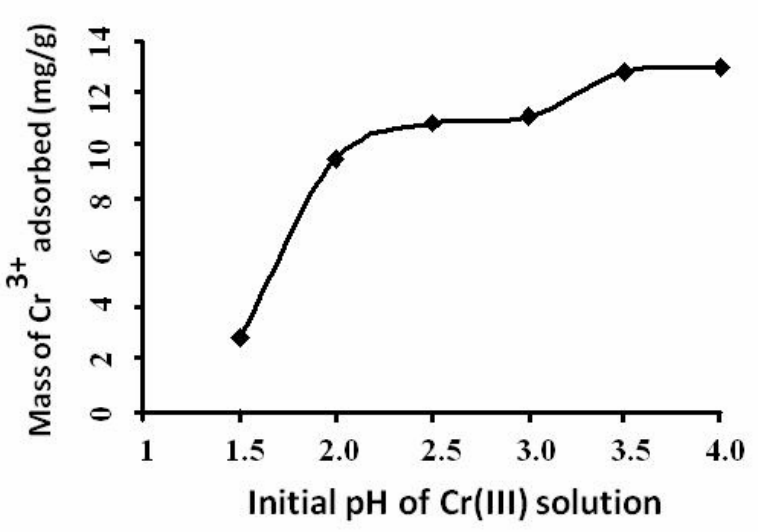
2. การดูดซับ Cr^{+3}

การเตรียมสารปนเปื้อนของ Cr^{+3} ในสารละลายสังเคราะห์สามารถดูได้จากวิธีการเตรียมในบทที่ 3

2.1 ผลของ pH สารละลายเริ่มต้น

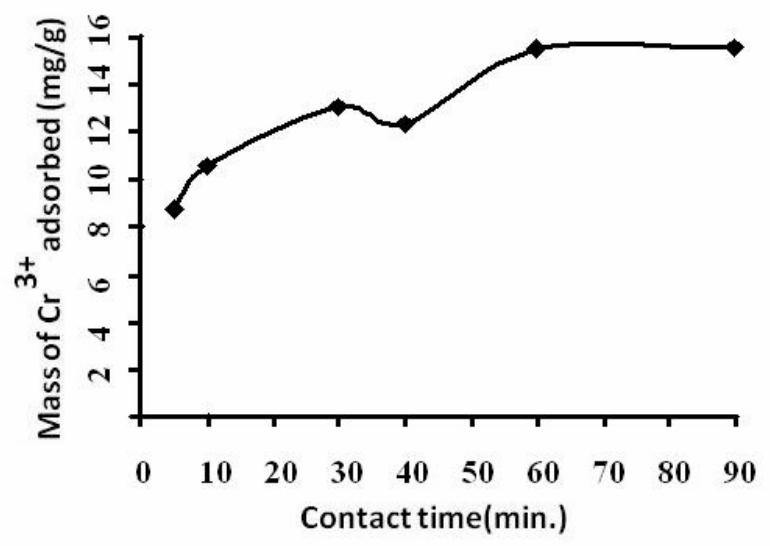
ผลของ pH สารละลายเริ่มต้นของ Cr^{+3} ที่มีผลต่อความสามารถในการดูดซับของถ่านกัมมันต์แสดงดังภาพที่ 4.9 พบว่าผลของการดูดซับไอออน Cr^{+3} มีค่าสูงขึ้นเมื่อ pH สารละลายเริ่มต้นสูงขึ้น การดูดซับเพิ่มจาก 2.79 ถึง 12.91 mg/g เมื่อค่า pH เพิ่มขึ้นจาก 1.5 ถึง 4.0 ตามลำดับ ประสิทธิภาพการดูดซับมากสุดของไอออน Cr^{+3} อยู่ในช่วง pH 3.5 ถึง 4.0 จากผลการทดลองจะเห็นได้ว่าประสิทธิภาพในการดูดซับของถ่านกัมมันต์จะมีค่ามากที่ระดับ pH สูง และที่ระดับ pH ต่ำค่าการดูดซับจะลดลงอย่างรวดเร็ว ทั้งนี้เนื่องจากที่ระดับ pH ต่ำความเป็นกรดสูง การดูดซับ Cr^{+3} จะอยู่ในลักษณะของเมตริก (matrix) สำหรับที่ระดับ pH สูงความเป็นกรดต่ำและที่สมดุลการดูดซับมากสุดโครเมี่ยมจะอยู่ในรูปของ Cr^{+3} และไม่ได้เปลี่ยนเป็นเฟสอื่นเช่น Cr^{+6} (Fahim et al., 2006) ค่า pH ของสารละลายเริ่มต้นมีผลต่อกระบวนการดูดซับ ซึ่งทำให้เกิดปฏิกิริยาทางไฟฟ้าสถิต (electrostatic interaction) ระหว่างตัวดูดซับ กับตัวถูกดูดซับ เมื่อค่า pH ของ Cr^{+3} เพิ่มขึ้นมากกว่า 4 สารละลายก็จะตกตะกอน ทำให้บดบังการแพร่ซึมหรือดูดซับของ Cr^{+3} บนพื้นผิวถ่านกัมมันต์ลดลง ดังนั้นค่าเงื่อนไขการดูดกลืนที่มากสุดสำหรับ Cr^{+3} อยู่ที่ pH = 3.5 ซึ่งค่า pH ที่ให้การดูดกลืนมากที่สุดนี้จะถูกเลือกเพื่อใช้เป็นเงื่อนไขสำหรับการทดลองในปริมาณอื่นๆต่อไป



ภาพที่ 4.9 แสดงความสัมพันธ์ระหว่างการดูดซับ Cr^{+3} กับค่า pH ของสารละลาย (ความเข้มข้นสารละลาย 100 mg/L, เวลาการดูดซับ 60 นาที, 0.6 g ของถ่านกัมมันต์/100 mL ของสารละลาย และอุณหภูมิ 30 $^{\circ}$C)

2.2 ผลของเวลาในการดูดซับ

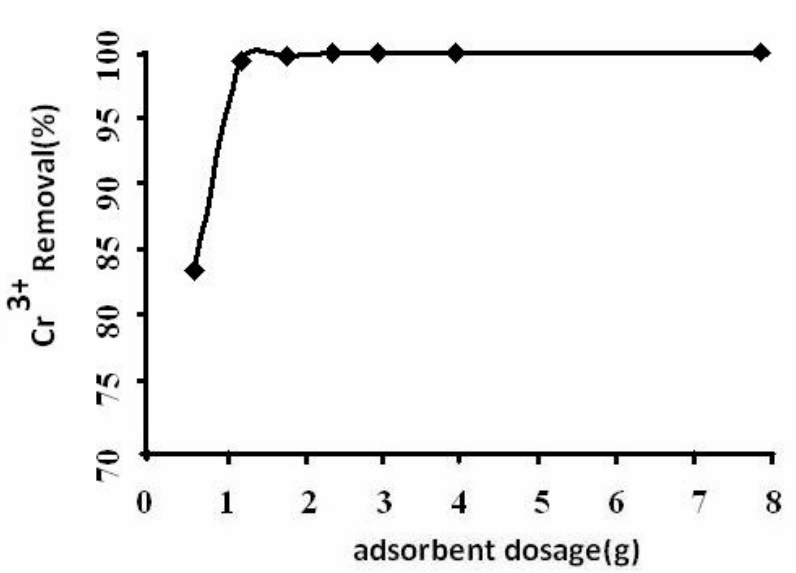
จากภาพที่ 4.10 แสดงผลของเวลาในการดูดซับสัมพันธ์กับมวลของ Cr^{+3} ที่ถูกดูดซับบนถ่านกัมมันต์ ในการทดลองใช้ถ่านกัมมันต์ 0.6 g สารละลาย 100 mL ค่า pH เริ่มต้น 3.5 ในช่วงเวลาทดลอง 5 ถึง 90 นาที จากผลการทดลองเมื่อเวลาการดูดซับเพิ่มขึ้นจาก 5 - 60 นาที ปริมาณของ Cr^{+3} ถูกดูดซับอย่างรวดเร็ว และความสามารถในการดูดซับเริ่มคงที่ที่เวลา 60 นาที และจะคงที่ต่อไปจนกระทั่งถึงเวลา 90 นาที ทั้งนี้เนื่องจาก affinity ของโลหะที่ถูกดูดซับขึ้นกับเวลาในการดูดซับเฉพาะตัวของโลหะนั้น (Balkaya and Bektas, 2009) ดังนั้นการดูดซับที่สภาวะสมดุลของ Cr^{+3} จะเกิดขึ้นในเวลา 60 นาที ซึ่งแสดงปริมาณการดูดซับมากที่สุด และเวลาการดูดซับที่เวลานี้จะใช้เป็นเงื่อนไขสำหรับการทดลองตัวแปรอื่นต่อไป



ภาพที่ 4.10 แสดงความสัมพันธ์ระหว่างการดูดซับ Cr^{+3} กับเวลาของการดูดซับ (ความเข้มข้นสารละลาย 100 mg/L, pH 3.5 ของ Cr^{+2}, 0.6 g ของถ่านกัมมันต์/100 mL ของสารละลาย และอุณหภูมิ 30 $^{\circ}C$)

2.3 ผลของปริมาณของถ่านกัมมันต์

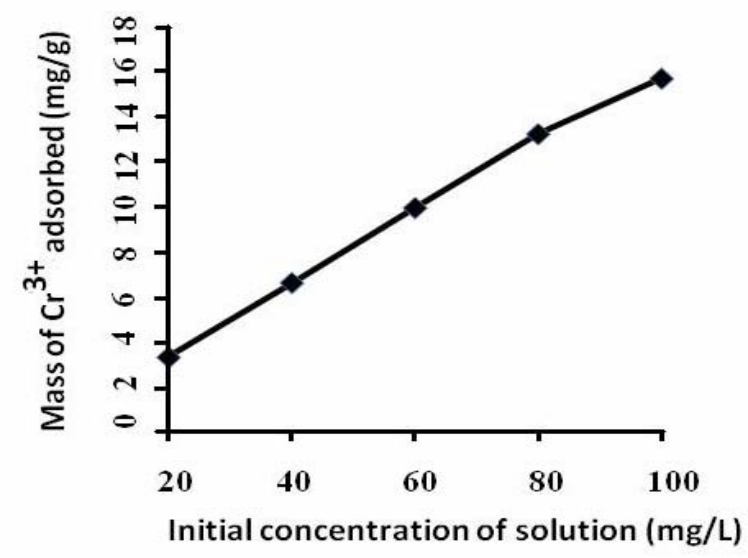
ผลของการใช้ปริมาณถ่านกัมมันต์ที่มีต่อเปอร์เซ็นต์การกำจัด Cr^{+3} แสดงดังภาพที่ 4.11 ในการทดลองจะเปลี่ยนปริมาณของถ่านกัมมันต์จาก 0.6 ถึง 8 g และใช้ค่า pH = 3.5 เวลาการดูดซับ 60 นาที และความเข้มข้นของสารละลาย 100 mg/L อุณหภูมิ 30 $^{\circ}C$ จากผลการทดลองที่ได้พบว่าเปอร์เซ็นต์การกำจัดโลหะ Cr^{+3} จะมีค่าเพิ่มขึ้นเมื่อปริมาณถ่านกัมมันต์เพิ่มขึ้น การกำจัดจะเพิ่มขึ้นอย่างรวดเร็วจนถึงปริมาณการกำจัดสูงสุดเกือบ 100% เมื่อใช้ถ่านกัมมันต์ปริมาณ 0.6 ถึง 1.2g และหลังจากนั้นการกำจัดจะคงที่ตลอดช่วงการทดลอง จะเห็นได้ว่าค่าเปอร์เซ็นต์การดูดซับสูงสุดมากกว่า 99% กับปริมาณของถ่านกัมมันต์ที่ใช้จำนวนเล็กน้อย (1.2 g) และเวลาที่ใช้ในการดูดซับระยะเวลาสั้นๆ 60 นาที เป็นสิ่งสำคัญอย่างมากสำหรับการนำไปประยุกต์ใช้ในการบำบัดน้ำเสียที่คุ้มค่าทางเศรษฐกิจ ดังนั้นจึงกล่าวได้ว่าเปลือกเมล็ดมะม่วงหิมพานต์สามารถผลิตเป็นถ่านกัมมันต์ที่มีประสิทธิภาพสูงในการใช้เป็นตัวดูดซับโลหะหนักอย่างเช่น Cr^{+3} ในสารละลายได้อย่างดียิ่ง



ภาพที่ 4.11 แสดงความสัมพันธ์ระหว่างการดูดซับ Cr^{+3} กับปริมาณของถ่านกัมมันต์ (ความเข้มข้นสารละลาย 100 mg/L, pH 3.5 ของ Cr^{+3},เวลาการดูดซับ 60 นาที และอุณหภูมิ 30 ^{o}C)

2.4 ผลของความเข้มข้นของสารละลาย

ความเข้มข้นของสารละลายเริ่มต้นเป็นตัวแปรที่สำคัญอย่างมากในกระบวนการดูดซับโลหะในสารละลาย ผลของความเข้มข้นของสารละลายเริ่มต้นที่มีต่อเปอร์เซ็นต์การดูดซับของ Cr^{+3} แสดงดังภาพที่ 4.12 ในการทดลองใช้การปรับเปลี่ยนความเข้มข้นของสารละลายจาก 20 ถึง 100 mg/L และใช้ถ่านกัมมันต์ 1.2 g ค่า pH = 3.5 และ เวลาการดูดซับ 60 นาที ผลการทดลองที่ได้พบว่าการดูดซับของโลหะบนถ่านกัมมันต์ ทั้งนี้เนื่องจากปริมาณความเข้มข้นของสารละลายสูงๆ จะมีปริมาณของ Cr^{+3} รวมกันอยู่สูงมากบนพื้นผิวของถ่านกัมมันต์และสอดคล้องเพียงพอกับพื้นที่ผิวสูงของถ่านกัมมันต์ จึงทำให้มีการดูดซับที่สูงตามไปด้วย ทั้งนี้พิจารณาจากข้อมูลในช่วงการทดลองนี้เท่านั้น (ความเข้มข้นของสารละลายจาก 20 ถึง 100 mg/L) แต่อย่างไรก็ตามหลังจากช่วงการทดลองนี้การดูดซับมีแนวโน้มจะคงที่เนื่องจากความสามารถในการดูดซับบนพื้นผิวของถ่านกัมมันต์มีการอิ่มตัวหรืออยู่ในสภาวะสมดุลสำหรับปริมาณความเข้มข้นของสารละลายเริ่มต้นของโลหะใดโลหะหนึ่ง



ภาพที่ 4.12 แสดงความสัมพันธ์ระหว่างการดูดซับ Cr^{+3} กับความเข้มข้นของสารละลาย (pH 3.5 ของ Cr^{+3},เวลาการดูดซับ 60 นาที และ 1.2 g ของถ่านกัมมันต์/100 mL ของสารละลายอุณหภูมิ 30 ^{o}C)

2.5 ไอโซเทอมของการดูดซับ

ไอโซเทอมของการดูดซับของ Cr^{+3} ถูกคำนวณโดยใช้สมการของ Freundlich และ Langmuir สมการนี้จะพบได้ในบทที่ 2 ค่าปริมาณต่างๆที่คำนวณได้อาศัยข้อมูลจากการทดลองการดูดซับและแสดงในตารางที่ 4.5 จากข้อมูลไอโซเทอม และค่าสัมประสิทธิ์รีเกจชั่น (regression coefficients) ในตารางที่ 4.5 พบว่ากลไกของการดูดซับ Cr^{+3} บนถ่านกัมมันต์เหมาะสมกับแบบจำลองของ Langmuir มากกว่า Freundlich โดยค่าความสามารถการดูดซับ Cr^{+3} ของถ่านกัมมันต์มีค่าเป็น 13.93 mg/g

เมื่อเปรียบเทียบค่าความสามารถในการดูดซับ Cr^{+3} ของถ่านกัมมันต์ที่ผลิตจากเปลือกเมล็ดมะม่วงหิมพานต์กับถ่านกัมมันต์ที่ผลิตจากวัสดุชีวมวลจากงานวิจัยของนักวิจัยท่านอื่นๆ ดังแสดงในตารางที่ 4.6 พบว่าถ่านกัมมันต์ที่ผลิตจากเปลือกเมล็ดมะม่วงหิมพานต์ในงานวิจัยนี้มีค่าความสามารถในการดูดซับ Cr^{+3} สูงกว่าถ่านกัมมันต์ที่ผลิตจากวัสดุชีวมวลอื่นๆ ดังนั้นถ่านกัมมันต์ที่

ผลิตได้จากงานวิจัยนี้สามารถนำไปประยุกต์ใช้ในการบำบัดน้ำเสีย หรืออุตสาหกรรมน้ำดื่มได้อย่างมีประสิทธิภาพสูง

ตารางที่ 4.5 แสดงค่าการดูดซับ Cr^{+3} โดยการคำนวณตามสมการของ Freundlich และ Langmuir

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

ตารางที่ 4.6 แสดงการเปรียบเทียบความสามารถในการดูดซับ Cr^{+3} ของถ่านกัมมันต์ที่หลากหลาย

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

บทที่ 5
สรุปผล และข้อเสนอแนะ

สรุปผล

ในงานนี้สามารถเตรียมถ่านกัมมันต์จากวัสดุเหลือใช้ทางการเกษตรได้แก่ เปลือกเมล็ดมะม่วงหิมพานต์ โดยวิธีการกระตุ้นทั้งทางเคมีโดยใช้ KOH และทางกายภาพด้วยกาซ CO_2 เพื่อให้ได้ถ่านกัมมันต์ที่มีค่าพื้นผิวสูงๆให้เหมาะสมกับการนำไปประยุกต์ใช้เป็นตัวดูดซับกาซไฮโดรเจน จากผลการวิจัยสามารถเตรียมถ่านกัมมันต์ที่มีคุณภาพสูงได้ค่าพื้นที่ผิวสูงสุด 1120 m^2/g โดยเผาที่อุณหภูมิ 850°C เป็นเวลา 2.30 ชั่วโมง และใช้สารกระตุ้นในอัตราส่วน KOH/Char = 4 ค่าพื้นผิวที่ได้นี้มีค่าสูงพอสมควร จึงทำให้ถ่านกัมมันต์จากเปลือกเมล็ดมะม่วงหิมพานต์ที่เตรียมได้นี้ สามารถนำไปประยุกต์ใช้งานได้หลากหลาย เช่น ใช้เป็นตัวดูดซับกาซ ใช้ในการบำบัดน้ำเสีย และใช้ในอุตสาหกรรมน้ำดื่มได้เป็นอย่างดี สำหรับรายละเอียดอื่นๆที่สำคัญที่ได้จากงานวิจัยสามารถสรุปได้ดังนี้

1. การวิเคราะห์โครงสร้างผลึกด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ ผลการทดลองพบว่าถ่านกัมมันต์ที่เตรียมได้ทุกๆชิ้นงานจะมีโครงสร้างเป็นแบบ amorphous และเปลือกเมล็ดมะม่วงหิมพานต์มีโครงสร้างผลึกที่ไม่สมบูรณ์ไม่สามารถชี้ชัดโครงสร้างที่แน่นอนได้ เนื่องจากประกอบด้วยสารอินทรีย์ต่างๆมากมายในโครงสร้าง แต่ถ่านกัมมันต์ที่เตรียมได้ในอัตราส่วน KOH/Char ต่างๆและที่เวลาแช่ต่างๆ จะมีลักษณะของโครงสร้างที่แสดงพีคพอจะปรากฏให้เห็นได้บ้างที่มุม 2θ = 26° and 43° และเมื่อตรวจสอบเทียบกับพีคมาตรฐาน (JCPDS) พบว่าพีคจะสอดคล้องกับโครงสร้างของแกรไฟต์ ซึ่งเป็นลักษณะโครงสร้างปรกติของถ่านกัมมันต์

2. ผลการตรวจสอบกลุ่มฟังก์ชั่นด้วยเทคนิคอินฟราเรดสเปคโตรสโกรปี พบว่าสเปกตรัมส่วนใหญ่จะอยู่ในกลุ่มของออกซิเจนที่เป็นลักษณะทั่วๆไปของวัสดุชีวมวล เช่น กลุ่ม carbonyl, phenolic hydroxyl, carboxyl และ lactone

3. ผลการตรวจสอบโครงสร้างจุลภาคด้วยกล้องจุลทรรศน์อิเลกตรอนแบบส่องกราด ข้อมูลที่ได้จากการตรวจสอบด้วยกล้อง SEM พบว่าโครงสร้างทางจุลภาคของผงละเอียดถ่านกัมมันต์ที่เผาอุณหภูมิ 850 องศาเซลเซียส ในบรรยากาศของก๊าซไนโตรเจน และ ก๊าซคาร์บอนไดออกไซด์ จะประกอบด้วยโครงสร้างที่เป็นรูพรุนจำนวนมากคล้ายกับรังผึ้ง โดยการเผาที่เวลาการกระตุ้นสูงจะมี

ปริมาณปริมาณรูพรุนเพิ่มขึ้น และเช่นเดียวกันเมื่ออัตราส่วนของสารกระตุ้นสูงขึ้นปริมาณรูพรุนก็เพิ่มขึ้นและมีการจัดเรียงตัวของรูพรุนเป็นระเบียบขึ้นด้วยเช่นกัน

4. ผลการตรวจสอบพื้นที่ผิว (BET) พบว่าค่าพื้นที่ผิวของผงละเอียดถ่านกัมมันต์ที่เผาอุณหภูมิ 850 $^{\circ}$C และเผาแช่เป็นเวลา 20, 40, 60, 90, 120 และ 150 นาที ในบรรยากาศของกาซไนโตรเจน และ กาซคาร์บอนไดออกไซด์ จะมีค่า BET เพิ่มขึ้นเมื่อเวลาการกระตุ้นสูงขึ้น และปริมาณของสารกระตุ้นสูงขึ้น โดยจะมีค่าสูงถึง 1120 m^2/g สำหรับถ่านกัมมันต์ที่เตรียมได้ที่เวลาการกระตุ้น 150 นาที และปริมาณสารกระตุ้นในอัตราส่วน KOH/Char = 4 ดังนั้นด้วยค่าพื้นที่ผิวที่สูงนี้ผู้วิจัยคาดหวังว่าสามารถนำถ่านกัมมันต์ที่เตรียมจากเปลือกเมล็ดมะม่วงหิมพานต์นี้ไปประยุกต์ใช้เป็นตัวดูดซับกาซได้

5. การทดสอบประสิทธิภาพการดูดซับโลหะหนัก Pb^{+2} , Cd^{+2} และ Cr^{+3} ในสารละลายสังเคราะห์บนถ่านกัมมันต์ การทดลองการดูดซับจะหาประสิทธิภาพการดูดซับด้วยเครื่องวัดการดูดซับแบบอะตอมมิก และจากสมการดูดซับของฟรุนดลิชและแลงเมียร์ โดยศึกษาผลของตัวแปรต่างๆ เช่น pH ของน้ำที่มีโลหะหนักปนเปื้อน เวลาในการดูดซับ และปริมาณของถ่านกัมมันต์ที่ใช้ดูดซับ พบว่าถ่านกัมมันต์ที่เตรียมจากเปลือกเมล็ดมะม่วงหิมพานต์นี้ สามารถดูดซับโลหะหนักทั้งสามนี้ได้อย่างมีประสิทธิภาพสูง ซึ่งสามารถดูดซับได้มากกว่า 99% และเกือบถึง 100% ดังนั้นถ่านกัมมันต์ที่ผลิตได้จากงานวิจัยนี้สามารถนำไปประยุกต์ใช้ในการบำบัดน้ำเสีย หรืออุตสาหกรรมน้ำดื่มได้อย่างมีประสิทธิภาพสูงเช่นกัน

ข้อเสนอแนะ

ในการดำเนินงานต่อเนื่องจากการวิจัยนี้ จะมีข้อเสนอแนะสำหรับงานในอนาคตที่ควรจะทำดังต่อไปนี้

1. ในการศึกษานี้ใช้เทคนิค SEM เท่านั้น สำหรับการตรวจสอบโครงสร้างทางจุลภาค ในงานต่อไปควรจะใช้เทคนิคของกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (Transmission Electron Microscopy (TEM)) ร่วมด้วย เนื่องจากเทคนิคนี้จะได้ข้อมูลโครงสร้างทางจุลภาคที่เล็กและละเอียดกว่า และจะได้ข้อสรุปที่เกี่ยวกับพัฒนาการของโครงสร้างทางจุลภาคที่ดียิ่งขึ้นกว่า

2. ควรจะทดลองการกระตุ้นโดยใช้สารเคมีชนิดอื่นบ้าง เช่น $ZnCl_2$, H_3PO_4 และอื่นๆ และควรจะทดลองเพิ่มอัตราส่วนของสารกระตุ้นเพิ่มขึ้นอีกเพื่อดูถึงแนวโน้มของการเปลี่ยนแปลง

3. ในงานต่อไปควรจะศึกษาเทคนิคการเตรียมโดยใช้วิธีไมโครเวฟ เนื่องจากใช้เวลาในการเผาน้อยลงทำให้ประหยัดเวลา และพลังงาน

4. ควรจะศึกษาการเตรียมวัสดุชีวมวลชนิดอื่นบ้างเช่น เมล็ด หรือเปลือกผลไม้ ต่างๆที่เหลือทิ้งจากการเกษตร

5. ควรทดสอบประสิทธิภาพการดูดซับสารปนเปื้อนในสารละลายชนิดอื่นๆบ้าง

6. ในการศึกษานี้ไม่ได้ทดสอบการดูดซับกาซไฮโดรเจนเพียงแต่เตรียมถ่านกัมมันต์ให้ได้พื้นที่ผิวสูงมากที่สุดที่จะเพียงพอในการดูดซับกาซไฮโดรเจน ดังนั้นในการศึกษาต่อไปควรจะทดสอบประสิทธิภาพในการดูดซับกาซไฮโดรเจนด้วย

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Adsorption of Lead(II) and Cadmium(II) ions from aqueous solutions by adsorption on activated carbon prepared from cashew nut shells

S. Tangjuank, N. Insuk, J. Tontrakoon, V. Udeye

***Abstract*—**Cashew nut shells were converted into activated carbon powders using KOH activation plus CO_2 gasification at 1027 K. The increase both of impregnation ratio and activation time, there was swiftly the development of mesoporous structure with increasing of mesopore volume ratio from 20-28% and 27-45% for activated carbon with ratio of KOH per char equal to 1 and 4, respectively. Activated carbons derived from KOH/char ratio equal to 1 and CO_2 gasification time from 20 to 150 minutes were exhibited the BET surface area increasing from 222 to 627 $m^2.g^{-1}$. And those were derived from KOH/char ratio of 4 with activation time from 20 to 150 minutes exhibited high BET surface area from 682 to 1120 $m^2.g^{-1}$. The adsorption of Lead(II) and Cadmium(II) ion was investigated. This adsorbent exhibited excellent adsorption for Lead(II) and Cadmium(II) ion. Maximum adsorption presented at 99.61% at pH 6.5 and 99.45% at optimum conditions. The experimental data was calculated from Freundlich isotherm and Langmuir isotherm model. The maximum capacity of Pb^{2+} and Cd^{2+} ions was found to be 28.90 $mg.g^{-1}$ and 14.29 $mg.g^{-1}$, respectively.

***Keywords*—**Activated carbon, Cashew nut shell, Heavy metals, Adsorption

1. Introduction

Water pollution is serious problem of the environment. The increasing in the use of major 20 heavy metals from over the past few decades has inevitably resulted an increasing flux of metallic substances in natural source of water. Resulting from many industries such as tannery, mining, alloying and battering produce significantly major hazardous heavy metal ions such as lead, cadmium and mercury [1]. All lead compounds are considered cumulative poisons. Acute lead poisoning can effect nervous system and gastrointestinal track [2]. The harmful of cadmium include number of acute and chronic disorders such as "itai-itai" disease, emphysema and hypertension [3]. Conventional technique for heavy metals removal water and wastewater including electroplating, evaporating, oxidation, reduction, membrane separation, ion exchange and adsorption. Among these methods, adsorption is worthy economical and effective [4]. Various adsorbents such as silica gel, alumina clay, synthetics polymer resins and carbonaceous materials are used in adsorption method [5]. The activated carbon is the major applying for removal heavy metals adsorption [6], [7]. Agriculture wasted is highly uses as raw material for produce the activated carbon because large quantity of unused and low cost on the production [8]. In recently, activated carbons can be commonly produced from coal, wood or agricultural wastes such as coconut and palm shell, corncob, rich husk, etc., activated by physical or chemical process. Because of their special pore structure, they have super adsorption capacity and are generally used in variety industrial and domestic fields, such water treatment, solvent decolourization, catalyst supports of fuel cell and surpercapacitors [9]. In recent years, there is growing interest in the production of activated carbons from agricultural by-products and residual wastes. In previous studies, many researchers found that activated carbons from coconut shells [10], and pistachio shells [11] by KOH activation and CO_2 gasification are essentially microporous with a fairly high surface area [12]. Chemical carbonization of baggage with concentrated sulfuric acid at a 4: 3 ratio and subsequent CO_2 activation at 900°C produced activated carbons with high surface areas (403-1433 $m^2.g^{-1}$) [13]. The above mentioned studies show that KOH activation and CO_2 gasification enhance high surface area in activated carbon. However, there are few reports on the preparation and characterization of activated carbons derived from cashew nut shells [14] - [16] but the study about how to prepare activated carbon from cashew nut shells with large surface area is scarce in literature. The cashew tree, Anacardium occidentale Linn., is a native plant of eastern Brazil and is introduced into other tropical countries such as India, Africa, Indonesia and South East Asia in the 16th century. It is now found widely in other parts of Central America and the Southern of Thailand, cashew nut shells are usually neglected and abundant agricultural waste. The cashew nut shells have found important commercial usage as the phenolic raw material for the manufacture of certain resins and plastics having unusual electric and frictional properties. Therefore, it is interesting to develop the cashew nut shells as activated carbons with large surface area.

The objectives of this work are to prepare activated carbons from cashew nut shells using KOH activation under N_2 and CO_2 atmosphere. The prepared activated carbon which characterized their properties from typical technique was use for removal of lead(II) and

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copper(II) ions in aqueous solutions by batch method. The parameters such as effect of initial pH of heavy metal solution, contact time, dosage of activated carbon, and initial concentration of heavy metals were studied.

2. Experimental

2.1. Preparation of activated carbon

Chars were prepared from cashew nut shells by carbonization in the absence of air. These chars were well mixed with water and KOH in a grass beaker with the weight ratios of KOH per char equal to 1 and 4. The mixed chars were dried in oven at 120°C for 24 h to obtain the dried mixtures consisting of chars and KOH. The dried mixtures were heated in oven from room temperature to 850°C (1027 K) with a rate of 15 °C.min^{-1}, and temperatures for 20 to150 minutes. When the time was up, the nitrogen gas was switch off and CO_2 immediately flowed into the oven. The activated carbons obtained were thoroughly washed with distilled water several times, dried at 110°C, cooled at room temperature and stored in desiccators for activated carbon characterization.

2.2. Characterization of the produced activated carbon

FT-IR spectrometer (Spectrum GH, Perkin Elmer) was employed to determine the presence of surface functional groups in samples and samples were analyzed as KBr pellets. The change of crystal structures was characterized by X-ray diffractionmeter (XRD) with CuK-α radiation (Siemens, D-500). The microstructure of activated carbon was investigated with Scanning electron microscope (LEO, Model 1455VP). The BET surface area of the activated carbon was obtained from the N_2 adsorption isotherm at 77K with adsorption meter (Micromeritics, Porous Materials, BET-2020). The yield was calculated by the following formula as in (1);

$$\%\text{yield} = (\text{weight of the final products})/(\text{weight of the initial samples}) \times 100. \quad (1)$$

2.3. Adsorption experiments

The activated carbon which has highest BET surface area (1127 m^2.g^{-1}) were chosen as adsorbent for adsorption of heavy metals solution. The adsorption of Pb(II) and Cd(II) ions from aqueous solution was investigated by batch method. The effect of initial pH, contact time and activated carbon dosage and initial heavy metals concentration were studied. The aqueous which aliquots of 50 mL of Pb(II) and Cd(II) solution of 40 mg.L^{-1} were poured into Erlenmeyer flask(100 mL) containing accurately weight amount of activated carbon which used as adsorbents. The required initial pH of solution were adjusted by adding 0.1 M HCl or NaOH. Then, the flasks were shaken continuously at 200 rpm by auto-shaker for prescribed length of time attain to equilibrium. After filtration through Whatman filter paper, Pb(II) and Cd(II) ions remaining in the solution were determined by atomic adsorption spectrometer(Varian SpectrAA 220).

The amount of metals ion adsorbed[17] was calculated in percentage(%) and metal uptake(q_e) as in (2) and (3);

$$\%\ \text{Adsortion} = (C_i - C_e)/C_e \times 100 \quad (2)$$

$$q_e = (C_i - C_e)\, V/1000\, w \quad (3)$$

where C_i is the initial concentration (mg.L^{-1})
C_e is metal concentrations at various time interval (mg.L^{-1})
V is the volume of the heavy metal solution (mL)
w is the mass of adsorbent(g)

The Freundlich equation [18]-[21] is in the linearise form as in (5) ;

$$\log q_e = 1/n\ (\log C_e) + \log k \quad (5)$$

where q_e is the metal ions adsorbed(mg.g^{-1}) at equilibrium
C_e are the equilibrium concentration(mg.L^{-1})
k is Freundlich constant with multilayer adsorption
n is adsorption intensity

The Langmiur equation [22] is in the form as in (6);

$$C_e / q_e = 1/ q_{max}\ K_L + Ce /q_{max} \quad (6)$$

where q_e is the metal ions adsorbed(mg.g^{-1})
C_e are the equilibrium concentration(mg.L^{-1})
q_{max} is monolayer adsorption capacity(mg.g^{-1})
K_L is Langmiur adsorption constant

Langmuir and Fruendlich isotherms were obtain from the experiments.

3. Results and Discussion

3.1. Effects of KOH/char and activation time

Fig. 1 shows the effects of the activation time on the yield of activated carbons. It can be seen that, an increase of activation time decreases the yield of activated carbons. For the activated carbons of group with KOH/char ratio equal to 4, the yield decreased from 82-64% with the increase of the activation time from 20–150 minutes. For the activated carbons of group with KOH/char ratio equal to 1, the yield decreased from 77-60% with the increase of the activation time from 20–150 minutes. The results indicate that with increase of the activation time the yield of group with KOH/char ratio equal to 1 are lower than that of group with KOH/char ratio equal to 4. This is due to the occurrence of the activation reaction between CO_2 and carbons, so the longer activation time favors the progress of activation reaction, which increases in the degree of burning of the produced carbon. However, a large amount of KOH enveloped the carbon, thus lowered the reaction between CO_2 and carbon, resulting of decrease in the degree of burning of the produced carbon.

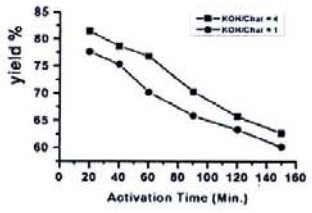

Fig. 1. Effect of activation time on yield(%) of the activated carbons.

3.2. Surface chemistry

The adsorptive capacity of the activated carbon is influenced by its surface chemical structure. The functional groups suggested most

often in activated carbon are carboxyl groups, phenolic hydroxyl groups, carbonyl groups and lactone groups [24]. The FTIR spectra of activated carbon are shown in Fig. 2. The spectra were recorded from 4000 cm^{-1} to 400 cm^{-1}. The FTIR spectrum of the raw cashew nut shell (Fig. 2a) was quite similar to that of rockrose [25], which is also a type of lignocellulosic materials. The band at about 3436 cm^{-1} was attributed to ν(O-H) vibrations in hydroxyl groups or surface-bonded water. The location of hydrogen-bonded OH groups is usually in the range of 3200-3650 cm^{-1} for alcohols and phenols. The band located around 2923 and 2852 cm^{-1} corresponded to ν(C-H) vibrations in methyl and methylene groups [26], [27]. The ν(C=C) vibrations can also be inferred from peak in the region of 1631 cm^{-1}. The band around 1457 cm^{-1} corresponded to carboxylate groups (-COOH). The band shows around 1113 cm^{-1} referred to the vibration of the C-O group in lactones [28]. The band at 1384 cm^{-1} could be attributed to ν(C-O) vibrations in carboxylate groups. The appearance of bands between 1300 and 900 cm^{-1} could be assigned to C-O stretching vibrations. Absorption due to γ(C-H) bending occurred at 776 cm^{-1} whilst γ(O-H) bending attributed to the absorptions at 579 cm^{-1}. For activated carbons with KOH/char ratio equal to 1 with activation time 20 min (Fig. 2b) and 60 min (Fig.2c), appearance of bands located at 2335 and 1740 cm^{-1} which could be assigned to the C=O stretching vibrations in ketones or carbonyl groups [29] while the bands at 2923 and 2852 cm^{-1} disappeared. The decreasing of the intensity of the peaks between 3436 cm^{-1} indicated a decomposition of the cellulose-based cashew nut shell structure and the loss of surface-bonded moisture. Besides these peaks, the other bands in all activated carbons were quite similar even though the magnitude of the bands decreased with increasing activation time, which suggested that they have similar structures. These trends were also consistent with the activated carbons with KOH/char ratio equal to 4 (Fig. 2d-2e). These results agree with the surface chemistries of other agricultural by-products, such as peach stones [30] and pistachio-nut shell [31].

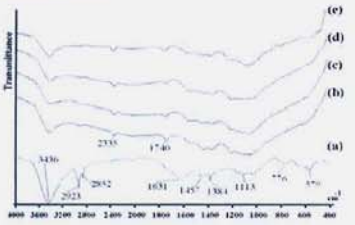

Fig.2. FTIR spectra of the cashew nut shell and activated carbons; (a) the cashew nut shell, (b) KOH/Char = 1 with activation time 20 min, (c) KOH/Char = 1 with activation time 60 min, (d) KOH/Char = 4 with activation time 20 min, (e) KOH/Char = 4 with activation time 60 min.

3.3. X-ray analysis

Fig. 3 shows the X-ray diffraction profile of the raw cashew nut shell and the prepared activated carbons at different times and KOH/Char ratios. The raw material (Fig.3a) had a less organized structure with no indication of any specific crystalline structure probably due to the various organic impurities and volatile matters present within the structure. For char (Fig. 3b), there appeared to have a peak at around $2\theta = 26^{\circ}$. Whilst at a furnace temperature of 850 °C, much of the volatiles and other impurities would have been released and therefore there was formation of any crystalline structures for activated carbons (Fig. 3c-3f). The results indicated that the diffraction profiles of all activated carbons exhibited broad peaks and the absence of a sharp peak revealed a predominantly amorphous structure, and two broad peaks seemed to appear at around $2\theta = 26^{\circ}$ and 43° which were similar to the peaks of crystalline carbonaceous structure such as graphite (JCPDS). In addition, increasing activation time (Fig. 3c-3f) resulted in slightly sharper peak at around 43°, signified an increasing regularity of crystal structure and resulted in better layer alignment. However, the XRD peaks of group of KOH/char ratio equal to 1 (Fig. 3c and 3d) and 4 (Fig. 3e and 3f) were very similar. This indicated that the KOH effect was not significant for development structure.

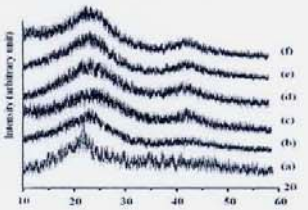

Fig.3. XRD patterns of the cashew nut shell, char and activated carbons; (a) Cashew nut shell, (b) Char, (c) KOH/Char = 1 with activation time 20 min, (d) KOH/Char = 1 with activation time 60 min, (e) KOH/Char = 4 with activation time 20 min, (f) KOH/Char = 4 with activation time 60 min.

3.4. Microstructure

Typical SEM microstructures of various conditions of activated carbon from cashew nut shell are shown in Fig. 4a-4g. The char surface (Fig. 4a) shows the irregular structure with prolonged slit pores of the order of 10 μm. Activation of the sample for KOH/Char equal to 1 produced the irregular structure with rough texture and a large numbe of shallow cavities on the surface (Fig. 4b-4d). With the increase of activation time from 20 to 120 minutes, the random arrays of pore structures had more appeared due to the progress of activation reaction between CO_2 and carbon and the release of the volatile. On the other hand, the increasing both of impregnation ratio and activation time, more pores appear in the interporous areas. With increasing of ratio of KOH/char from 1 to 4 resulted in significantly different of surface and pore structures as observed in Fig. 4e - 4g. For the ratio of KOH/Char equal to 4 with activated time 20 min (Fig. 4e), the surface was enveloped with an amount of KOH and interspersed with generally large pores due to some of the volatiles being evolved. When the activation time was increased from 20 to 120 minutes, decreased the amount of KOH on the surface (analogous to release of volatiles), and there are many uniformly pore structures and becoming honeycomb shape as shown in Fig. 4f-4g. This is because at prolonged activation time favors the progress of activation reaction between CO_2 and carbon, the surface was destroyed by violent activation and large pore numbers were created with increased activation time (analogous to release of volatiles) [32]. Meantime, there were the development of porosity due to reaction between KOH and carbon. This is attributed to the fact that the most of KOH seeped deeply into the interior of char; while at higher KOH/Char ratio, the more severe etch of the wall takes place to create a great quantity of micropores, resulting in an increase in the pore volume [33]. This difference in the development of pore structure can also exhibit the apparently larger BET surface area of the resulting activated carbons produces with higher impregnation ratio of KOH. Furthermore, the SEM result shows that the activated carbon appears to have well developed macropores of the order of 10-30 μm.

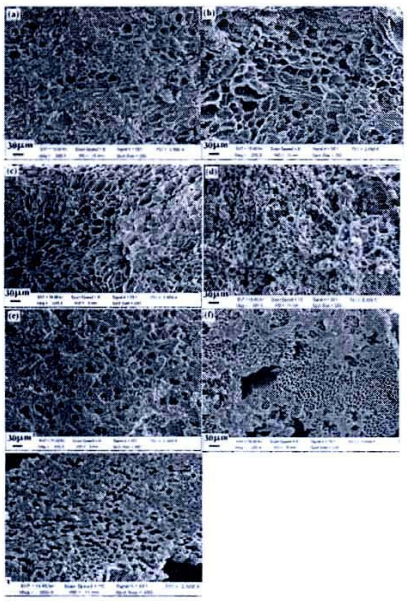

Fig.4. SEM micrographs of the char and activated carbons; (a) Char, (b) KOH/Char = 1 with activation time 20 min, (c) KOH/Char = 1 with activation time 60 min, (d) KOH/Char = 1 with activation time 120 min, (e) KOH/Char = 4 with activation time 20 min, (f) KOH/Char = 4 with activation time 60 min, (g) KOH/Char = 4 with activation time 120 min.

3.5. Surface area

The effect of KOH/Char has shown in table. 1. It can be seen that the activated carbon with KOH/char ratio equal to 4 and CO_2 gasification time from 20 to 150 min exhibited higher BET from 682 to 1120 $m^2.g^{-1}$ and pore volume from 0.3675 to 0.5789 $cm^3.g^{-1}$. This is due to at a longer CO_2 activation time, there is an sufficient amount of CO_2 reacting with the carbon to produce pores, while at higher KOH/Char ratio, the more severe etch of the wall takes place to create a great quantity of micropores, resulting in an increase in the pore volume and the high BET is obtained. In the classification by the International Union of Pure and Applied Chemistry (IUPAC), pores are classified as micropores(< 2 nm diameter), mesopores (2-50 nm diameter) and macropores (>50 nm diameter). It can be seen from table.1 that all activated carbons prepared at different ratio of KOH/Char are composed mainly of mesopore with a pore size about 2.1–2.3 nm; with increasing of KOH/Char, the ratio of mesopore volume and the pore volume increase. For the activated carbon with KOH/char ratio of 4 with activation time of 20-150 minutes, there was swiftly the development of mesoporous carbon with increase of mesopore volume ratio from 28-46%, with the average pore size being 2 nm, while mesopore volume ratio of KOH/char ratio of 1 increases slowly from 21-28%. With increasing activation time, probably due to the violent attack of carbon by chemical materials, the opening of pores is clearly damaged and party burnt, resulting in the widening of pore diameters, i.e. the increasing of mesopore volumes and decreasing of micropore volumes. These results indicate that the increase in activation time and the KOH/Char weight ratio produces an increase in pore and mesopore volumes. Therefore, in this work cashew nut shells activated carbon had predominantly mesopores, which make them more suitable for liquid-phase adsorption for example wastewater treatment or drinking water purification. It was found that the KOH activation could provide the activated carbon with relatively high levels of BET surface area when compared to other activation methods. Based on this observation, it can suggest that cashew nut shell is a good material for the preparation of a high quality activated carbon.

Table 1 Physical properties of activated carbons derived from cashew nut shells under different.

Sample KOH/Char	Gasification time (min.)	BET ($m^2.g^{-1}$)	Pore volume ($cm^3.g^{-1}$)	Average pore size (nm)
	20	222	0.1127	20.35
	40	263	0.1321	20.11
	60	272	0.1389	20.48
1	90	285	0.1450	20.36
	120	553	0.2802	20.26
	150	627	0.3142	21.46
	20	682	0.3675	21.57
	40	699	0.3682	21.07
	60	819	0.4258	20.80
4	90	828	0.4431	21.42
	120	995	0.5677	21.63
	150	1120	0.5789	22.57

3.6. Adsorption Efficiency

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The effect of initial pH on the adsorption is exhibited in Fig. 4. The result of Pb(II) and Cd(II) ions from Fig. 5 exhibited in the high range 97.50 to 99.13 %. The maximum adsorption efficiency for both of Pb(II) and Cd(II) ion was obtained at pH 6.0-6.5 respectively. The pH of the solution at the equilibrium increased initial pH from 6.0-6.5 to 7.0-7.75. The pH of the initial solution are affected variables in the adsorption process that treated surface charge of the adsorbent and degree of specification and ionization of activated carbon. Between pH 6.0-6.5, the surface is negative charge on the surface of the adsorbent increase there for Pb^{2+} and $Cd2^{+}$ could be enhanced the physical sorption on active site. Thus, the optimum condition value were chosen at 6.0 for Cd(II) and 6.5 for Pb(II) adsorption for further experiments.

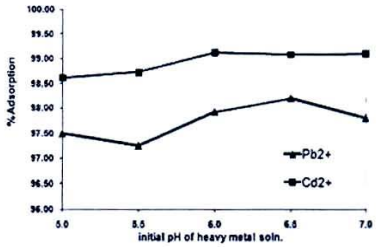

Fig. 5. Effect of initial pH on adsorption of Pb(II) and Cd(II) solutions(initial concentration 40 $mg.L^{-1}$, contact time 30 min. , 0.6 g Activated carbon/solution 50 mL and temp. 303 K).

The effect of the contact time on adsorption of Cd(II) and Pb(II) ions is presented in Fig. 6. For Cd(II), the adsorption equilibrium are obtained at 30 to 120 minutes which showed high range of adsorption of 99.68-99.83%, respectively. The percentage removal of Cd(II) ions increase rapidly from 5 to 30 minutes and then

close to constant value of adsorption efficiency although further increasing contact time till 120 minutes. Thus, the equilibrium contact time of 30 minutes for Cd^{2+} adsorption could be required because of the adsorpbate diffused around adsorbent particle and penetrated into internal pore. Though, the equilibrium of the contact time on adsorption of Pb(II) ion was attained after shaking 5 to 30 minutes, then desorption are received. However, it could be re-adsorbed at high efficiency are shown at 90 to 120 minutes. However, from the results, the agitation time required for uptake of Pb(II) ions and Cd(II) ion were fixed at 30 minutes for another next parameter to make sure that the equilibrium was accomplished. As seen from Fig. 5, Pb^{2+} ions exhibited greater attributed than Cd^{2+} ions.

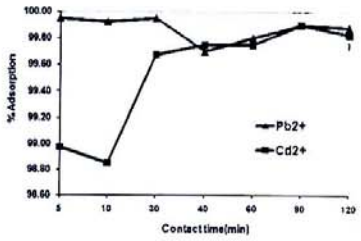

Fig. 6. Effect of contact time on adsorption of Pb(II) and Cd(II) ions (initial concentration 40 $mg.L^{-1}$, initial pH of heavy solution of Pb(II) 6.5 and Cd(II) 6.0, 0.6 g Activated carbon/ solution 50 mL and temp. 303 K).

of activated carbon dosage on adsorption of Cd(II) and Pb(II) ions is shown in Fig. 7. For both of heavy metal ion adsorption, the optimum of adsorbent were chosen as 0.6 g per 50 mL of solution. However, the increasing of removal adsorption percentage while increasing adsorbent dosage up to certain quantity and then seem to be almost constant. Thus, sufficiency site are mainly essential for adsorption of heavy metal solution. The high BET surface of activated carbon prepared from cashew nut shell which total external and internal active pore site could be indicated predomitary the adsorption efficiency. Because of very tiny of adsorbent with short contact time are the important point for economical wastewater treatment application [20]. Therefore, the high percentages of adsorption could be indicated that activated carbon from cashew nuts that play as excellent adsorbent.

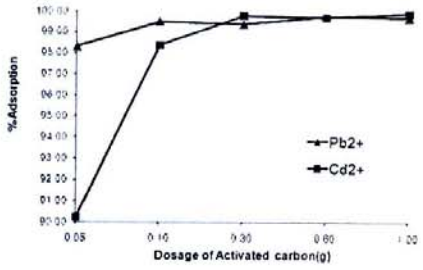

Fig. 7. Effect of activated carbon dosage on adsorption of Pb(II) and Cd(II) ions (initial concentration 40 $mg.L^{-1}$, initial pH of heavy solution of Pb(II) 6.5 and Cd(II) 6.0, contact time 30 min. and temp. 303 K).

The effect of initial concentration on the percentage removal of Pb(II) and Cd(II) ions by activated carbon prepared from cashew nut shell is shown in Fig. 8. where it is seen that the adsorption of Pb(II) ions decrease from 99.9% to 99.28% and CdII) ions is decrease from 99.6% to 91.45% , respectively,. For this case, the increase of solution concentration leads to a significantly decrease of the adsorption. Cadmium ions has significantly decrease of adsorption capacity more than Pb(II) ions. This was due to high initial concentrations the number of mole of heavy Pb(II) and Cd(II) ions available to the surface are very high, so functional adsorption become dependent on initial concentration. This characteristic indicated that surface saturation was dependent on initial metal ions concentration.

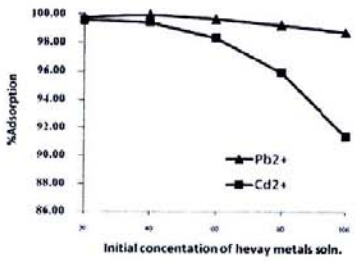

Fig. 8. Effect of initial concentration of heavy metals solution on adsorption of Pb(II) and Cd(II) ions (initial pH of heavy solution of Pb(II) 6.5 and Cd(II) 6.0, contact time 30 min., 0.6 g Activated carbon/solution 50 mL and temp. 303 K).

Freundlich and Langmuir constant and regression coefficient calculated from the adsorption data are given in Table 2. The values of regression coefficient(R^2) of both model close to linear are suitable for describing the adsorption of lead [34]. Hence, the adsorption both of heavy metals activated carbon prepared from cashew nut shell seem to be favorable. But cadmium adsorption fitted the Freundlich more than Langmuir model. The adsorption capacity of activated carbon prepared from cashew nut shells for uptake of Pb(II) and Cd(II) ions is 28.90 and 14.29 $mg.g^{-1}$, respectively.

Table 2 Values of Freundlich and Langmuir constants for adsorption of Pb(II) and Cd(II) ions.

Heavy metals	Freundlich constant				Langmiur constants		
	q_{max}	K	$1/n$	R^2	Adsorption capacity q_{max} (mg/g)	K (L/mg)	R^2
Lead(II)	1.320	0.859	0.168	0.945	28.90	0.0029	0.922
Cadmium(II)	1.390	0.289	0.161	0.933	14.29	0.1280	0.845

The comparison of adsorption capacity of various adsorbents for lead and cadmium ions taken from literatures are showed in Table 3. From these results could be assess the quantitatively the binding capacities of prepared activated carbon from cashew nut are competitive when compare other adsorbent. However, prepared activated carbon exhibited preferred Pb(II) ions adsorption more than Cd(II) ions adsorption.

Table 3 Comparison of adsorption capacity of various sorbent for Pb(II) and Cd(II).

Sorbent	Adsorption capacity(mg/g)		pH	C_0(mg/L)	Reference
	Pb(II)	Cd(II)			
Coconut shell carbon	26.50	-	4.5	50	[35]
Eichhornia activation	16.58	9.30	3.0	50	[1]
Hazelnut husk A.C.	13.05	-	5.7	40	[17]
Ceiba Pentandra hulls	-	19.50	5.7	80	[20]
Cashew nut shells A.C.	28.90	14.29	6.0-6.5	40	This study

4. CONCLUSIONS

A high BET surface area activated carbons could be prepared from cashew nut shells by KOH activation plus CO_2 gasification. FTIR spectrum of activated carbons exhibited the presence of different oxygen groups, and aromatic carbon structures. The X-ray diffraction profiles showed a predominantly amorphous structure, and two broad peaks seemed to appear at around $2\theta = 26^\circ$ and 43° which were similar to the peaks of crystalline carbonaceous structure such as graphite. SEM photographs showed that the structure of activated carbons composed of a great porous with honeycomb shaped and increased with increase of KOH/char ratio and gasification time. Increasing activation time from 20 to 150 min resulted in higher values of BET surface area, pore volume and ratio of mesopore volume. The activated carbons prepared at an activation time of 150 minutes with KOH/char ratio to 4 yielded the highest BET surface area(1120 $m^2.g^{-1}$). The optimum conditions of lead and lead showed highly 99.61% and 99.45%, respectively. The adsorption capacity of both of heavy metals exhibited high values that use as beneficial adsorbent. The study indicated that activated carbon prepared from cashew nut shell could be used as an effective adsorbent for the treatment of lead and cadmium aqueous wastewater.

Acknowledgment

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Full Length Research Paper

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

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

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

INTRODUCTION

Chromium (III) is an essential microelement that can be toxic in large doses(100 mg/L) (Khawaja, 1998). The toxicity of chromium compounds depends on the oxidation state of the metal. Occupational exposure to chromium (VI) has been associated with increased incidence of lung cancer. The efficacy of chelating therapy in chromium poisoning has not been proven (US, 1998). Trivalent chromium compounds are considerably less toxic than the hexavalent compounds and are neither irritating nor corrosive under normal conditions. However, all forms of chromium can be toxic at high levels. People who are allergic to chromium may have asthma attacks after breathing high levels of chromium (III) in air (Song et al., 2000; Alaerts et al., 1989). Repeated or prolonged skin contact may cause irritation. In severe cases, skin allergy can occur with itching, redness and/or an eczema-like rash. Chromium (III) compounds that entered the body can be inhaled or ingested. Both chromium (III) and chromium (VI) have high chronic toxicity to aquatic life. A long-term exposure to trivalent chromium is known to cause allergic skin reaction and cancer (Bansal et al., 1979). Many studies have investigated the adsorption of trivalent chromium and hexavalent chromium on activated carbon (Ramos et al., 1995; Valdimir and Danish, 2002). Cost Effective adsorbents for environmental treatment of metal containing is required. A low cost adsorbent is defined as by-product or waste material from industrial process and agricultural. Many processes were used for metal removal from wastewater such as ion exchange (Tiravanti et al., 1997), coagulation/flocculation (Song et al., 2004), filtration and membrane (Fabianil et al., 1996; Hafez et al., 2002). Activated carbons prepared from agriculture wastes are more effective due to some specific characteristics with high BET surface area (Kuniawan et al., 2006). Thus, low cost activated carbon can be used as adsorbent for the removal of heavy metals. Few studies performed Cr(III) adsorption on activated carbon. They reported the optimum pH value at 5 and the capacity of adsorption can be fitted to the Langmuir isotherm (Huang and Wu, 1977; Alaerts et al., 1989; Ramos et al., 1995).

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

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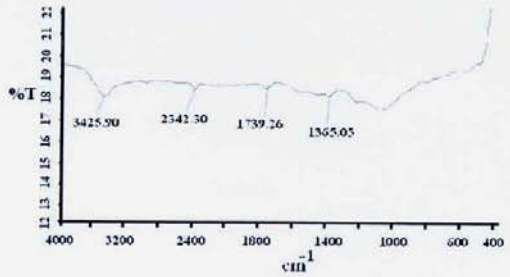

Figure 1. FT-IR spectrum of activated carbon derived from cashew nut shells.

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

MATERIALS AND METHODS

Preparation of activated carbons

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

Characterization of the produced activated carbon

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

Adsorption experiments

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

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

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

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

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

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

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

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

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

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

Langmuir and Fruendlich isotherms were obtained from the experiments.

RESULTS AND DISCUSSION

Characteristics of the adsorbent

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

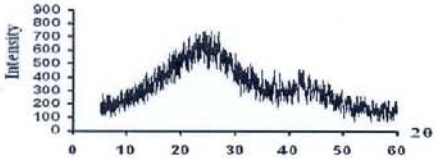

Figure 2. X-ray diffraction of activated carbon derived from cashew nut shells

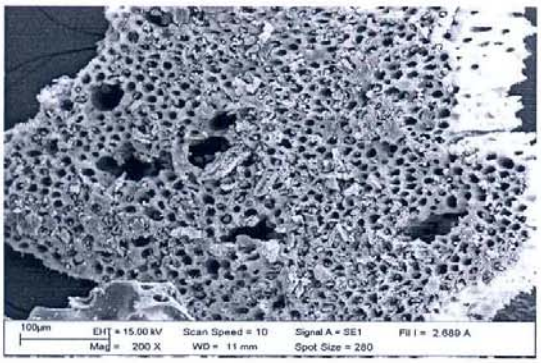

Figure 3. Scanning electron micrograph of activated carbon derived from cashew nut shells.

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

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

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

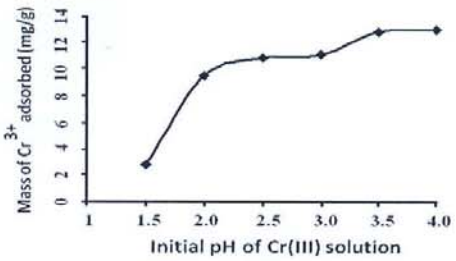

Figure 4. Effect of initial pH on adsorption capacity of Cr(III) solution (initial concentration 100 mg/L, contact time 60 min. and 0.6 g activated carbon/ solution 100 mL).

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

Effect of initial pH of solution

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

Effect of contact time

The equilibrium time is the one parameter for an economic wastewater treatment. The contact time in the

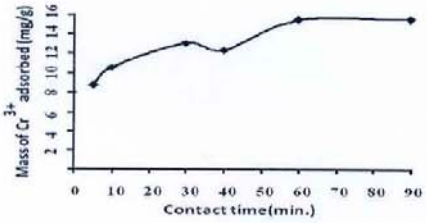

Figure 5. Effect of contact time on adsorption capacity of Cr(III) solution (initial concentration 100 mg/L, initial pH 3.5 of Cr(III) solution and 0.6 g activated carbon/ solution 100 mL).

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

Effect of adsorbent dosage

The effect of the adsorption of Cr(III) ions on dosage was studied by varying amount of adsorbents while keeping pH(3.5), contact time(60 min), initial concentration of Cr(III) solution(100 mg/L), shaking speed(200 rpm) and temperature(30℃) constant. A dosage of the adsorbent has a great influence for adsorption process. As seen from Figure 6 which shows the effect of adsorbent dosage on removal of Cr(III), the percentage of Cr(III) removal was increasing with the increase in adsorbent dosage. The removal was increasing significantly as dosage increased from 0.6 - 1.2 g and then tends to constant as almost 100%. The Cr(III) removal values were found to be 84% and more than 99% for adsorbents dosage of 0.6 and 1.2 g, respectively. The effect of adsorbents dosage on adsorption capacity of Cr(III)

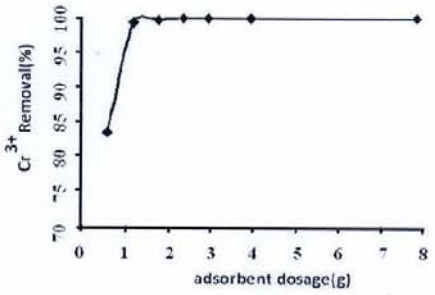

Figure 6. Effect of adsorbents dosage on % removal of Cr(III) ions for aqueous solutions (initial concentration 100 mg/L, initial pH 3.5 of Cr(III) solution and contact time 60 min).

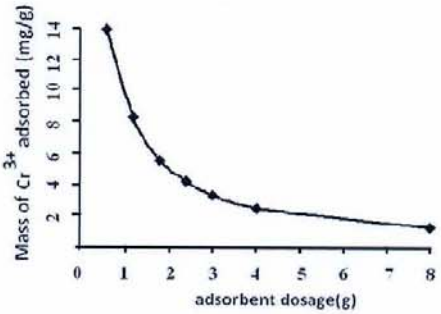

Figure 7. Effect of adsorbent dosage on adsorption capacity of Cr(III) solution(initial pH 3.5 of Cr(III) solution, contact time 60 min. and initial concentration of Cr(III) solution 100 mg/L).

solution is shown in Figure 7. The results indicate that the Cr(III) adsorption capacity of activated carbon decreased with increasing adsorbent dosage. This implies that the amount of the number of binding site increased which resulted in a split of the flux of Cr(III) aqueous solution concentration and the solute concentration on the surface area of activated carbon (Huang and Wu, 1975; Montanher et al., 2005). This decrease may be ascribed to the electrostatic interactions and interference of binding site which have an influence to reduce adsorbent densities (Cheng and Yang, 1975).

Effect of initial concentration of Cr(III) solution

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

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

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

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

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

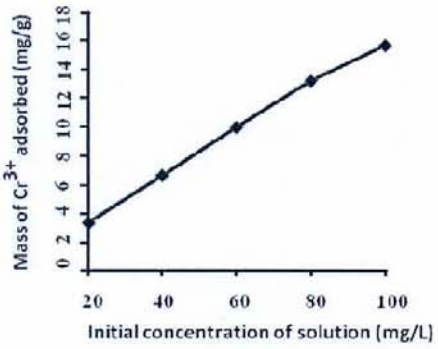

Figure 8. Effect of concentration of Cr(III) solution on adsorption capacity(initial pH 3.5 of Cr(III) solution, contact time 60 min. and 1.2 g activated carbon/solution 100 mL).

on adsorption capacity is represented in Figure 8. The concentrations varying from 20 to 100 mg/L were studied. It is seen that increasing the initial Cr(III) concentration resulted in increase in Cr(III) adsorbed on activated carbons. This is because at high initial concentration the number of Cr(III) ions available to the surface sufficient area was high. This adsorption indicates that surface saturation replies on initial concentration.

Adsorption isotherm

The adsorption isotherms of trivalent chromium were calculated. Experimental data was fitted to both Freundlich and Langmuir models. In the Langmuir model, monolayer adsorption capacity; q_{max} (mg/g) of activated carbon prepared from cashew nut shells and other parameters were determined following linearized form of Equation 3. The heterogeneous adsorption capacity; q_e (mg/g) was determined following from Equation 2. The parameter calculated from the adsorption data is exhibited in Table 2. As can be seen from isotherms and regression coefficients, Cr(III) adsorption fitted well with the Langmuir model more than the Freundlich model. The adsorption capacities q_{max} (mg/g) and k_L of the activated carbon for the uptakes of Cr(III) ions were 13.93 mg/g and 0.0100, respectively. The comparisons of the Cr(III) ions adsorption capacity (%) with different adsorbents taken from literature are presented in Table 3. The results of the present work show that the adsorption capacity was higher than those in the other works. Hence activated carbon derived from cashew nut shells would be useful for the economic treatment of wastewater containing chromium metals.

Conclusions

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

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

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