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# Application of Coconut Shell's Activated Carbon for Heavy Metal Removal from Wastewater

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**Abstract:** This study was conducted with batch and continuous column type laboratory experiments to remove heavy metals and organic matter by using activated carbon of coconut shell (ACCS). Synthetic wastewater was used to evaluate the heavy metal removal capability at a starting pH of 6.5. The sorbent dosages in the predetermined synthetic solutions were 10, 16.7 and 20$gL^{-1}$. In the batch tests, the column was continuously operated for 14 days at 100 to 125$Lh^{-1}$ until equilibrium concentration was achieved. Moreover, the laboratory column showed removal efficiency (RE) of 100% without any desorption. The data fit the Freundlich isotherm model. The batches with low heavy metal concentrations of Cd, Cu and Zn exhibited an RE of approximately 99%, whereas 87 to 100% of Pb was removed from most of the batches, indicating the superior effectiveness of the procedure. In addition, the full-scale column filter with a 10L ACCS filter was capable of reducing about 30% of the total organic carbon (TOC) and 50% of hydrogen peroxide ($H_2O_2$) from semiconductor wastewater at a continuous flow rate of approximately 125L $h^{-1}$.

**Key words:** Activated Carbon · Coconut Shell · Heavy Metal · Isotherm · Sorbent

## INTRODUCTION

Adsorption using commercial activated carbon is an effective but expensive purification and separation technique used in industry, especially in water and wastewater treatments to remove heavy metals [1, 2]. The heavy metals discharged into the aqua-environment present a special concern as they are bounded to bioaccumulation and excessive concentrations are associated with various diseases in humans and animals.

Here, activated carbon of coconut shell (ACCS) and a full-scale column filter packed with ACCS were used in a laboratory, batch and column study. Walnut, hazelnut, almond and pistachio shell-based activated carbon was used to remove Cd, Cu, Pb and Zn from aqueous solution [1]. Activated carbon from palm shell also has Pb adsorption ability [3]. The paper mulberry bio-char was more effective and exhibited a higher adsorption potential for cadmium, copper, chromium, lead and zinc than commercially available silica powder [4]. Granular activated carbon is used to remove only Pb from wastewater by reverse fluidized technology, where removal efficiency increases with bed height and detention time [5]. Activated carbon from algae marine Gracilaria is capable to remove heavy metal ($Ni^{2+}$) from aqueous solutions [6]. *Platanus orientalis* leaves were used to remove Cd from aqueous solution, where the ash of these leaves showed more favorable than living ones [7]. The main objective of this study was to evaluate the efficiency of ACCS as a sorbent for metal retention in laboratory tests under well-controlled experimental conditions. After getting promising results obtained from batch tests, a set of columns were developed to investigate the possibility of using ACCS under continuous flow conditions.

## MATERIALS AND METHODS

**Sorbents:** Sorbent materials with a similar particle size were used as particle size may have an effect on the removal of heavy metals [8, 9]. ACCS was sieved to the desired particle size (0.6 ~ 1mm) and dried at 40°C for 3h without additional treatment before being used in the batch experiments [7].

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Table 1: USEPA limit values and initial concentrations (°C) of heavy metals

| | Concentrations (μg $L^{-1}$); [[a] used for 20g $L^{-1}$ sorbent dosage] | | | |
|---|---|---|---|---|
| | Cd | Cu | Pb | Zn |
| USEPA | 2 | 13 | 65 | 120 |
| Batch 1 | 7671; 1767[a] | 8992; 1807[a] | 8775 | 9394; 1979[a] |
| Batch 2 | 3834; 882[a] | 4299; 902[a] | 4402 | 4905; 900[a] |
| Batch 3 | 1567; 214[a] | 1703; 246[a] | 2608 | 2786; 476[a] |
| Batch 4 | 763; 120[a] | 893; 116[a] | 1762 | 1959; 339[a] |
| Batch 5 | 409; 22[a] | 463; 30[a] | 894 | 958; 256[a] |
| Batch 6 | 94; 9[a] | 128; 14[a] | 474 | 506; 142[a] |
| Batch 7 | 43; 3[a] | 51; 6[a] | 105 | 102; 72[a] |
| Batch 8 | 11 | 23 | 61 | 75 |

**Heavy Metal Concentrations:** In this study, we attempted to use realistic concentration ranges where the lowest values were below or about US Environmental Protection Agency (USEPA) fresh water acute limits [10] and the highest values were significantly higher, as shown in Table 1. The purpose was to evaluate and compare the sorbents at both highly and slightly polluted conditions, since some sorbents are effective at rather high concentrations but are less efficient at low concentration [8].

**Batch Experiments:** Sorption experiments were carried out using synthetic solutions in 50 ml beakers at room temperature (28±1°C). The required concentrations of Cd, Cu, Pb and Zn were obtained by step-by-step diluting their stock commercial solutions to the desired concentrations. The ionic strength of the water samples was controlled using 0.01M NaCl and the pH changes during the experiments were minimized using 0.003M $NaHCO_3$ [8]. Before starting the batch experiments, the pH of all solutions was adjusted to 6.5 using strong acid or base solutions. Afterwards, sorbent dosages were set at 10, 16.7 and 20g $L^{-1}$ [8] in the predetermined synthetic solutions. The solutions and sorbents were then mixed by gently shaking the batches in a mechanical shaker at 100 rpm for 24h. The pH values were checked after the completion of the shaking to identify any possible pH variations from the starting values. Later, the batches were taken from the shaker and filtered through 0.45μm filter paper, after which the filtrates were acidified to pH 1.5 ~ 2 and stored at 4°C until the heavy metal measurements. One set was also run as a control batch with sorbent but without any heavy metal addition. All the chemicals used were reagent grade and were used without any further purification.

**Column Experiment:** The fixed bed columns were packed with ACCS with a particle size range of 0.6 ~ 1mm and used as up-flow reactors. Influent water was pumped through the ACCS-packed column with peristaltic pump. The column had an inner diameter of 55mm with a 25mm high layer of glass beads and a 95mm high layer of ACCS. Fig. 1 shows a schematic diagram of the column [11]. The columns were operated using upward flow at room temperature and air free distilled water (without heavy metals) was run through the columns for 24h prior to starting the experiments in order to wet the columns and establish equilibrium between the adsorbent and water. Uniform solution distribution, minimized pressure gradients and reduced channeling and fouling of the adsorbent were achieved by using this design and operation procedure [11-13]. During the 14-day experiment, flow rates were set at 100 to 125mL $h^{-1}$ and inflow heavy metal concentrations of 1.6, 1.7, 2.6 and 2.8mg $L^{-1}$ of Cd, Cu, Pb and Zn were used, respectively.

**Full-Scale Column Study:** An ACCS-packed column filter with an effective volume of 10L was studied. A continuous downward flow of contaminated water at 125L $h^{-1}$ was provided throughout the 45-day study with a starting pH of 3±0.08. Semiconductor industrial wastewater with a significant concentration of total organic carbon (TOC) and hydrogen peroxide ($H_2O_2$) was used directly. In the influent (Inf.), Iron (Fe) (<0.05mg $L^{-1}$), aluminium (Al) (<0.1mg $L^{-1}$) and Cu (<0.05mg $L^{-1}$) showed very low concentrations. Samples were collected fortnightly and stored until measurement.

**Analyzing Sorption Data:** For ACCS, the solid phase heavy metal concentration, $q_e$ (μg $g^{-1}$), was determined by analyzing the corresponding heavy metal concentration before and after the treatment using equation (1):

$$q_e = \frac{C_0 - C_e}{X} \quad \text{Equation (1)}$$

where $C_e$ is the equilibrium heavy metal concentration in the solution (μg $L^{-1}$) and $X$ the sorbent dosage (g $L^{-1}$).

The metal removal efficiency percentage [2, 14] of the adsorbent was defined by Equation (2), while Equation (3) was used as the linear form of the Freundlich isotherm to fit the sorption data:

$$RE(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{Equation (2)}$$

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad \text{Equation (3)}$$

where $K$ is correlated with the quantity of sorbate associated with the sorbent and $n$ is the Freundlich isotherm constant related to the sorption strength [6, 7 & 15].

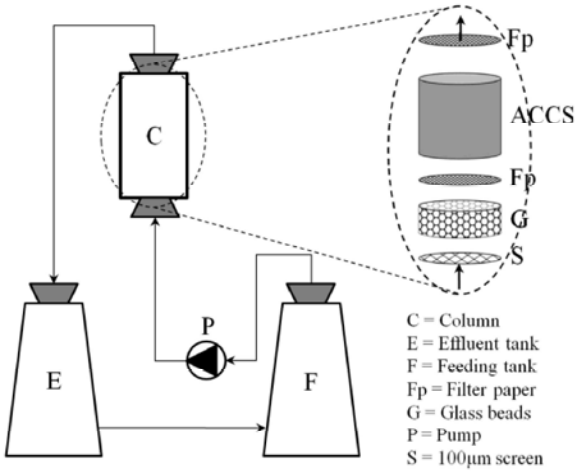


Fig. 1: Schematic diagram of the adsorption column and the column detail

## RESULTS AND DISCUSSION

**Physical Properties:** The removal of heavy metals from wastewater by agricultural wastes is a green chemistry method for improving environment cleanliness [2]. Fig. 2 shows an image, taken by environmental scanning electron microscope (E-SEM), showing the satisfactory surface of an ACCS particle with voids to adsorb heavy metals. The Fourier transform infrared (FTIR) spectra revealed indicated the different surface structures of the carbon such as aliphatic, aromatic and cyclic as observed by the bands at 1460 $cm^{-1}$ and over the 1320-1100 $cm^{-1}$ range. All the analyzed spectra possessed bands at 3300-3500 $cm^{-1}$, revealing the presence of alcoholic, phenolic or acidic OH with hydrogen bonding. The peaks at 2000-2100 $cm^{-1}$ were attributed to the C=C group and those at 2200-2300 $cm^{-1}$ to the C=N group. The bands at 2000-2300 $cm^{-1}$ were considered to correspond to C=N=S or C=N=C. These results indicated that carbon possesses a similar structure to that of standard activated charcoal, but has greater capacity to remove heavy metals [2].

**Equilibrium Concentrations for Batch Tests:** The results of the simultaneous removal of Cd, Cu, Pb and Zn using different sorbent dosages are presented in Fig. 3 on a double logarithmic scale for batch tests. As expected, the amount of heavy metal removed increased with increasing initial heavy metal concentration in all of the batches. For the Zn adsorption, a satisfactory removal was observed at the sorbent dosage of 20g $L^{-1}$ for all batches. Three and two batches at a sorbent dosage of 16.7 and 10g $L^{-1}$, respectively, showed removal below USEPA limits. In other cases, the batches with relatively low heavy metal concentrations showed better results for all sorbent dosages.

**Removal Efficiency (RE) in Column Test:** The removal efficiencies of the heavy metals in the column test are shown in Fig. 4. For the $C_e$ measurement, samples were collected at 1, 6, 18, 36, 72, 96, 168 and 317h after the starting time. Pb showed an RE of 94% after 1h whereas Cu showed an RE of nearly 100% after 6h. To check the desorption criteria, the column was run continuously for 14 days. No desorption was observed as the column showed satisfactory results while maintaining a constant $C_e$ for 14 days.

**Full-Scale Column Filter:** Table 2 shows the influent and effluent concentration of semiconductor wastewater during the study. The heavy metal concentration was nearly the same in the effluent as in the influent, indicating the absence of any leaching inside the column. Moreover, TOC and $H_2O_2$ were reduced by approximately 30 and 50%, respectively, with respect to the influent levels. The continuous flow exhibited better long-term performance in heavy metal removal and other experimented parameters, thereby demonstrating the longevity of the column. The $H_2O_2$ efficiency was reduced by nearly 33% on the third day of study. Subsequently, RE of $H_2O_2$ was maintained nearly constant at around 50%.

**Influence of Dosage:** The RE was corrected for the mass of adsorbent in the batches and is given as the amount of metal ion removed per unit sorbent dosage (g $L^{-1}$). Fig. 5 shows the RE per dosage of adsorbent versus the amount of sorbent dosage, while the other parameters are maintained constant. The figure shows that the RE per dosage of the adsorbent generally improved with decreasing dose for Cd, Cu and Pb, while for Zn it very slightly increased with increasing sorbent dosage.

**Removal Efficiency (RE) of Heavy Metals:** The heavy metal RE from contaminated water at various sorbent dosages is shown in Fig. 6. To investigate the relation, mean values for all batches at different sorbent dosages were divided by the respective dosage. The RE of Pb was above 87% for all the batches at a sorbent dosage of 16.7g $L^{-1}$ while at a sorbent dosage of 20g $L^{-1}$, RE was increased by 57% or more in all batches except batch 1,

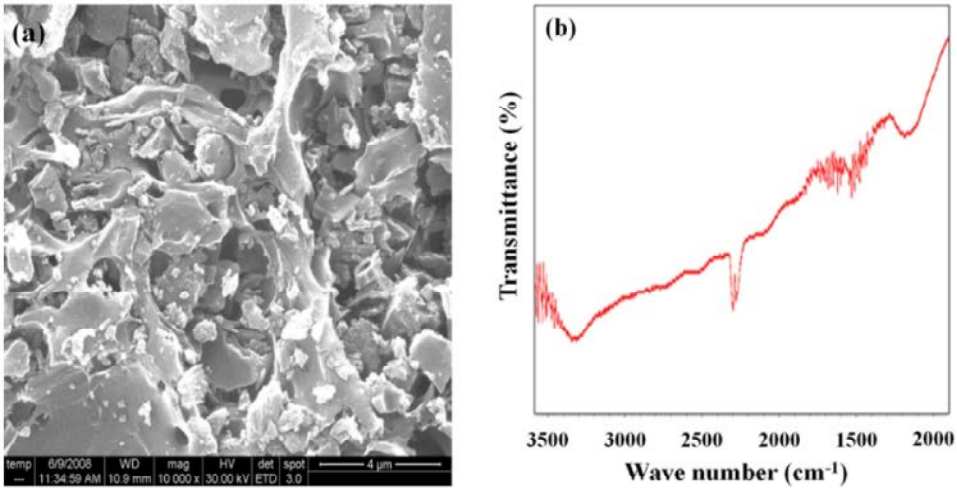


Fig. 2: E-SEM image of ACCS before being used as a sorbent (panel (a)) and FTIR spectra of ACCS (panel (b))

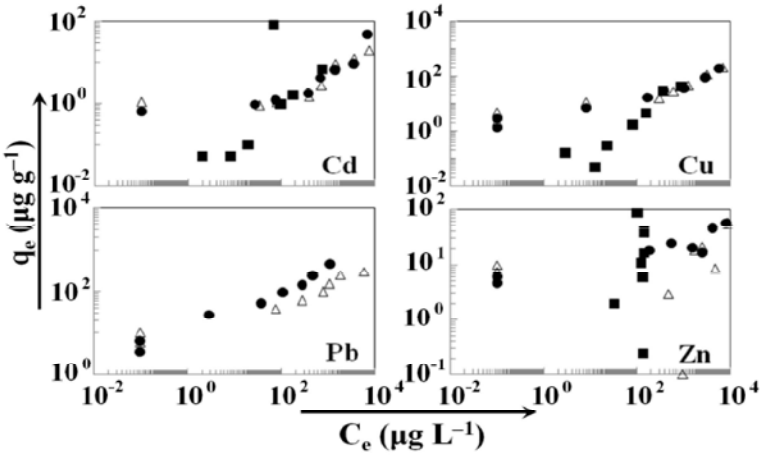


Fig. 3: Cd, Cu, Pb and Zn removal using different sorbent dosages (■ 20g $L^{-1}$, • 16.7g $L^{-1}$, Δ 10g $L^{-1}$)

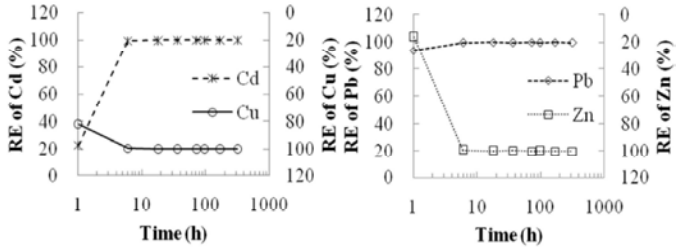


Fig. 4: Removal efficiency (RE) according to time for Cd, Cu, Pb and Zn

Table 2: Influent and effluent properties of full-scale column

| | 2008-04-15 | | 2008-04-29 | | 2008-05-13 | | 2008-05-27 | |
|---|---|---|---|---|---|---|---|---|
| Properties (mg $L^{-1}$) | Inf. | Eff. | Inf. | Eff. | Inf. | Eff. | Inf. | Eff. |
| TOC | 1.243 | 0.837 | 1.103 | 0.759 | 1.004 | 0.709 | 0.977 | 0.63 |
| $H_2O_2$ | 10 | 5 | 10 | 5 | 15 | 10 | 10 | 5 |
| Fe | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| Al | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Cu | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |

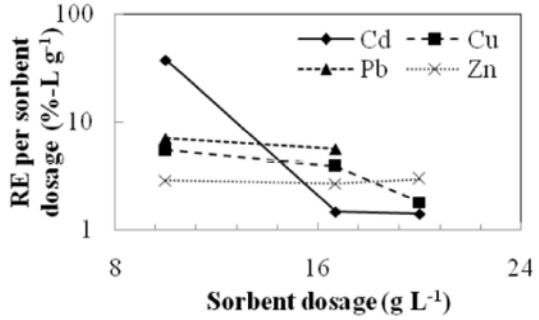


Fig. 5: Influence of sorbent dosage on heavy metal removal efficiency (RE)

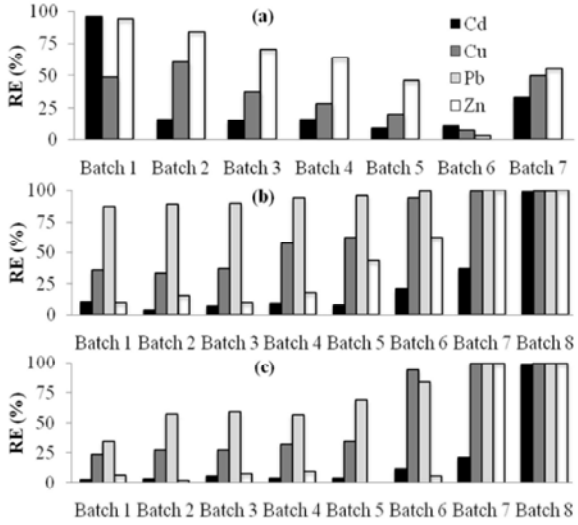


Fig. 6: Effect of sorbent dosages [(a) 20g $L^{-1}$, (b) 16.7g $L^{-1}$ and (c) 10g $L^{-1}$] on removal efficiency (RE) of Cd, Cu, Pb and Zn.

Table 3: Freundlich isotherm constants for different sorbent dosages

| | Sorbent dosage (g $L^{-1}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 20 | | | 16.7 | | | 10 | | |
| Heavy metals | *K* | 1/*n* | $r^2$ | *K* | 1/*n* | $r^2$ | *K* | 1/*n* | $r^2$ |
| Cd | 0.02 | 1.01 | 0.53 | 0.59 | 0.33 | 0.68 | 0.79 | 0.26 | 0.57 |
| Cu | 0.01 | 1.22 | 0.88 | 4.04 | 0.37 | 0.94 | 6.03 | 0.32 | 0.87 |
| Pb | - | - | - | 13.50 | 0.45 | 0.98 | 14.81 | 0.32 | 0.95 |
| Zn | 0.20 | 0.78 | 0.05 | 7.59 | 0.18 | 0.86 | 6.18 | 0.02 | 0.00 |

which showed an RE of 35%. The RE of Cu was mostly above 55% at a sorbent dosage of 16.7g $L^{-1}$. At higher sorbent dosages, the adsorption of low concentrated heavy metals was around 99%. The RE of Cd and Zn was relatively low for most of the batches at all conditions. Zn showed better RE at a sorbent dosage of 16.7g $L^{-1}$ in batch 6 while a very low RE was achieved at a sorbent dosage of 20g $L^{-1}$, indicating the effect of sorbent dosage.

**Sorption Isotherm:** Table 3 shows Freundlich isotherm constants with the $r^2$ values for all sorbent dosages investigated in this study. For Zn, at the sorbent dosages of 10 and 20g $L^{-1}$, the $r^2$ values were very low, indicating a poor correlation. For others, the $r^2$ values of = 0.5 signify statistically significant correlation. Although $r^2$ = 0.5 shows a fair correlation, using the estimated Freundlich isotherm for prediction is considered highly uncertain unless $r^2$ is close to 1 [8]. Accordingly, Pb showed the

most correlated result to fit the isotherm. Cu showed a better correlation than Cd as $0.87 = r^2 = 0.94$. Furthermore, the isotherm maintained the correlation with $r^2 = 0.5$ for Cd.

## CONCLUSIONS

The present study results have demonstrated the potential effectiveness of ACCS in heavy metal removal. Satisfactory results were achieved for heavy metal RE in both for the batch and continuous studies. The heavy metal RE was dependent on the sorbent dosages with lower sorbent dosages exhibiting better RE than higher dosages. ACCS was found to be suitable for batch treatment with low heavy metal concentrations. No sorbent leaching occurred during the batch tests and full-scale studies, indicating an acceptable adsorbent quality. The porous surface and FTIR spectra revealed properties similar to those of standard activated carbon.

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