

Removal of toxic metals (Cd²⁺ and Pb²⁺) from wastewater on study of adsorption isotherm by using activated peanut hull

Tin Htwe Mu¹

Abstract

Removal of Pb(II) and Cd(II) from aqueous solution was essential as it is toxic. In this research, peanut hull was used as adsorbent. Peanut hull samples were collected from Kyanpya village in Minbu Township, Magway Region. The collected peanut hulls were washed with water and then dried in sunlight and then cut into 1-2 cm length pieces. The cut peel was made into powder by blender and meshed with (500 μm) sieve. Raw peanut hull was activated using 1 M HCL solution. The powders (100 g) were placed in 500 mL of 1M HCl for 4 hours. The sample solution was filtered and thoroughly washed with distilled water to reach at pH 7 and dried in hot air oven at 100°C for 5 hours. Then, the activated peanut hull was calcinated at different temperatures (300 and 500 °C). Some physicochemical properties (moisture, pH and bulk density) were determined. The moisture content of acid treated peanut hull was 0.28 ± 0.016 %, APHC-300 and APHC- 500 were found to be 0.18 ± 0.010 and 0.16 ± 0.012 . The bulk density of acid treated peanut hull was 0.583 ± 0.49 lb ft⁻³, APHC-300 and APHC- 500 were detected 0.907 ± 0.77 and 0.867 ± 0.63 lb ft⁻³. The instrumental measurements were used (SEM, EDXRF). The metal adsorption parameter of the effects of adsorbent dosages on the removal efficiency was studied. The percent of Cd (II) adsorbed increase with an increased in weight of APHC- 300 sample and APHC-500. The adsorption data were simulated by adsorption isotherm. The Freundlich constant (K_f) related to the sorption capacity which is a measure of the maximum adsorption showed that the APHC-300 and APHC-500 had higher mass capacity for Cd (II) 0.0841mg g^{-1} and 0.1009mg g^{-1} , the lowest mass capacity for Pb (II) 0.0285mg g^{-1} and 0.0148mg g^{-1} respectively. The graph was obtained linear relationship and obeyed the Langmuir isotherm parameters and the sorption capacities were affected. Therefore, the activated peanut hull may be used for reduce toxic metals from wastewater.

Keywords: Peanut hull, metals adsorption, sorption isotherm

Introduction

Peanut hulls have a high potential as a roughage source. In years of drought where limited forage and roughage sources prevail, they provide an alternative to hay especially in the Southeastern United States where peanut production thrives. In whole form, peanut hulls are quite cumbersome and difficult to transport (Waller., 2009). Peanut hulls vastly improve their logistics and storage; given they are readily available in the Southeast; this makes them an ideal feedstuff. However, for them to be acceptable, they must work as an effective fiber source (Hill., 2002).

Adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk. Adsorption is a term which is completely different from Absorption. While absorption means uniform distribution of the substance throughout the bulk, adsorption essentially happens at the surface of the substance. When both Adsorption and Absorption processes take place simultaneously, the process is called sorption. Adsorption process involves two components, Adsorbent and

¹Dr., Associate Professor, Department of Chemistry, University of Magway

Adsorbate. Adsorbent is the substance on the surface in which adsorption takes place. Adsorbate is the substance which is being adsorbed on the surface of adsorbent. Adsorbate gets adsorbed. Adsorption has been widely used in the removal of metal ions from aqueous media.

Heavy metals are individual metals and metal compounds that can impact human health. Eight common heavy metals are discussed in this brief: arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver (Babel *et al.*, 2003). These are all naturally occurring substances which are often present in the environment at low levels. In large amounts, they can be dangerous. Generally, humans are exposed to these metals by ingestion (drinking or eating) or inhalation (breathing). Working in or living near an industrial site which utilizes these metals and their compounds increases one risk of exposure, as does living near a site where these metals have been improperly disposed.

Freundlich isotherm is the most utilized isotherm in wastewater treatment. It has been reported that data for the adsorption involving adsorbates within a liquid phase is the best by using this isotherm (Ho, 2006). The parameters in Freundlich isotherm are related to the equilibrium concentration of the adsorbate. The relation between the amount of adsorbate adsorbed on to the adsorbent surface and the equilibrium concentration of the adsorbate in solvent at equilibrium at a constant temperature may be estimated by various adsorption isotherm models.

The determinations of lead and cadmium onto acid treated peanut hull char at 300°C and acid treated peanut hull char at 500°C were determined using atomic absorption spectrophotometer (Stavin, 1968). The aim of this research, the acid treated peanut hulls was used as adsorbent for the removal of heavy metal from aqueous solutions.

Materials and Methods

Materials

An 8.9 mL of concentrated HCl solution was dissolved in distilled water and volume made up to 1L in a volumetric flask. 1M HCl acid solution was obtained. A stock solution of 1000 ppm was prepared by dissolving (0.1599 g) of lead (II) nitrate in deionized water and volume made up in 100 mL volumetric flask. The cadmium stock solution corresponding to 1000mg/L of Cd²⁺ was prepared by dissolving 0.23g of cadmium (II) sulphate in distilled water and diluting to 100 mL in a standard volumetric flask. Acid treated peanut hull char 300°C and 500°C were used in this researched.

Methods

The collected peanut hulls (RPH) were dried in sunlight and then cut into 1-2 cm length pieces. The cut pieces were made into powder by blender and meshed with (500 µm) sieve. The powders (100 g) were placed in 500 mL of 1M HCl for 4 hours. The sample solution was filtered and thoroughly washed with distilled water to reach at pH 7 and dried in hot air oven at 100°C for 5 hours. The dried peanut hulls powder was cooled, weighed and stored in airtight bottle to avoid moisture. The dry acid-treated peanut hulls (APH) were converted into a peanut hulls char by calcinating at different temperature: 300°C (APHC-300) for 3 hr and at 500 °C (APHC-500) for 2 hr. The following equations were used to calculate the percentage uptake (% sorption).

$$\text{Sorption (\%)} = \frac{c_0 - c_e}{c_0} \times 100 \quad c_0 = \text{initial concentration of Cd}^{2+} \text{ ion}$$

$$c_e = \text{final concentration of Cd}^{2+} \text{ ion}$$

Results and Discussion

Determination of Some Physicochemical Properties of RPH, APHC-300 and APHC-500

1 g of acid treated peanut hull sample was placed into a beaker and 100 mL of distilled water was added to this sample. The sample solution was heated at 80° C for 2 min. Then, the sample solution was gently shaken and filtered off. The filtrate was cooled at room temperature and the pH of sample was determined by using pH meter. Clean and dry graduated cylinder (10 mL size) was weighed and the raw peanut hull sample was filled into the cylinder. The total weight of cylinder including sample was again weighed. Cylinder was placed in a tapping box and cylinder was tapped until no more reduction volume. Minimum volume was recorded and bulk density of peanut hull sample was calculated. 1 g of acid treated peanut hull sample was accurately weighed in the porcelain crucible. It was kept in the oven at 130° C for 1½ hr. Then, it was taken out and allowed to cool down at room temperature in desiccators. After cooling the sample, it was weighed again. Similarly, the determinations of (APHC-300 and 500) samples were carried out in these determinations. The moisture content of APH was 0.28 ± 0.016%, APHC-300 and APHC- 500 were found to be 0.18 ± 0.010 % and 0.16 ± 0.012 %. In Table 1, the data of bulk density of acid treated peanut hull was found to be 0.583 ± 0.49 lb ft⁻³ and the bulk density of APHC – 300 and APHC – 500 were found to be 0.907 ± 0.77 lb ft⁻³ and 0.867 ± 0.63 lb ft⁻³ respectively. Therefore, the bulk density of APHC-300 and APHC- 500 are small different. Because the two samples are char, the pore size is nearly the same. Therefore, the bulk density of APHC-300 and APHC- 500 are small and different. Because the two samples are char, the pore size is nearly the same.

Characterization for RPH, APHC-300 and APHC-500 by SEM and EDXRF Technique

In Figure 4(b) APHC-500, the electron micrographs also revealed that the particles are irregular shape and its surface exhibits a micro-rough texture, which can promote the adherence of metal than APHC-300°C Figure 4(a).

Energy dispersive X-ray fluorescence (EDXRF) spectrometer can analyse the elements from Al to U under vacuum condition. It can be utilized for qualitative identification and quantitative estimation of elements in solid, powders and liquids with appropriate sample preparation techniques. Figure 5 and Table 2 showed the EDXRF spectrum of the APHC- 300 °C. The Si (20.495%), Al (18.350%), Ca (18.225%), Fe (14.807 %), Cu (6.079%), K (3.254%) and Cr (0.969%) were found in APHC at 300°C. In Figure 6 and Table 2, Si (23.384%), Al (16.793%), Ca (16.037%), Fe (13.287 %) and Cu (6.710%) were found to be EDXRF spectrum of the APHC- 500°C.

Effect of dosage carried out onto APHC- 300 and APHC-500 by using Cd²⁺ ion solution

In this research, the effect of dosage of APHC- 300 and APHC-500 on adsorption of Cd (II) were studied at pH 7 for 2 hr of contact time (Table 3). It was found that the percent Cd (II) adsorbed increased with an increase in weight of APHC- 300 sample and APHC-500 (Figure 7). At the small values of dosage, the percent Cd (II) adsorbed increased more rapidly up to 0.25 g of samples.

Effect of dosage carried out onto APHC- 300 and APHC-500 by using Pb²⁺ ion solution

In this research, the effects of dosage of APHC- 300 and APHC-500 on adsorption of Pb (II) were studied at pH 5 for 2 hr of contact time (Table 4). It was found that the percent Pb (II) adsorbed increased from 18.76- 63.90% with an increase in weight of APHC- 300 sample from 0.1-2.0g. In APHC-500°C, it was found that the percent Pb (II) adsorbed increased with an increase in weight of samples (Figure 8). From the small weight of dosage to large weigh, the percents are increased more rapidly, up to 0.5g of sample. From 0.5 g sample, the percent is increased steadily with increase weigh.

Adsorption Isotherm for Pb (II) and Cd (II) Adsorption onto APHC-300 and APHC-500

Adsorption isotherms for Pb (II) and Cd (II) ions were studied using the equilibrium concentration of the metal ions. In Table 5, the correlation coefficient of R² value for Cd (II) on APHC-300 and APHC-500 nearly one, therefore the linear relationship was obtained. The Freundlich model was found to better fit the experimental data of Cd (II) ion sorption by APHC-300 and APHC-500 than Pb (II) ion. The Freundlich constant (K_f) related to the sorption capacity which is a measure of the maximum adsorption showed that the APHC-300 and APHC-500 had higher mass capacity for Cd (II) 0.0841mg g⁻¹, 0.1009 mg g⁻¹, and the lowest mass capacity for Pb (II) 0.0285 mg g⁻¹ and 0.0148 mg g⁻¹ respectively. The selectivity order for metal ions toward the APHC-300 sample is Cd > Pb. This may be due to the ionic size of Cd (II) that is smaller than the size of Pb (II) ion.

Table 6 shows the comparison of the Langmuir isotherm parameters for Pb (II) and Cd (II) ions. According to the figure, the R² value of the Langmuir isotherm parameters for Pb (II) and Cd (II) ions on APHC-300 and APHC-500 were obtained nearly one. These results were consistent with the equilibrium result of kinetic experiments performed at different dosage of sorbent.



Figure 1 The Photograph of Acid Treated Peanut Hull (APH)



Figure 2 The Photograph of Acid Treated Peanut Hull Char at 300°C (APHC-300)

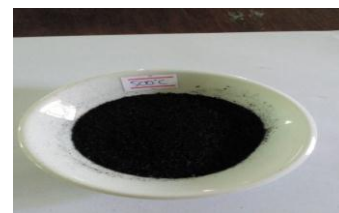


Figure 3 The Photograph of Acid Treated Peanut Hull Char at 500°C (APHC-500)

Table 1. Some physicochemical properties of APH, APHC-300 and APHC-500

Samples	Bulk Density (lb ft ⁻³) ($\bar{x} \pm s$)	Moisture Content (%) ($\bar{x} \pm s$)
Acid Treated (APH)	0.583 ± 0.49	0.28 ± 0.016
Acid Treated char at 300°C (APHC-300)	0.907 ± 0.77	0.18 ± 0.010
Acid Treated char at 500°C (APHC-500)	0.867 ± 0.63	0.16 ± 0.012

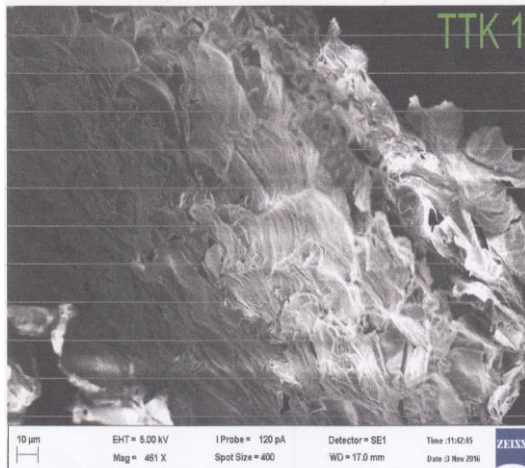


Figure 4(a) SEM photograph of APHC – 300

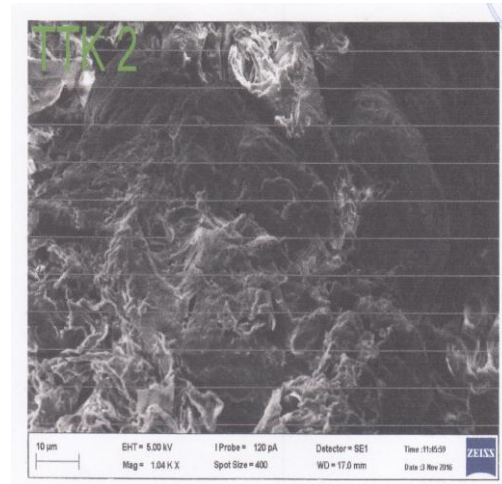


Figure 4(b) SEM photograph of APHC – 500

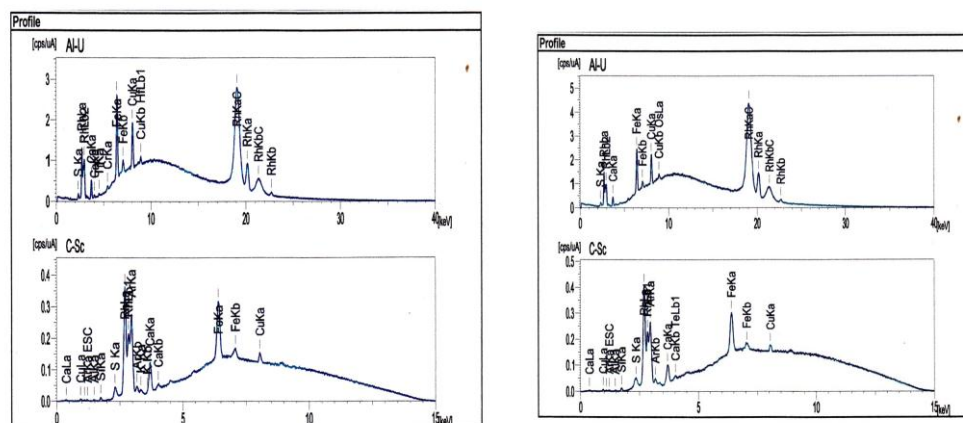


Figure 5 EDXRF Spectrum of APHC-300 Figure 6 EDXRF Spectrum of APHC-500

Table 2. The relative Abundance of Elements in EDXRF Spectrum of APHC- 300 and APHC-500

Elements	APHC-300	APHC-500
Si	20.495	23.384
Al	18.350	16.793
Ca	18.225	16.037
Fe	14.807	13.287
Cu	6.079	6.710
K	3.254	-
Cr	0.969	-

Table 3. Effect of Dosage on Sorption of Cd²⁺ Ion onto APHC- 300 and APHC-500

No	Dosage (gm)	Removal (%) of APHC-300	Removal (%) of APHC-500
1	0.1	46.82	44.84
2	0.25	61.06	58.62
3	0.50	80.78	78.86
4	1.0	83.34	83.98
5	2.0	86.26	86.84

Table 4. Effect of Dosage on Sorption of Pb²⁺ Ion onto APHC- 300 and APHC-500

No	Dosage (gm)	Removal (%) of APHC-300	Removal (%) of APHC-500
1	0.1	18.76	21.64
2	0.25	20.64	23.52
3	0.50	39.80	40.74
4	1.0	52.48	49.16
5	2.0	63.90	65.28

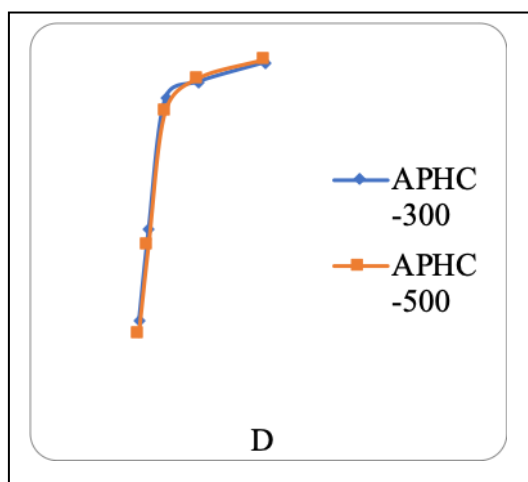


Figure 7 Effect of Dosage on Sorption of Cd²⁺ Ion onto APHC-300 and APHC-500

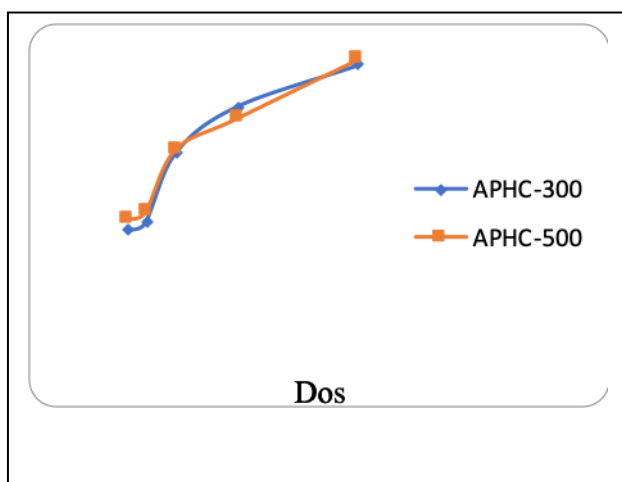


Figure 8 Effect of Dosage on Sorption of Pb²⁺ Ion onto APHC- 300 and APHC-500

Table 5. Freundlich Isotherm Parameters on APHC -300 and APHC-500

Freundlich isotherm parameters	APHC-300		APHC-500	
	Pb ²⁺ Ion	Cd ²⁺ Ion	Pb ²⁺ Ion	Cd ²⁺ Ion
1/n	1.260	1.501	1.473	1.409
R ²	0.677	0.891	0.657	0.923
k _f (mg g ⁻¹)	0.0285	0.0841	0.0148	0.1009

Table 6. Langmuir Isotherm Parameters on APHC -300 and APHC-500

Langmuir isotherm parameters	APHC-300		APHC-500	
	Pb ²⁺ Ion	Cd ²⁺ Ion	Pb ²⁺ Ion	Cd ²⁺ Ion
Sorption coefficient, K_L (L mg ⁻¹)	0.0143	0.0338	0.0152	0.030
Correlation coefficient, R^2	0.923	0.889	0.927	0.950
Sorption capacity, q_{max} (mg g ⁻¹)	2.3641	4.5045	2.2371	5.3191

Conclusion

In this research, acid treated peanut hull char at 300°C (APHC-300) and acid treated peanut hull char at 500°C (APHC-500) were used as adsorbents. Physicochemical properties of the APHC-300°C and APHC- 500°C samples were determined. The moisture content of APHC-300 and APHC- 500 was found to be about 0.03% and 0.02 %. The bulk density of APH was found to be 0.583 ± 0.02 lb ft⁻³ and the bulk density of APHC-300 and APHC-500 were found to be 0.907 ± 0.01 and 0.86 ± 0.01 lb ft⁻³ respectively. Therefore, the bulk density of APHC-300 and APHC- 500 is small and different. Because the two samples are char, the pore size is nearly the same.

In APHC-500, the SEM micrograph of the electron micrographs also revealed that the particles are irregular shape and its surface exhibits a micro-rough texture, which can promote the adherence of metal than APHC-300°C. 20.495 % of Si was highest and 0.969 % of Cr was lowest on APHC-300 in EDXRF spectrum. Similarly, 23.384 % of Si was highest and 6.710 % of Cu was lowest in EDXRF spectrum of the APHC- 500°C.

The effect of dosage of APHC- 300 on adsorption of Pb (II) was found that the percent Pb (II) adsorbed increased from 18.76- 63.90% with an increase in weight of APHC- 300 sample from 0.1-2.0g. In APHC-500°C, it was found that the percent Pb (II) adsorbed increased with an increase in weight of samples. At the small values of dosage, the percent Cd (II) adsorbed increased more rapidly up to 0.25 g of each samples. The Freundlich isotherm parameters for Pb (II) and Cd (II) ions onto APHC-300 and APHC-500, the correlation coefficient of R^2 value for Cd (II) on APHC-300 and APHC-500 nearly one, therefore the linear relationship was obtained. The Freundlich model was found to better fit the experimental data of Cd (II) ion sorption by APHC-300 and APHC-500 than Pb (II) ion. The Freundlich constant (K_f) related to the sorption capacity which is a measure of the maximum adsorption showed that the APHC-300 and APHC-500 had higher mass capacity for Cd (II) 0.0841mg g⁻¹, 0.1009 mg g⁻¹, and the lowest mass capacity for Pb (II) 0.0285 mg g⁻¹ and 0.0148 mg g⁻¹ respectively. The selectivity order for metal ions toward the sample is Cd > Pb. This may be due to the ionic size of Cd (II) that is smaller than the size of Pb (II) ion. The sorption capacities for Cd (II) are more capable than Pb (II) onto APHC-300 and APHC-500.

The comparison of the Langmuir isotherm parameters for Pb (II) and Cd (II) ions, the R^2 value of the Langmuir isotherm parameters for Pb (II) and Cd (II) ions on APHC-300 and APHC-500 were obtained nearly one. The graph obtained linear relationship.

According to experimental data, the acid treated peanut hull in APHC-500 had more efficiency than APHC-300 for the removal of Cadmium from aqueous solution. Effect of pH and dosage of Cd (II) performed onto APHC-500 were consistent with the adsorption isotherm process of Freundlich. These results were consistent with the equilibrium result of adsorption isotherm performed at different pH and dosage of sorbents. Therefore, the acid treated peanut hull char will be used for removal of heavy metals from wastewater.

Acknowledgements

The author would like to thank Rector Dr Khin Mg Oo, Pro-rectors Dr Win Soe and Dr Than Than Oo, University of Magway for their guidance to do this paper. In addition, I would like to express my gratitude to Dr Thidar Aung, Professor and Head of Chemistry Department, University of Magway for their kind encouragement.

References

- Babel, S. and Kurniawan, T. A. (2003). "Low- Cost Adsorbents for Heavy Metal Uptake from Contaminated Water", *J. Hazard. Mater.*, **97**, 219-243
- Hill, G. M. (2002). "Peanut by Products Fed to Cattle." *J. Vet. Clin. Good Anim.*, **18**, 295-315
- Ho, Y.S. (2006). "Second-order Kinetic Model for the Sorption of Cadmium onto Tree Fern: A Comparison of Linear and Non-linear Methods", *Water Res.*, **40**, 119-124
- Stavin, W. (1968). "Atomic Absorption Spectroscopy", John Wiley & Sons Inc., New York, 183-184
- Waller, J. C. (2009). "By Products and Unusual Feedstuffs." *J. Feedstuffs*, **38**, 18-22