Adsorption of Cadmium (II) and Lead (II) by Agricultural Wastes

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Abstract

As heavy metal pollution becomes a growing concern in the world, many environmentally friendly ways to remove heavy metals have been studied. Agricultural waste is an option for this purpose. In this paper, four agricultural wastes were studied towards their ability to adsorb Pb(II) and Cd(II) from aqueous solutions at concentrations of 1, 2.5 and 5 mg/L, viz. rice straw, sweet rice straw, sugar cane bagasse, and activated carbon from sugar cane bagasse as a reference. Carbon from sugar cane bagasse showed better adsorption efficiencies for Pb(II) and Cd(II) than the other three adsorbents (rice straw, sweet rice straw, and sugar cane bagasse). Adsorption activity on Pb(II) was: rice straw ≈ sweet rice straw > bagasse, while on Cd(II): sugar cane bagasse ≈ rice straw ≈ sweet rice straw. However, the adsorption capacities of the three types of adsorbent do not much lower than the activated carbon, where as the activated carbon is much costly. The higher the initial concentrations of Cd(II) and Pb(II) solutions, the lower % of metal adsorbed, even though the mg of metals adsorbed/g adsorbent increased.

Key words: adsorption,, Cd,, Pb, rice straw, sweet rice straw, sugar cane bagasse

1. INTRODUCTION

With the increase in environmental awareness and governmental policies, there has been a push toward development of new efficient and environmentally friendly ways to combat contaminations of heavy metals in water. Many methods have been suggested for water remediation, including flocculation, ultra filtration, activated charcoal, chemical precipitation, electro-deposition, cementation, solvent extraction, and ion exchange resins. However, more cost-effective and environmentally friendly remediation systems are necessary (Kohar *et al.*, 2004).

Bioremediation has emerged as a technology for the removal of heavy metal contaminants using living organisms. Various researchers have conducted studies using living microbial and fungal systems to remove heavy metals from contaminated water (Gardea-Torresdey *et al.*, 1998, Kapoor and Viraraghavan, 1998).

Recently, plants have been studied for their ability to remove contaminants from the environment. *Eichhornia crassipes* (water hyacinth), *Alternanthera philoxeroides* (alligator weed), *Pistia stratiotes* (water lettuce), and *Potamogetton crispus* (pondweed), have been used in experimental works to treat polluted effluent (Schneider and Rubio, 1999). Bioremediation works well at low concentrations, but the toxicological effects of high levels of metal contaminations limit living systems. However, dead systems offer many advantages over living systems and can be obtained inexpensively. Dead or inactivated systems may be more practical because: (a) they don't require treatment with nutrients to maintain the biological activity of the organisms, (b) Problems of metal toxicity on plant metabolism, plant deterioration, odor liberation, and insect proliferation are avoided, (c) The dried biomass has advantages in conservation, transport, and handling and is much ready for using in wastewater units as a simple adsorbent material, (d) It is possible to re-cover the adsorbed heavy metals by elution techniques and to reuse the adsorbent material, (e) Immobilized biomaterial have also proven to accumulate metals from contaminated waters under flow conditions (Gardea-Torresdey, 1998a).

However, besides the natural biomasses discussed above, since the year of 1970s some studies have also been performed using various agricultural wastes, such as peanut skins and hulls, sugar cane bagasse, barley straw, oat by products, rice bran, rice husk, rice hull, rice straw (pretreated or untreated)), etc, The studies were on a variety of heavy metals such as Hg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, and Cr^{3+} (Friedman and Waiss (1972), Larsen and Schierup (1981), Suemitsu *et al.*, (1986), Shashikanth and Miss (1993), Marshall *et al.* (1993), Marshall *et al.* (1995), Gardea-Torresdey *et al.*, (2000), Kohar *et al.* (2005)). When the availability and cost are put into consideration, the agricultural wastes appear to be more reasonable heavy metal adsorbents than the natural biomasses. If the natural biomass is chosen as adsorbent on a large scale, it needs to be cultivated before it is available for a mass need. Land for planting, which is costly, is required, while the agricultural waste is available freely after harvest time.

Based on the issues above, a study on the adsorption ability of rice straw, sweet rice straw, sugar cane bagasse and carbon of sugar cane bagasse (as a reference) on Cd(II) and Pb(II) was conducted. The soaking time was run in one hour, for all experiments, since previous experiments had shown this to be the optimum time for reaching equilibrium adsorption of Cd(II) and Pb(II) (Kohar *et al.*, 2005). The metal content in the sample solutions were also measured by ICPS to asses the initial concentrations.

2. MATERIALS AND METHOD

Materials

Materials which were used in this research included:

- Rice straw and Sweet Rice straw (from Trawas area, East Java)
- Sugar cane Bagasse (Kedawung Sugar Factory, Pasuruan)
- Standard Solution of Cd(II) and Pb(II) 1000 mg/L, p.a (Merck, Germany)
- Demineralized water (Faculty of Pharmacy, The University of Surabaya)
- Concentrated HNO_3 and NaOH p.a (Riedel de Haen, Germany)
- Argon (*welding grade*)

Instrumentation

The followings are instruments which were used during the implementation of this research:

- Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) 3410 + (Fisons):
  - Fast Pump Time : 10,0 seconds
  - Rinse Time : 30,0 seconds
  - Flush Time : 30,0 seconds
  - Plasma Flow : 0,80 L/Min
  - Coolant Flow : 7,50 L/Min
  - Carrier Flow : 0,80 L/Min
  - Nebulizer Type : Conical (P/N AR: 35-07-C2)
- Analytical balance (Sartorius)
- pH meter C6 840 (Schott)
- Glass wares

Methods

Preparation of Adsorbents

Rice straw and sweet rice straw were washed with demineralized water, drained, and sun dried. Then they were milled and sieved to obtain particle sizes of 0,9 - 1,5 mm. Sugar cane bagasse was soaked in demineralized water, washed, sun dried, milled and sieved as for the straw. Carbon from sugar cane bagasse was washed with demineralized water, and sun dried. The particle size of carbon sugar cane bagasse was in the range of 0,425-0,6 mm

Preparation of Standard Solutions Pb(II) and Cd(II)

Working standard solutions of 0,5; 1; 2,5; 5; and 10 mg/L were prepared by diluting the standard solutions of Pb(II) and Cd(II) (1000 mg/L). The solutions were analyzed by ICPAES at the wavelengths of 220,353 and 228,802 nm for Pb and Cd, respectively. Calibration curves were made from the obtained data.

Analysis of Samples Pb(II) and Cd(II) in The Solution After Treatment with The Adsorbents

Samples of Pb(II) and Cd(II) were made in 3 concentrations: 1, 2,5 and 5 mg/L (representing low, medium and high concentrations, and also accurately measured by ICPAES), and pH was adjusted to 5 by adding 0,1 N NaOH solution. To each 100 ml of Pb(II) and Cd(II) sample solutions was added 0.5 g adsorbent (rice straw, sweet rice straw, sugar cane bagasse or carbon from sugar cane bagasse, accurately weighed), and was soaked for 1 hour.

The supernatant was collected and Pb(II) and Cd(II) concentrations were measured using AES at the wavelengths of 220,353 and 228,802 nm. The pH values were measured using a pH meter. Initial concentrations of Pb(II) and Cd(II) solutions were also measured. The treatment and analysis for the samples were conducted in triplicate.

Preparation of Blank Solutions

The same procedure was applied as in samples Pb(II) and Cd(II), but the metal solution was replaced by demineralized water which was adjusted at pH 5.

The results were presented as mg of metals adsorbed/g adsorbent and % metals adsorbed. The initial concentrations were in mg/L, and the sample solutions were in 100 ml. Therefore the concentration of metals adsorbed was converted to mg/100 ml and then the weight of adsorbent was taken into account. The data were analyzed by Multivariate ANOVA.

3. RESULT AND DISCUSSION

The result of calibration curve between intensity and concentration of Pb(II) showed in the Figure 1. And Figure 2 showed the calibration curve for Cd(II).

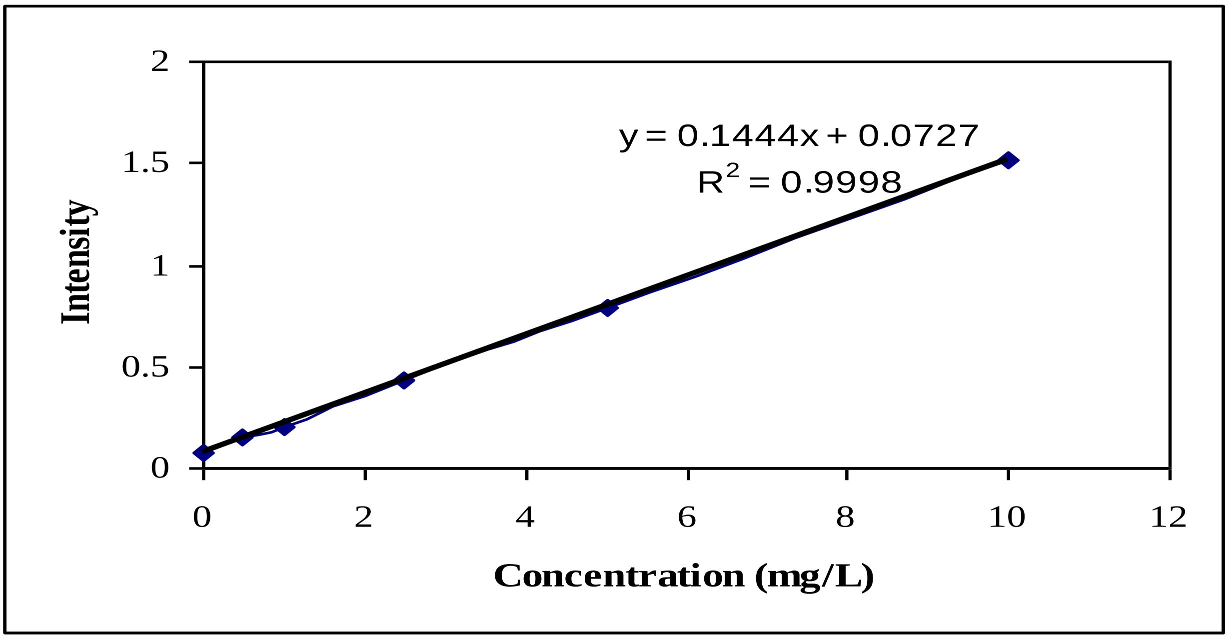

Figure 1. Calibration Curve of Pb(II) Standard Solutions

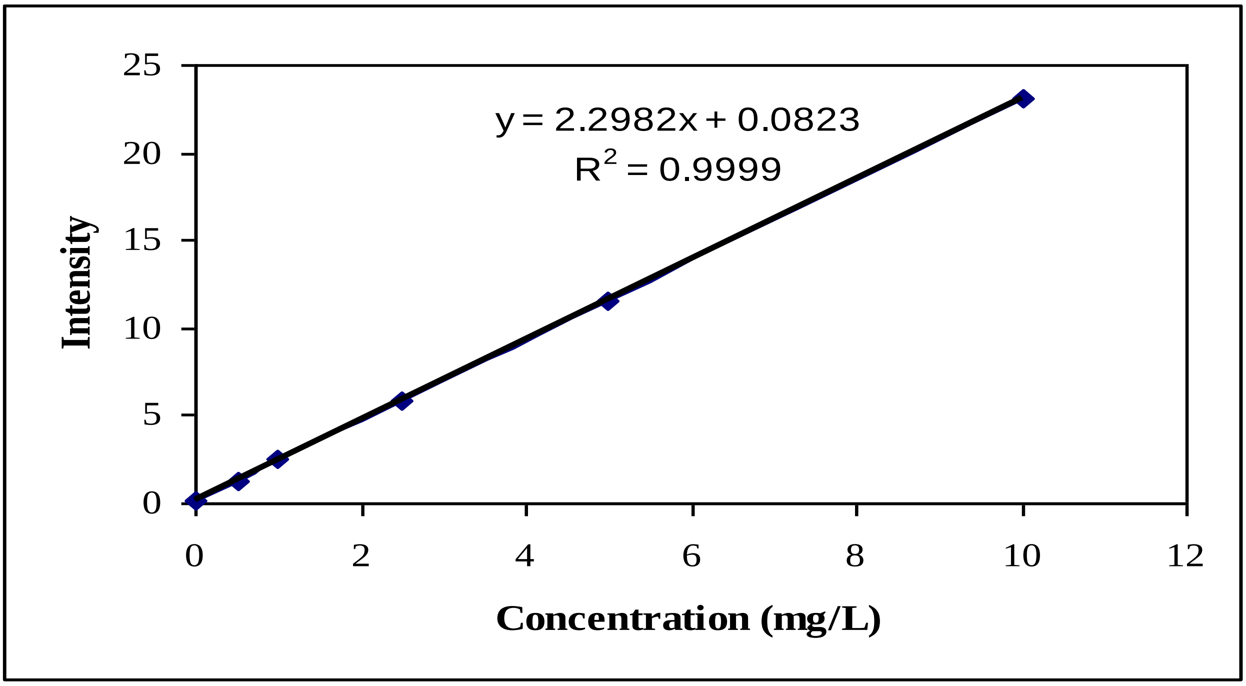

Figure 2. Calibration Curve Cd(II) Standard Solutions

Table 1. Average of mg Pb(II) Adsorbed/g Adsorbent and % Adsorbed (n = 3)

Adsorbents	mg Pb(II) adsorbed/g adsorbent	% Pb(II) adsorbed	pH (initial)	pH (final)
Initial conc. ± 1.0 mg/L				
Rice straw	0.14±0.01 (CV=5.09 %)	72.76 ± 3.915 (CV 3.98 %)	6.63 ± 0.05 (CV 0.68 %)	6.02±0.06 (CV 1.01 %)
Sweet rice straw	0.14 ± 0.01 (CV=4.03 %)	72.27 ± 2.33 (CV=3.23 %)	6.54 ± 0.11 (CV=1.65 %)	6.38 ± 0.15 (CV=2.32 %)
Sugar cane bagasse	0.16 ± 0.01 (CV=3.35 %)	70.22 ± 2.27 (CV=3.23%)	6.04 ± 0.05 (CV=0.77 %)	6.04 ± 0.04 (CV=0.60 %)
Carbon from bagasse	0.19 ± 0.00 (CV=0.87 %)	94.07 ± 0.29 (CV=0.30 %)	7.06 ± 0.04 (CV=0.62 %)	7.68 ± 0.06 (CV=0.80 %)
Initial conc. ± 2.5 mg/L				
Rice straw	0.35 ± 0.02 (CV 5.69 %)	72.09 ± 3.84 (CV 5.33%)	5.95±0.03 (CV 0.51 %)	6.11±0.04 (CV 0.65 %)
Sweet rice straw	0.35 ± 0.02 (CV=6.13 %)	67.63 ± 4.33 (CV=6.40 %)	5.95 ± 0.03 (CV=0.51 %)	6.15 ± 0.07 (CV=1.14 %)
Sugar cane bagasse	0.37 ± 0.05 (CV=13.55 %)	60.32 ± 2.92 (CV=4.84 %)	5.92 ± 0.02 (CV=0.34 %)	6.05 ± 0.04 (CV=0.58 %)
Carbon from bagasse	0.44 ± 0.02 (CV=3.79 %)	83.21 ± 0.32 (CV=0.39 %)	7.55 ± 0.04 (CV=0.47 %)	7.65 ± 0.02 (CV=0.27 %)
Initial conc. ± 5.0 mg/L				
Rice straw	0.65 ± 0.02 (CV=3.19 %)	67.32 ±2.19 (CV=3.25 %)	6.34 ± 0.13 (CV=2.10 %)	6.46 ± 0.06 (CV=0.89 %)
Sweet rice straw	0.64 ± 0.02 (CV=3.28 %)	66.86 ± 2.26 (CV=3.38 %)	6.47 ± 0.06 (CV=0.93 %)	6.35 ± 0.16 (CV=2.54 %)
Sugar cane bagasse	0.51 ± 0.01 (CV=1.50 %)	35.75 ± 1.69 (CV=4.72 %)	6.04 ± 0.05 (CV=0.77 %)	6.04 ± 0.04 (CV=0.60 %)
Carbon from bagasse	0.75 ± 0.00 (CV=0.10 %)	71.62 ± 1.63 (CV=2.28 %)	6.56 ± 0.03 (CV=0.40 %)	6.83 ± 0.10 (CV=1.48 %)

Table 2. Average of mg Cd(II) Adsorbed/ g Adsorbent and % Adsorbed (n = 3)

Adsorbents	mg Cd(II) adsorbed/ g adsorbent	%Cd(II) adsorbed	pH (initial)	pH (final)
Initial conc. ± 1.0 mg/L				
Rice straw	0.14 ± 0.002 (CV=5.09 %)	71.74 ± 1.83 (CV=2.55 %)	5,99 ± 0,02 (CV=0,33 %)	5.61 ± 0.02 (CV=0.27 %)
Sweet rice straw	0.14 ± 0.00 (CV=0.32 %)	71.52 ± 1.10 (CV=1.54 %)	5.92 ± 0.01 (CV=0.10 %)	5.85 ± 0.04 (CV=0.60 %)
Sugar cane bagasse	0.16 ± 0.01 (CV=4.79 %)	71.48 ± 3.85 (CV=5.38 %)	5.41 ± 0.03 (CV=0.47%)	5.40 ± 0.09 (CV=1.58 %)
Carbon from bagasse	0.20 ± 0.00 (CV=1.95 %)	93.64 ± 2.74 (CV=2.92 %)	7.07 ± 0.06 (CV=0.80 %)	7.82 ± 0.05 (CV=0.59%)
Initial conc. ± 2,5 mg/L				
Rice straw	0.31 ± 0.01 (CV=3.23 %)	66.64 ± 1.87 (CV=2.81 %)	5.74 ± 0.15 (CV=2.59 %)	5.87 ± 0.04 (CV=0.68 %)
Sweet rice straw	0.31 ± 0.01 (CV=3.38 %)	62.71 ± 1.96 (CV=53.12 %)	6.81 ± 0.02 (CV=0.25 %)	6.47 ± 0.28 (CV=4.40 %)
Sugar cane bagasse	0.38 ± 0.01 (CV=3.80 %)	64.91 ± 3.70 (CV=5.70 %)	5.84 ± 0.13 (CV=2.24 %)	5.44 ± 0.03 (CV=0.49 %)
Carbon from bagasse	0.49 ± 0.02 (CV=3.30 %)	91.89 ± 3.51 (CV=3.82 %)	8.02 ± 0.03 (CV=0.33 %)	7.96 ± 0.05 (CV=0.63%)
Initial conc. ± 5.0 mg/L				
Rice straw	0.62 ± 0.03 (CV=4.04 %)	63.71 ± 4.57 (CV=7.17 %)	5.65 ± 0.19 (CV=3.41 %)	5.63 ± 0.15 (CV=2.58 %)
Sweet rice straw	0.59 ± 0.00 (CV=0.73 %)	60.43 ± 0.18 (CV=0.29 %)	6.12 ± 0.03 (CV=0.47 %)	6.07 ± 0.06 (CV=0.9934. %)
Sugar cane bagasse	0.59 ± 0.01 (CV=1.71 %)	49.34 ± 1.04 (CV=2.10 %)	5.83 ± 0.04 (CV=0.69 %)	5.88 ± 0.10 (CV=1.62 %)
Carbon from bagasse	0.84 ± 0.01 (CV=1.36 %)	78.01 ± 1.45 (CV=1.86 %)	6.96 ± 0.06 (CV=0.92 %)	6.97 ± 0.08 (CV=1.15 %)

The pH of the solutions were adjusted to pH 5, as in the previous studies the optimum adsorption was achieved at pH 5 (Kohar, 2005). There was a slight drop of pH after treatment with rice straw and sweet rice straw at lower and higher concentrations of Pb(II) solutions. While as with sugar cane bagasse and carbon the pH did not change or tended to slightly increase.

As like Pb(II), Cd(II) also showed the same pattern in the pH, at lower and higher initial concentration of Cd(II) solutions, the pH decreased after treatment with rice straw and sweet rice straw, but at medium concentration sweet rice straw also showed a decrease in pH. While with bagasse and carbon at lower concentration it tend to increase, but at medium concentration sugar cane bagasse showed a de-crease in pH, while carbon did not. However, in higher concentration sugar cane bagasse showed a slight pH decrease and carbon was on the contrary.

The adsorption mechanism is not clear, however, it could be postulated that adsorption of heavy metals in an organic adsorbent could happen chemically or physically. Plants mostly consist of cellulose, hemicellulose, lignin and other organic compounds. Cellulose is a polymer of hydrocarbon chains and it has carboxylic or phenolic hydroxyl groups in its structures. Heavy metal ions can attach to two adjacent hydroxyl group in the adsorbent, and therefore release 2 hydrogen ions into the solution (Randal *et al.*, 1974), and so, theoretically it would lower the pH of the solution. Another possibility of adsorption is by physical mechanism, where the heavy metals ions become trapped in the pore of the adsorbent. It might be well that the two mechanisms occurred simultaneously. The decrease of pH in rice straw and sweet rice straw might explain that a chemical mechanism predominates with those adsorbents.

Table 3. Statistical Analysis of The Adsorption of Cd(II)and Pb(II) by Several Adsorbents

Type of adsorbent	Average of % Pb(II) adsorbed	Average of % Cd(II) adsorbed
Sugar cane bagasse	55,43 a	61,91 a
Sweet rice straw	68,92 b	64,89 a
Rice straw	70,72 b	67,36 a
Carbon from bagasse	82,97 c	87,85 b
LSD 5% =	2,58	7,10

Note: Notations a, b, and c are to show whether there are significant different between samples. Values followed by different letter meaning that they are significantly different by LSD test at = 0.05.

Table 3 showed that carbon from sugar cane bagasse has the highest adsorption ability than the other three adsorbents. It may be suggested that the carbon has smaller particle size than the other three adsorbents. The adsorption ability of the four adsorbents toward different metals (Cd and Pb) was also different. Sugar cane bagasse showed a poor adsorption ability to adsorb Pb(II), while on Cd(II), sugar cane bagasse, rice straw and also sweet rice straw did not show a significant difference.

Table 4. Statistical Analysis the Effect of Initial Concentration Elevation of Cd(II) and Pb(II) to the % Adsorbed

Concentrations	Average of % Pb(II) adsorbed	Average of % Cd(II) adsorbed
High Initial Concentration	60,39 a	62,87 a
Medium Initial Concentration	70,81 b	71,54 b
Low Initial Concentration	77,33 c	77,10 b
LSD 5% =	2,23	6,15

Note: Notations a, b, and c are to show whether there are significant different between samples.
Values followed by different letter meaning that they are significantly different by LSD test at α = 0,05.

When the initial concentrations of the metal solutions were increased, the mg of metal adsorbed/g adsorbent was also increased, however, the % adsorbed decreased. This phenomenon is likely due to saturation of the active sites of the adsorbents. Table 4 also showed that the decrease of % adsorbed of Pb(II) occurred from the medium concentration to high concentration of the initial concentrations of Pb(II), as for Cd(II), the decrease of % adsorbed which occurred at the medium and high concentrations did not show any significant different.

4. CONCLUSION

Carbon from sugar cane bagasse was the best Cd(II) and Pb(II) adsorbent when compared to the four other adsorbents. The adsorption activities of rice straw and sweet rice straw on Pb(II): were not significantly different, while sugar cane bagasse showed the least activity. Cd(II) adsorption did not show any significant different between sugar cane bagasse, rice straw and sweet rice straw. Carbon from sugar cane bagasse showed higher activity on the adsorption of Cd(II) and Pb(II). However, it needed a special treatment for activated carbon preparation, which. might need an extra cost Besides, the other three adsorbents still showed good activity on the adsorption of Cd(II) and Pb(II).

The higher the initial concentrations of Cd(II) and Pb(II) solutions, the lower percentage of metal adsorbed, even though the mg of metals adsorbed/g adsorbent increased. This might be due to saturation on the active sites of the adsorbents. The percentage of Pb(II) adsorbed at lower concentration was best adsorbed by carbon from sugar cane bagasse.

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