ADSORPTION OF HEAVY METALS Pb, Cd, Hg, Ag, Fe, and Zn FROM SOLUTION BY RICE STRAW

PENJERAPAN LOGAM BERAT Pb, Cd, Hg, Ag, Fe, dan Zn DARI LARUTAN OLEH JERAMI PADI

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Abstract

As rice straw is abundantly available in Indonesia and other tropical developing countries as an agricultural waste. This material may be used as a simple and environmentally friendly way to remove heavy metals from contaminated water sources for human use. In this paper, untreated rice straw was studied towards its ability to adsorb several heavy metals Pb, Cd, Hg, Ag, Fe, and Zn ions from aqueous solutions at concentrations of 2 ppm and 20 ppm, in individual and mixed solutions. In individual solutions at 2 ppm, the order of metal sorption by straw when calculated on a weight basis is Zn > Pb > Cd > Ag > Fe > Hg, at 20 ppm it is Pb > Fe > Cd > Zn > Hg > Ag. The selective order of the metal sorption at 2 ppm is: Cd > Zn > Pb > Ag > Fe ≈ Hg; while at 20 ppm, the order is Pb > Fe > Ag > Hg > Cd > Zn. Interestingly, in mixed solution experiments competitions between metals were occurred. The adsorption of the metals was also in line with the decrease of pH of the solutions, especially for Hg, suggesting that chemical reactions i.e. the release of H^+ was occurred. Further studies on the potentials of rice straw to filter out heavy metals from contaminated water are warranted.

Keywords:Rice straw, heavy metals elimination, mixed heavy metals solution, adsorption.

Abstrak

Jerami padi sangat banyak dihasilkan di Indonesia dan negara-negara tropis lainnya sebagai limbah pertanian. Bahan ini dapat digunakan sebagai sarana yang sederhana dan ramah lingkunagan untuk menghilangkan unsur logam berat dari sumber air terkontaminasi, yang akan digunakan untuk keperluan sehari-hari. Dalam tulisan ini dipelajari kemampuan jerami padi yang tidak diolah untuk menjerap beberapa unsur logam berat Pb, Cd, Hg, Ag, Fe dan Zn dari larutan pada konsentrasi 2 dan 20 ppm, dalam larutan tunggal maupun campuran. Dalam larutan tunggal pada konsentrasi 2 ppm urutan penjerapan logam adalah Zn > Pb > Cd > Ag > Fe > Hg, pada konsentrasi 20 ppm adalah Pb > Fe > Cd > Zn > Hg > Ag. Urutan penjerapan selektif logam pada 2 ppm adalah: Cd > Zn > Pb > Ag > Fe ≈ Hg; sedangkan pada 20 ppm, urutannya menjadi Pb > Fe > Ag > Hg > Cd > Zn. Jika unsur logam dicampur dalam larutan, terjadi persaingan (kompetisi) penjerapannya pada jerami padi. Penjerapan logam berat juga terjadi seiring dengan menurunnya pH dari larutan, terutama pada Hg. Hal ini menunjukkan adanya reaksi kimia yaitu terjadinya pelepasan H^+. Karena itu perlu dilakukan penelitian lebih lanjut mengenai kemampuan jerami padi untuk menyaring unsur logam berat dari air yang terkontaminasi.

Kata kunci: jerami padi, penjerapan logam berat, campuran logam berat, penjerapan.

1. INTRODUCTION

Heavy metals contamination of ground and surface water is of growing concern in many parts of the world, particularly in developing countries in which large populations have to use these sources for drinking and cooking water. Lead and cadmium are perhaps now the two most dangerous trace elements in our environment since they are so widespread due to industrial pollution and because they pose a variety of severe health risks.

Many studies had been conducted to eliminate heavy metals from water resources, such as flocculation, filtration using activated charcoal, and ion exchange, precipitation by chemicals, etc. However, because of the high cost of these methods, the development of a more cost-effective and environmentally friendly remediation system is necessary (Gardea-Torresdey *et al.*, 1996). In order to find more cost-effective and environmentally friendly methods, several studies had been carried out, by using living and dried plants, and agricultural wastes, such as *Eichhornia crassipes* (water hyacinth), *Alternanthera philoxeroides* (alligator weed), *Pistia stratiotes* (water lettuce) (Schneider& Rubio, 1999) various kinds of bark (Randall *et al.*, 1974, Gardea-Torresdey *et al*, 1998, Larsen & Schierup, 1981), alfalfa (Gardea-Torresdey *et al*, 1996) etc. Agricultural waste has also been studied, such as soybean hulls, sugarcane bagasse, rice hulls, rice straw, barley straw etc. (Friedman & Waiss, 1972, Kumar & Dara, 1980, Larsen & Schierup, 1981, Suemitsu *et al.*, 1986, Marshall *et al.*, 1995, Gardea-Torresdey *et al*, 2000).

Tarley *et al.* (2004), has conducted a study of the potensiality of rice husks for removing Cd(II) and Pb(II). Soediman *et al.* (1998) found that rice husk pretreated with 10% NaOH solution showed good adsorption on Cd(II) and Pb(II), and pretreated rice straw showed good results as well.

Kohar *et al.* (2002, 2002a) carried out a study of rice husk and straw pretreated with difference concentration of NaOH solution, and then compared it with rice straw as is. It turned out that pretreated rice straw did not give significant improvement in terms of mg metals adsorbed per g adsorbant.

Rocha *et al.* (2009), were tested the capasity of rice straw after treated with NaOH solution to produce a carbonaceous adsorbent to remove Cu(II), Zn(II) and Hg(II) from aqueous solution. This adsorption process reached the equilibrium before 1.5 hours, with maximum adsorption at pH 5. Kohar *et al.* (1997, 1998) also found that the optimum pH for the adsorption of Cd(II) and Pb(II) by rice husk and straw were also at pH 5-6.

Indonesia is facing substantial heavy metal pollution of ground and surface water in industrialized areas, but it also has vast numbers of padi fields. On the other hand, the production of rice is over 50 million tons per year, and the resulting rice straw is considered agricultural waste that is usually burnt in the fields, thus yielding a lot of smog. Yet, rice straw has not received much attention as a potential remover of heavy metals so far, and the results appear to be inconclusive. Kumar and Dara (1980) compared rice straw and rice husk with sugar cane bagasse, onion skin and garlic skin and found onion skin to be the best adsorption material. Marshall *et al.*(1993) found the adsorption capacity of rice straw for Zn to be lower than that of soybean hulls and cottonseed hulls, but higher than that of sugar cane bagasse. Another issue when using plant material or agricultural waste for heavy metal adsorption is whether to use the materials as is, or to first subject them to modification by chemical treatment. Larsen and Schierup (1981) used three types of barley straw (*Hordeum vulgare*): (1) Dried and ground in a mill, referred to as straw (untreated).(2) Dried, ground, boiled, and washed three times in demineralized water, referred to as straw (washed). (3) Treated as in (2) and mixed with pulverized $CaCO_3$ (2:1), referred as straw (washed) + $CaCO_3$. Other authors proposed soaking in NaOH solutions of 3-8 % [15,18]. It has been postulated that water treatment and alkali treatment will remove lignin and hemicelluloses, respectively, thus making the adsorptive sites more easily and abundantly available. However, when Kohar *et al* carried out a study on the adsorption of Pb and Cd using pretreated and untreated straw, they found out that the adsorption of Pb and Cd in mg metal adsorbed/g of adsorbent for pretreated straw (straw/H_2O and straw/NaOH) were significantly lower than the mg metal adsorbed/g untreated straw.

Given the fact that rice straw is plentifully available at virtually no cost in Indonesia and other tropical developing countries, we decided to more systematically evaluate the potentials of this agricultural waste product for the removal of heavy metals from contaminated waters. This paper investigates competitive activity of rice straw as is (straw/untreated) on several heavy metals.

2. METHODS

Materials:

Rice straw was obtained from padi fields near Surabaya, East Java. In the laboratory, this straw was washed with demineralized water to remove dirt and soil. It was then dried under the sun and cut and milled to particles of approximately 0.5-2 mm. This material was called straw/untreated. Nitric acid, analytical grade, was from Riedel De Haen, Saelze, Germany. Lead nitrate, cadmium acetate, mercury nitrate, silver nitrate, ferric nitrate and zinc acetate were analytical grade (Merck). Metal solutions of suitable concentrations (around 2 ppm and 20 ppm) were made in demineralized water.

Instrumentation:

pH values were measured with a GC-840 pH meter (Schott, Mainz, Germany).Metal concentrations were measured by atomic-emission spectrometry (AES), using an induced-coupled–plasma instrument (Fisons, model 3410 ARL, USA), with argon as reactant gas. The wavelengths for Pb, Cd, Hg, Ag, Fe, and Zn were 283.306, 228.802, 253,652, 328,068, 259,940 and 213,856 nm, respectively. Calibration curves were made using working solutions of different concentrations, in the range of 1-20 ppm in mixed standard solutions.

Adsorption/batch experiments:

These were carried out in the capacity (or equilibrium) mode: To 200 ml of sample solution, containing either Pb, Cd, Hg, Ag, Fe, and Zn ions in the order of 2 ppm or 20 ppm, was added 1 gram of straw material (untreated). The solutions were gently shaken for 1 hour and then filtered through Whatman 41 filter paper. The filtrate was analyzed by ICP-AES at the appropriate wavelength. In addition, the pH of the aqueous solution was also measured before and after the experiment as the initial and final pH.

Blank experiments were carried out by shaking the adsorbent of choice with 200 ml demineralized water for 1 hour and then filtered as described above. The filtrate was analyzed for its metal content and its pH (this is referred to as the initial pH).

Competitive experiments

To 200 ml of sample solution, containing mixed solutions of Pb, Cd, Hg, Ag, Fe and Zn ions in the order of 2 ppm or 20 ppm, was added 1 gram of straw material (untreated). The solutions were gently shaken for 1 hour and then filtered through Whatman 41 filter paper. The filtrate was analyzed by ICP-AES at the appropriate wavelength. After the experiments, the pH values were also measured. Blank experiments were also conducted as in the individual solutions experiments.

Column Experiments

Column (internal diameter 5cm, height 50 cm) was packed with 10 gram of straw, then demineralized water was run into the column, after the packing, the height of straw in the column was 30 cm.

15 L of heavy metals solutions with concentration of 20 ppm of each metals was run continuously into the column. Volume of each fraction collected was 300 ml at flow rate of 3.5 L/h.

The concentration of heavy metals in each fraction was determined by ICP-AES, and the pH was also determined by means of a pH meter.

Competitive column experiments:

A mixture solution of the appropriate metals was run into the column, giving the concentration of each metals in the mixture was 20 ppm. The condition of the column was as above.

Calculations

Adsorptions were expressed in % metal adsorbed and mg and mol of metals adsorbed per gram straw (untreated).

3. RESULT AND DISCUSSION

Tables 1 and 2 show that there were only a slight difference occurred on the adsorption when lower concentration of the metals (2 pm) was used; only Hg showed an increased in adsorption when it was in mixed solution with other metals.However, when an increase of the initial concentration was applied, Hg also showed an increase in the adsorption (from no adsorption it increased to 1.82 mg Hg adsorbed/g straw when the initial concentration was increased 10 fold).The order of metal sorption by straw when calculated on a weight basis is Zn > Pb > Cd > Ag > Fe > Hg when lower concentration of metals was applied (2 ppm), while in a higher concentration of metals the order was changed: Pb > Fe > Cd > Zn > Hg > Ag.

When the heavy metals were put in a mixture the selective order of the metal sorption in lower of various heavy metals concentration was as follows: Cd > Zn > Pb > Ag > Fe ≈ Hg; while at higher concentrations, the order was Pb > Fe > Ag > Hg > Cd > Zn.

Mixed solution showed that there were was a competition occurred in the active sites of the straw. Even though the amount of mg metals adsorbed/g straw were changed, some showed a decrease, some an increase, the total amount of the metals adsorbed was not much differed.

When an observation was made on the bases of % adsorbed of the metals in mixed solution, it can be seen that at lower concentration of the metals, the adsorption of each metal was increased a bit, in line with the decrease of the pH, also Hg showed some adsorption (from 0 up to 28.93%,the pH decreased 0.02 and 0.06 unit respectively).

When the concentration of the metals were increased 10 fold, the % adsorbed of each metal was varied, from as low as 20.59% for Zn, to 90.76% for Fe (in mixed solution). The highest % adsorbed showed the strongest adsorption affinity of the metal to straw, so that the order of metal sorption became: Fe > Ag > Pb > Hg > Cd > Zn.

At lower concentration (2 ppm), the % adsorbed was not much changed when the metals put together in the solution, but at higher concentration,the amount of metalspresent in the solution was increase, so that the chance of collision between metals and the active sites also increased, while the active sites available was still plenty, and as the result the % adsorbed also increased except for the metals which does not have a strong affinity to the adsorbent.In this case Cd and Zn showed a low affinity.

Table 1. Results of capacity experiments using initial solution of metal 2 ppm.

	Individual Solution					Mixed solution				
	pH					pH				
Metals	Initial	Final	mg metals adsorbed /g straw	mol metal adsorbed /g straw	% adsorb-ed	Initial	Final	mg metals adsorbed/ g straw	mol metal adsorbed/ straw	% adsorb-ed
Pb	7.25	7.25	0.39	1.88	89.58	6.34	6.28	0.37	1.79	94.30
Cd	7.01	7.09	0.37	3.29	90.24	6.34	6.28	0.47	0.42	90.28
Hg	7.01	6.99	-	-	-	6.34	6.28	0.14	0.70	28.93
Ag	6.89	6.83	0.31	2.87	71.51	6.34	6.28	0.31	2.87	81.96
Fe	6.42	6.44	0.19	3.42	44.18	6.34	6.28	0.15	2.69	58.31
Zn	6.80	6.67	0.43	6.58	87.24	6.34	6.28	0.44	6.73	85.96
Total			1.69	18.04				1.88	15.20	

Table 2. Results of capacity experiments using initial solution of metal 20 ppm.

	Individual Solution					Mixed solution				
	pH					pH				
Metals	Initial	Final	mg metal adsorbed/ g straw	mol metal ad-sorbed/g straw	% adsorb-ed	Initial	Final	mg metal adsorbed/ g straw	□mol metal adsrobed/g straw	% adsorb-ed
Pb	6.95	6.59	2.67	12.89	88.45	6.77	4.25	3.30	15.93	77.22
Cd	7.06	6.68	2.52	22.42	83.85	6.77	4.25	1.13	10.05	25.16
Hg	6.83	6.40	1.82	9.07	52.68	6.77	4.25	2.11	10.52	73.49
Ag	7.06	6.86	1.58	14.65	50.00	6.77	4.25	2.62	24.29	88.47
Fe	6.63	4.50	2.62	46.91	87.22	6.77	4.25	2.98	53.36	90.76
Zn	6.94	6.46	2.28	34.88	75.83	6.77	4.25	0.87	13.31	20.59
Total			13.49	140.8				13.01	127.46	

Table 3. Results of column experiments

	Individual Solution					**Mixed solution**				
	pH					pH				
Metals	Initial	Final	mg metal adsorbed /g straw	mol metal adsorbed/ g straw	Mid point volume (ml)	Initial	Final	mg metal adsorb-ed/g straw	mol metal adsorbed/ g straw	Mid point volume (ml)
Pb	6.93	5.32	17.73	85.57	9.20	7.87	3.73	4.03	19.45	1.65
Cd	6.78	5.89	9.01	80.16	5.25	7.87	3.73	1.84	16.37	0.75
Hg	7.26	4.50	13.00	64.81	6.60	7.87	3.73	13.34	66.50	5.55
Ag	7.46	5.00	5.15	47.74	2.70	7.87	3.73	1.51	14.00	0.60
Fe	6.51	3.30	5.66	101.35	3.45	7.87	3.73	6.09	109.05	2.40
Zn	5.80	4.97	13.00	198.87	6.60	7.87	3.73	1.27	19.43	0.50
Total			63.55	578.50				28.08	244.80	

According to Sun and Shi (1998) the space of the ion may be the main factor that determines the competition of the ions, and in this experiments Cd is a bulkier ion and so may Zn, compared to the other ions. At lower concentration of heavy metals solutions (2 ppm) the pH was barely changed, however, at higher concentration of the metals, there was a visible change in the pH, especially in the mixed solution. Randal *et al.* (1974)have proposed that heavy metals are bound to either carboxylic or phenolic hydroxyl groups in the organic material, andthey also suggested that heavy metal ions were attached to two adjacent hydroxyl groups, thereby releasing two hydrogen ions into the solution. This should theoretically, lower the pH in the solution during and after the experiments.This theory may explain the change in the pH in these experiments. At lower concentration there was only a slight change in pH; on some metals (Pb and Cd) there was no change at all, even though some adsorptions were still occurred. As the concentrations of the metals were low, the reactions of metals to the phenolic/carboxylic groups of the organic materials were also small, thus giving only a very small change in the pH. When the metal were mixed, the total amount of the metals in the solution became bigger, that way the chance of possible reaction in the solution also add up, and in turn, the H^+ released were also added, even though the increase in pH was not too significant at low concentration. However, when the concentrations of the metals were raised 10 fold, the decrease of pH was more obvious, especially in the competitive experiments, and this also applied in the column experiments.It is interesting to observe the adsorption of Hg to straw. When it was put by itself in the solution, there was only a fraction of a change in pH occurred, and there was no adsorption. But in a mixed solution, where the decrease of pH was more obvious, it showed some adsorption ability of the straw to adsorbed Hg, even at lower concentration. When the concentration was raised 10 fold, even in individual solution Hg showed some increase in adsorption, more over in the competitive experiments, while the adsorption of other metals decreased, the amount of Hg adsorbed/g straw increased. It can also be seen in the column experiments, 4 out of 6 metals in the mixed solution showed a decrease of the amount of metals adsorbed/g straw, only Hg and Fe showed a slight increase in the mg of metals adsorbed/g straw. The decrease of pH in the individual solutions also showed interesting phenomenon: the pH decrease of Pb^{2+}, Cd^{2+}, Hg^{2+}, and Zn^{2+}, which have 2 positive charges were about the same (0,36, 0,38, 0,43, and 0,48 unit pH respectively), while Ag^{+} which has only one positive charge gave the smallest decrease in pH (0,10 unit), and Fe^{3+} which has 3 positive charges showed the biggest pH increased (2.13 unit pH).The amount of metals adsorbed/g straw in column experiments was by far larger than that of in the batch experiments because the amount of straw was increased and also the process was running continuously using a much larger volume of solution (200 ml compared to 15 L) even though the initial concentration was the same (20 ppm).In column competitive experiments the amount adsorbed of most metals droppeddrastically, only Hg and Fe showed a small increase, intotal, the amount of mg/g adsorbed and also the umol metal adsorbed also dropped to about a half. The final pH also dropped drastically to 3.73 unit pH. In other study by Kohar *et al.*(1997)the adsorption of Pb and Cd in low pH was very low as well, whereas the optimum pH for Pb and Cd was at pH 5. Study on column experiments need to be explored in a more thorough research.

4.CONCLUSIONS

Rice straw was studied as adsorbent for the removal of different metal ions in solutions.The amount of metals adsorbed/g straw increased with the increase of initialconcentrations of the metals and also with that of the straw.pH also played important role in the adsorption of heavy metals by straw, which showed that chemical reactions were occurred in the adsorption, even though there was also a possibility that the adsorption was going through physical adsorption. Competitive adsorption was occurred in mixed solution.

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