ELIMINATION OF CADMIUM AND LEAD MIXTURE IN SOLUTION BY PRETREATED RICE STRAW AND HUSK

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Abstract:

An experiment on the activity of pretreated rice straw and husk in eliminating heavy metals from solution has been conducted. The rice straw and husk were soaked in 3% NaOH solution, drained and then washed with demineralised water until the washing became neutral (the results were referred to as ***straw*** *and* ***husk****). The pretreated rice straw and husk (****straw*** *and* ***husk****) were mixed (stirring and without stirring) separately with Cd and Pb solution in time series. It was found that Cd was adsorbed more than Pb and* ***straw*** *was more active than* ***husk****. On the other hand, the stirring process and time series did not give much effect on* ***straw****, while the activity of* ***husk*** *increased with the increase of time period.*

Key words: *Heavy metals, husk, straw, elimination, adsorption.*

Abstrak:

Dalam penelitian ini dilakukan studi untuk mengetahui aktivitas jerami dan sekam padi yang telah diolah dengan larutan 3% NaOH. Jerami dan sekam padi direndam dengan larutan 3% NaOH, ditiriskan, dan kemudian dicuci dengan air bebas mineral sampai air euciannya menjadi netral (hasilnya disebut sebagai **jerami** dan **sekam**). Jerami dan sekam padi yang telah diolah (**jerami** dan **sekam**) masing-masing dicampur dengan larutan Cd dan Pb (dengan cara pendiaman dan pengadukan). Hasilnya menunjukkan bahwa Cd lebih terjerap dari pada Pb, dan j**erami** lebih aktif dari pada **sekam**. Selain itu pengadukan dan waktu proses tidak banyak berpengaruh pada **jerami**, sebaliknya aktivitas **sekam** meningkat dengan bertambahnya waktu pengadukan atau pendiaman.

Kata kunci: penjerapan, eliminasi, logam berat, jerami, sekam.

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I. Introduction

Contamination of water with heavy metals is still a serious problems. With the increasing number of industries, the problem becomes worse and worse. As the installation of waste water treatment units are still very costly, people have been trying to seek for cheaper means in eliminating heavy metals from water sources. Friedman and Waiss (1972) had studied the mercury uptake from water by agricultural products and by-products such as tannin in walnut expeller meal and peanuts skin, and proteins, as in woll and feathers. While in 1981, Larsen dan Schierup conducted a study using barley straw to eliminate heavy metals from solution, and it was found that straw has an activity to adsorb heavy metals from solution (Larsen & Schierup, 1981). Marshall et al. 1993 also studied the ability of rice milling byproducts (hulls and bran) to adsorbed metal ions from aqueous solution; he continued his study (1995) using soybean and cottonseed hulls, rice straw and sugarcane baggase. According to their publications, the adsorption capacity of those materials for Zn(II) were: soybean hulls > cottonseed hulls > rice straw > sugarcane baggase. Then in 1995 an experiment was carried out in Indonesia to test the activity of rice husk on the adsorption of heavy metals Cd and Pb (Wiwik, data unpublished). This experiment was then followed by other experiments using pretreated rice husk to test its activity on the elimination of Cd and Pb in solution and in waste water samples as well. Firstly, the husk was treated using 10% NaOH solution and it showed twice as much elimination of Cd and Pb than the elimination caused by rice husk prior treatment, while at the same time the amount of husk used could be reduced by 10 fold (Eko, 1996, R. Soediatmoko S. et. al., 1998).

The above mentioned experiments were continued by trials using much less NaOH in the treatment of rice husk and then rice straw was also taken into consideration (Kohar and Idfi, in press). It was found out that using 2% NaOH solution has already increased the activity of husk in adsorbing Cd and Pb in solution. However, treatment of husk with 1% and 2% NaOH solutions showed a much lower activity than that of straw. The study also showed that the highest % adsorbed of Cd and Pb was obtained by soaking 3% and 4% w/v straw in the metal solutions; and the straw was pretreated with 3%, as well as with 4% NaOH solution. In all those experiments the heavy metals were treated separately. Therefore, in this study Cd and Pb were treated in a mixture, in a 1 to 10 composition, using husk and straw pretreated with 3% NaOH solution and the concentrations of husk and straw used are 4% and 6% w/v, together with a variation of soaking and stirring times.

II. Materials and Method

Materials:

Rice straw and husk (collected from padi field in Sukolilo area, Surabaya, East Jawa), demineralised water (Faculty of Pharmacy Laboratory, University of Surabaya), Argon (Samator, *welding grade*), $Cd(NO_3)_2.4H_2O$, $Pb(NO_3)_2$ (E.Merck, Darmstadt), NaOH pro analysis (Riedel de Haen).

Instrumentations: :

Inductively Coupled Plasma Spectrometer (**ICPS**, Fison, model 3410 ARL), pH meter (CG 840 - Schott Gerate), and glass apparatus.

Method:

Sodium hydroxide 3% : NaOH (600 g) was dissolved in demineralised water to make 20 L solution.

Treatment of straw and husk:

Rice straw (cut to about 2 cm long) and husk were soaked in hot water, drained, and then soaked in 3%NaOH solution for several days.The soaked straw and husk then was drained and washed with demineralised water until the washing became neutral (checked with pH meter), and then dried under the sun. The result was referred to as **straw** and **husk**.

Standard solution of Cd and Pb :

Standard solution of Cd: $Cd(NO_3)_2.4H_2O$ (160.1 mg) was dissolved in demineralised water to make 2.5 L solution. This solution was diluted to make 8 other solutions with different concentrations: 0.012 ppm., 0.047 ppm. 0.234 ppm., 0.465 ppm., 0.934 ppm., 2.334 ppm., 4.668 ppm., and 9.335 ppm. of Cd.

Standard solution of Pb: $Pb(NO_3)_2$ (801.4 mg) was dissolved in demineralised water to make 2.5 L solution. This solution was diluted to make 8 other solutions with different concentrations: 0.1 ppm., 0.401 ppm. 2.005 ppm., 4.011 ppm., 8.021 ppm., 20.053ppm., 40.106 ppm., and 80.213 ppm. of Pb.

Sample solution of Cd and Pb:

A solution containing 3.68 ppm. Cd and 38.793 ppm. Pb in 20 L was made . The content of Cd and Pb in the sample solution was checked by **ICPS**.

*Treatment on Cd and Pbsample solution by **straw** and **husk***:

Pb and Cd sample solution (50,0 ml) was mixed with **straw** and **husk** (4% and 6% w/v, stirring and without stirring), for 1h., 2h., 3h. and 4 h., then filtrated using Whatman 41 filter paper. The Cd and Pb content in the filtrates were analysed by **ICPS** at 228.802 nm and 283.306 nm for Cd and Pb repectively.

Blank experiment : exactly the same as the ones in the sample treatment, using 50,0 ml demineralised water only, treated with **straw** and **husk**.

In another publication (Kohar and Idfi, 2002), it was shown that when a concentration of 4% **straw** or **husk** was used to treat individual metal solutions, the adsorption of Cd and Pb were higher than that of 1% concentration. Therefore, in this study the concentration of **straw** and **husk** used are of 4% and 6%, to see wether the increase of concentration by 2% will give considerable rise in adsorption.

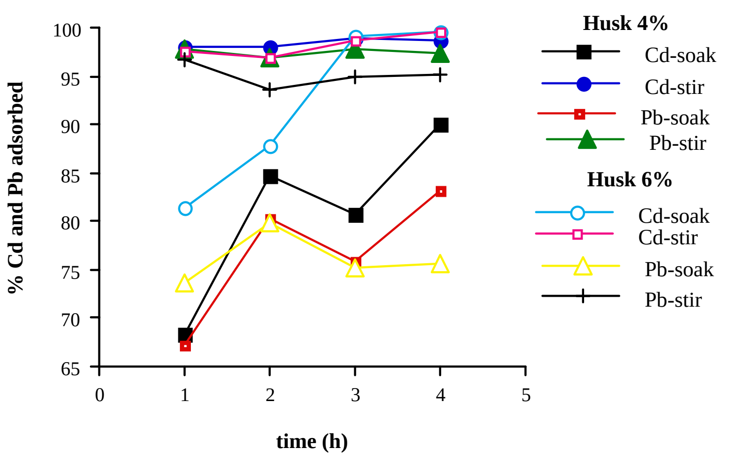
III. Result and Discussion

Table 1. % Cd and Pb adsorbed by **husk** (4% w/v, with and without stirring).

	Without stirring								Stirring (100 rpm)							
	%Cd adsorbed				%Pb adsorbed				%Cd adsorbed				%Pb adsorbed			
	1h	2h	3h	4h	1h	2h	3h	4h	1h	2h	3h	4h	1h	2h	3h	4h
1	67.99	84.93	85.04	89.47	69.99	77.44	79.22	82.50	98.85	98.80	98.94	98.05	97.14	97.93	97.44	97.56
2	65.34	83.01	85.40	86.99	67.49	78.21	79.89	79.26	97.94	98.31	99.17	98.26	97.27	97.37	97.09	97.88
3	65.96	82.69	77.93	92.03	65.83	76.74	72.68	82.08	99.05	97.81	97.85	98.91	98.25	95.59	97.88	97.47
4	66.29	83.28	79.30	89.81	64.64	80.20	71.70	81.24	99.33	96.85	98.76	98.15	97.34	97.26	97.00	97.90
5	69.66	83.04	78.58	92.09	63.98	79.25	78.68	87.20	97.26	97.42	99.09	98.00	97.88	97.86	96.69	95.74
6	69.77	85.47	80.06	89.64	67.66	80.54	71.43	85.58	99.22	98.52	98.76	98.74	97.81	96.97	97.56	94.12
7	70.63	86.58	80.87	87.03	67.40	86.46	73.97	78.86	94.87	98.09	99.11	99.91	99.17	95.44	99.17	98.88
8	68.22	82.88	80.52	91.36	67.01	79.09	78.49	84.89	99.54	98.46	98.59	98.05	97.71	98.44	96.93	96.86
9	69.70	87.99	80.86	92.77	69.59	82.57	74.88	89.04	97.63	97.33	98.80	99.17	97.11	96.24	98.56	97.59
10	68.98	87.56	79.10	89.29	67.76	83.37	77.24	81.03	96.39	97.76	99.89	98.52	97.93	96.02	98.46	99.10
Av	68.25	84.74	80.77	90.05	67.14	80.39	75.82	83.17	97.99	97.94	98.90	98.58	97.76	96.91	97.68	97.31
SD	1.83	2.06	2.54	2.02	1.91	2.99	3.26	3.39	1.51	0.61	0.51	0.62	0.62	1.04	0.82	1.47

Table 2. % Cd and Pb adsorbed by **husk** (6% w/v, with and without stirring).

	Without stirring								**Stirring (100 rpm)**							
	%Cd adsorbed				%Pb adsorbed				%Cd adsorbed				%Pb adsorbed			
	1h	2h	3h	4h	1h	2h	3h	4h	1h	2h	3h	4h	1h	2h	3h	4h
1	81.73	86.32	99.78	99.46	70.38	77.84	77.19	74.70	96.50	96.35	98.52	99.44	96.22	93.62	95.81	95.00
2	78.41	84.95	98.85	99.76	75.39	75.19	77.07	74.71	97.57	97.02	98.55	99.41	97.01	93.61	95.86	95.27
3	82.21	84.04	98.87	99.46	72.63	76.27	74.99	74.72	97.81	96.18	98.24	99.48	96.37	93.77	94.61	95.52
4	81.97	87.64	98.67	99.61	73.53	79.36	74.31	75.29	98.68	96.46	98.09	99.61	98.81	92.60	95.07	94.98
5	75.09	89.51	98.48	99.70	70.90	83.04	73.70	76.67	97.74	96.70	98.22	99.61	97.51	93.70	94.61	95.27
6	85.69	87.01	98.83	99.72	71.42	86.86	74.12	75.58	97.66	96.89	99.24	99.68	96.20	93.67	94.69	94.41
7	78.98	87.36	99.11	99.57	77.61	80.40	74.02	76.71	97.29	97.29	97.96	99.57	93.89	94.56	95.19	95.20
8	85.27	88.95	99.15	99.59	74.26	78.79	77.21	77.56	98.02	97.18	99.18	99.78	98.71	94.69	94.12	95.57
9	81.56	91.88	99.25	99.52	73.71	80.09	73.36	74.85	98.00	97.44	99.28	99.80	96.15	92.87	94.27	94.95
10	83.28	91.09	99.41	99.61	76.95	79.74	76.88	75.00	95.61	97.18	99.41	99.76	96.15	93.70	95.17	94.68
Av	81.42	87.88	99.04	99.60	73.73	79.76	75.29	75.58	97.49	96.87	98.67	99.61	96.74	93.68	94.94	95.09
SD	3.21	2.52	0.38	0.10	2.50	3.33	1.61	1.03	0.86	0.43	0.55	0.14	1.42	0.64	0.59	0.36



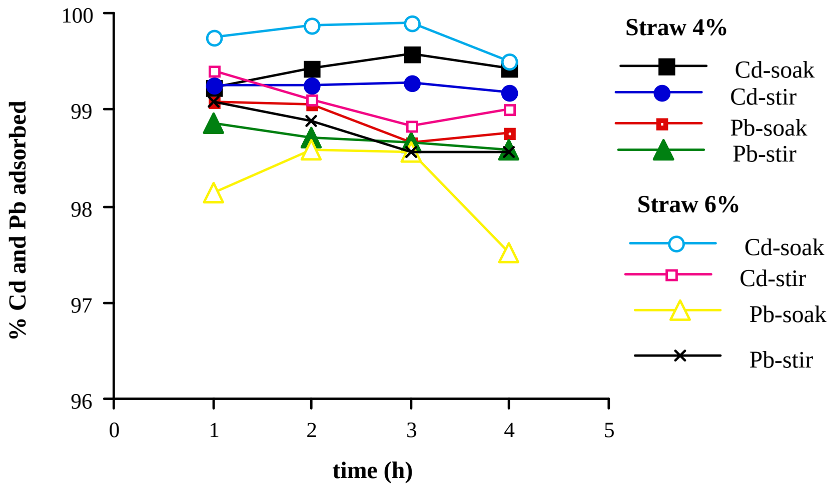
Graph 1. % Cd and Pb adsorbed by **husk** (4 and 6% w/v, with and without stirring).

Table 3. % Cd and Pb adsorbed by **straw** (4% w/v, with and without stirring/ soaked).

	Without stirring								Stirring (100 rpm)							
	% Cd adsorbed				% Pb adsorbed				% Cd adsorbed				% Pb adsorbed			
	1 h	2 h	3 h	4 h	1 h	2 h	3 h	4 h	1 h	2 h	3 h	4 h	1 h	2 h	3 h	4 h
1	99.10	99.56	99.02	99.32	98.40	99.09	97.99	99.52	99.37	99.32	99.43	98.67	98.88	98.77	98.73	97.86
2	99.13	99.51	99.97	99.43	99.23	99.07	98.51	99.65	99.37	99.18	99.13	98.40	98.98	98.80	98.73	98.01
3	99.16	99.38	99.86	99.54	98.90	98.09	98.67	98.62	99.21	99.10	99.02	99.27	98.84	98.53	98.38	97.86
4	99.21	99.46	99.99	99.51	99.17	99.31	98.55	99.75	99.21	99.99	99.16	98.67	98.67	98.67	98.63	97.84
5	99.24	99.48	99.10	99.46	99.09	99.02	98.47	99.75	99.13	99.08	99.48	99.35	98.92	98.63	98.82	98.82
6	99.08	99.40	99.16	99.54	99.09	99.25	99.02	99.89	99.24	99.02	99.43	99.46	98.77	98.61	98.50	98.98
7	99.05	99.32	99.97	99.51	99.13	99.29	98.69	99.96	94.24	99.16	99.13	99.46	99.11	98.61	98.57	98.98
8	99.97	99.40	99.78	99.40	99.46	99.17	98.80	99.77	99.24	99.24	99.46	99.46	98.92	99.02	99.53	99.92
9	99.13	99.29	99.83	99.07	99.07	99.29	98.71	93.62	97.32	99.21	99.51	99.48	98.90	98.71	98.07	98.82
10	99.16	99.38	99.16	99.67	99.19	99.00	99.11	97.10	99.21	99.21	99.16	99.51	98.82	98.73	98.55	98.73
Av	99.22	99.42	99.58	99.44	99.07	99.06	98.65	98.76	99.25	99.25	99.29	99.17	98.86	98.71	98.65	98.58
SD	0.27	0.08	0.41	0.16	0.28	0.36	0.31	2.01	0.08	0.27	0.19	0.42	0.12	0.14	0.37	0.68

Table 4. % Cd and Pb adsorbed by **straw** (6% w/v, with and without stirring).

	Without stirring								Stirring							
	%Cd adsorbed				%Pb adsorbed				%Cd adsorbed				%Pb adsorbed			
	1h	2h	3h	4h	1h	2h	3h	4h	1h	2h	3h	4h	1h	2h	3h	4h
1	99.70	99.81	99.89	99.13	97.97	98.42	98.57	98.69	99.37	99.16	98.72	99.16	98.82	98.69	98.49	98.92
2	99.67	99.86	99.89	99.62	97.97	98.51	98.40	97.31	99.35	98.99	98.88	98.99	98.82	98.80	98.59	98.47
3	99.67	99.89	99.89	99.56	97.78	98.65	98.57	97.64	99.35	99.21	98.91	98.97	98.84	98.92	98.63	98.63
4	99.73	99.86	99.84	99.65	97.03	98.61	98.57	97.53	99.46	99.08	98.75	98.99	99.25	98.82	98.44	98.63
5	99.78	99.89	99.92	99.67	98.07	98.77	98.59	97.72	99.43	99.08	98.83	98.99	99.07	98.96	98.51	98.63
6	99.78	99.84	99.94	99.04	98.07	98.51	98.59	98.61	99.40	99.02	98.75	98.97	99.29	98.94	98.55	98.38
7	99.75	99.86	99.89	99.48	98.26	98.71	98.51	97.58	94.40	99.10	98.91	98.94	99.02	99.09	98.63	98.38
8	99.81	94.94	99.89	99.62	99.23	98.61	98.57	97.70	99.46	99.18	98.91	98.97	99.19	98.84	99.63	98.61
9	99.84	99.86	99.86	99.62	98.55	98.42	98.61	97.43	97.48	99.05	98.88	98.99	99.33	98.84	98.55	98.32
10	99.81	99.89	99.89	99.62	98.34	98.69	98.61	97.91	99.43	99.08	98.83	99.02	99.13	98.92	98.57	98.65
Av	99.75	99.87	99.89	99.50	98.13	98.59	98.56	97.81	99.41	99.10	98.84	99.00	99.09	98.88	98.57	98.55
SD	0.06	0.03	0.03	0.23	0.56	0.12	0.06	0.47	0.05	0.07	0.07	0.06	0.18	0.11	0.08	0.18



Graph 2. % Cd and Pb adsorbed by **straw** (4 and 6% w/v, by with and without stirring).

Data obtained was analysed by Anova: Two - Factor With Replication (Excell, version 5.0), followed by least significant different.

Using analysis of varian to compare the activity of **straw** and **husk**, it showed that :

1. When 4% w/v of adsorbent was used, **straw** was more active than **husk** in eliminating Cd from solution ($F = 2962.054 > F_{crit} = 3.974$). Even in the 1-hour experiment **straw** has already reached more than 99% elimination, and it was increasing only slightly in the longer time period, while **husk** showed a time-dependent elimination. The result increased from 1-hour to 4-hour experiment, and the activity is less than **straw**.

This results was obtained in the non stirring/soaking process. In the stirring process, time did not show significant difference ($F = 2.464 < F_{crit} = 2.732$), and **straw** showed a slightly higher acitivity than **husk** ($F = 35.441 > F_{crit} = 3.974$). In the stirring process, time did not showed significant change in the activity of **straw**, as it has reached its maximum i.e more than 99%. As for **husk** time still contributed in increasing the activity eventhough it was not very obvious.

The difference was more obvious in their activity in eliminating Pb, especially in the non-stirring process ($F = 2030.695 >>> F_{crit} = 3.974$). Again, **straw** did not show time-dependency, but **husk** showed quite an increase in addition of time.

2. Using 6% w/v of adsorbent did not cause an increase in the activity of **straw**, but showed an effect on **husk**. The activity of husk was also affected by the stirring process. The increase of concentration of **husk** also gave rise to its activity, but it also increased the secondary waste. So it is not advisable to use this concentration.

In comparing the stirring and non-stirring process, it was found that if the result has already reached 99 % and over, stirring did not help much. However, when non-stirring process was applied and the elimination only reached 80% or less, stirring could increase the elimination of metals from solution, as the stirring process will increase the contact between heavy metal ions with the active sites of the adsorbents.

In all experiments, Cd was adsorbed more than Pb and **straw** was more active than **husk**.

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