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Research Article

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Adsorption Capacity of Pb (II), Cd (II), and Cr (VI) from Aqueous Solution Using Coffee Industry Waste

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ABSTRACT

Industrial coffee waste as coffee husk was evaluated as a new biosorbent to eliminate toxic lead, cadmium and chromium from water and wastewater. Without any chemical treatment, coffee husk was washed, dried and grounded into powder for use in the experiment. The result indicated that optimum adsorption capacity of Pb^{2+}, Cd^{2+}, dan Cr^{6+} were obtained at concentration of biosorben was 50 mg/50 mL with pH 6.6; 5.6and 4.4 and contact time were81.1; 55.5 dan 96.7 minute. Adsorption capacity of Pb^{2+}, Cd^{2+} dan Cr^{6+}were 261.30 mg/g, 108.81 mg/g dan 45.38 mg/g respectively.

Keywords: Coffee industry waste; Biosorbent; Lead; Cadmium; Chromium

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INTRODUCTION

The *Coffea Arabica* (Arabica) and *Coffea Canephora* (Robusta) plant species are providing the 75% and 25% of the world production respectively [1]. The processing of coffee generates significant amount of agricultural waste. The main coffee industry by-products are the spent coffee grounds, the coffee silver skin and the coffee husk. In coffee production countries, the coffee wastes are source of serious pollution and environmental problem. Several researches have been conducted for the revalorization of the coffee industry waste. Coffee wastes have been used as a low cost adsorbent in water treatment for heavy metals removal from industrial effluents [2].

In some industrial effluent, the concentration of heavy metals is higher than the safe permissible limits, which affects the biosphere. The excessive release of heavy metals into the environment is a major concern worldwide. Heavy metals contamination of water is a serious threat to the globe ecosystem. These pollutants could remove by adsorbent prepared from pyrolyzed coffee residues and clay [3].

Several physicochemical processes have been studied, including adsorption. Natural materials that are available in large quantities or certain waste product from industry or agricultural operation may have potential as inexpensive sorbents [4]. Biosorption can be considered as an ecofriendly and economical waste water treatment that has been proven to be highly efficient to remove low metal concentration [5]. The effectiveness of biosorption for the removal of heavy metals has been shown in a number studies. Exhausted coffee compounds on metal ion sorption Cr(III), Cu(II), Ni(II) [6]. Petiolar felt-sheath of palm to sorption of heavy metal (Pb^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}) and mandarin peels to toxic metal [7,8].

The adsorption lead (II) and Cd(II) on peels banana has been studied [9]. Chitosan as biosorbent for removal Pb^{2+} , Ni^{2+}, Cd(II), Cr (III) and Cr (VI) [10,11], Orange peel as biosorbent to adsorption of Cu (II) [12], Palm oil fruits for Copper [13], Cu(II) by *Thuja orientalis* [14].

Biosorption of strontium can use spent coffee ground [15], Cr (III) by coffee dust [16], Cd by black gram husk (*Cicer arientinum*) [17]. The adsorption of Cu(II) and Pb(II) from aqueous solution by chemical modified spent coffee grained. Spent coffee grains were modified with citric acid solution to increase the quantify of carboxylatic groups improving its metal adsorption capacity [5].

Coffee husk is probably the major residues from the handling and processing of coffee [18]. The potential of spent coffee ground for the removal of copper has been investigated as a low-cost adsorbent for biosorption of heavy metals. Among agro-waste, coffee husk (by product of brewing coffee) have the potential to be used as biosorbent for removing heavy metals from aqueous solution [2,5].

The aim of this study was to evaluate the potential use of the coffee husk as a biosorbent of Pb(II), Cd(II) and Cr (III) in aqueous solution.

EXPERIMENTAL SECTION

Materials

Samples of coffee husk were collected from Pangalengan, West Java Province, Indonesia.

Optimization Adsorption

Optimization of adsorption at room temperature with concentration of Pb(II), Cd(II)and Cr(VI). Variation of pH, time, than weight of adsorbent with simulation. Optimization method was used is *Central Composite Design* (CCD) with range of pH 2-7, time of 10-120 minutes and weight of adsorbent was 50-500 mg. Analysis of CCD was shown in Table 1.

Table 1: Design of optimization response surface central composite design for adsorption of Pb, Cd dan Cr

No.	pH	Time (minute)	Adsorbent (mg)
1	3.01349	32,297	141.214
2	5.98651	32,297	141.214
3	3.01349	32,297	408.786
4	5.98651	32,297	408.786
5	3.01349	97,703	141.214
6	5.98651	97,703	141.214
7	3.01349	97,703	408.786
8	5.98651	97,703	408.786
9	2	65	275
10	7	65	275
11	4.5	65	50
12	4.5	65	500
13	4.5	10	275
14	4.5	120	275
15	4.5	65	275
16	4.5	65	275
17	4.5	65	275
18	4.5	65	275
19	4.5	65	275
20	4.5	65	275

Optimum condition obtained with adsorbate concentration was 50 mg/L. Analysis of cation used atomic absorption spectrophotometer (AAS).

Isotherm Adsorption

Amount of 50 ml of Pb^{2+}(optimum pH) with concentration 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120 and 140 mg/L. Each of solution was added to erlenmeyer 100 mL. Solution was agitated with shaker at 150 rpm for optimum time. Solution was filtered with Whatman 42, and concentration of Pb(II) was detected by AAS. The same treatment was done for adsorbate that contained of Cd and Cr.

Adsorption capacity was calculated with equation :

$$Q_e = \frac{(Co - Ce)\, xvol\ adsorbat(L)}{weight\ of\ adsorben(g)}$$

Co=initial concentration (mgL^{-1})
Ce=final concentration of solution in equilibrium (mgL^{-1})
Qe=concentration of adsorbate on adsorben in equilibrium (mg/g)
Adsorption capacity (mg/g)=a/b
a=weight of initial adsorbate (mg)-weight of final adsorbate (mg)
b=Weight of adsorbent (g)

RESULTS AND DISCUSSION

Characterization of Biosorbent Coffee Husk

Biosorbent from coffee husk was characterized to ability of adsorption of heavy metal. The characterization was shown in Figure 1.

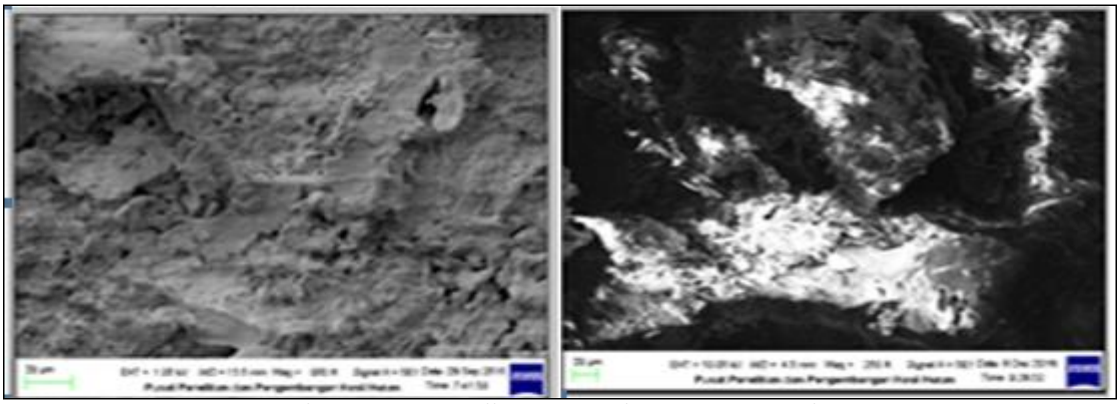

Figure 1: Morfologi biosorbent coffee husk (a) before adsorption (b) after adsorption

Figure 1 shown of biosorbent coffee husk before and after adsorption. Morphology biosorbent coffee husk before adsorption for 50x, appeared rough surface due to the particle size uneven and the color was dark. Biosorbent after adsorption was shown shine and bright surface. It is proved adsorption of metal ion onto surface of biosorbent. Characterization with SEM-EDX and FTIR was shown in Table 2.

Table 2: Characterization of SEM-EDX dan FTIR

Biosorbent	Ratio of element (%)					Absorbance (cm^{-1})
	C	O	K	Cu	Al	
Coffe husk	57,09	32,67	1,62	4,30	4,33	3265
						2918; 2847
						1606; 1524

Characterization using *Scanning electron microscopy EDX* was obtained component carbon, oxygen, potassium, cuprum and aluminium. Carbon and oxygen were the dominant in biosorbent and classified in organic compounds. Characterization of functional group with IR was obtained adsorption at 3265 (cm^{-1}). It showed functional groups of hydroxyl, aromatic, alkene, alkuna, amida and amina. Adsorption was sharp act wave number 2918 dan 1847 cm^{-1}. In this peak was stretching vibration for alkana, aldehyde dan karboxylate. Wave number of primary amina and secondary amina for bending vibration.

Optimization of Adsorption Pb, Cd dan Cr with Biosorbent of Coffee Husk

Optimization of adsorption was done by batch system with variation of metal ion with 20 conditions. Variation of experiment was design by minitab program with *Response Surface Central Composite Design* (Table 1). Data of experiment was shown in Table 3.

Table 3: Adsorption capacity at variation of experiment for adsorbate of Pb, Cd dan Cr

No	Condition treatment			Adsorption capacity mg/g (eg)		
	pH	Weight	Time	Pb	Cd	Cr
1	4.5	500	65	17.96	4.74	4.87
2	4.5	275	120	33.98	7.8	8.88
3	3.01	408	97	8.73	3.73	6.01
4	7	275	65	27.76	8.75	8.91
5	4.5	275	10	33.16	7.33	8.88
6	5.98	141	97.7	57.69	12.52	17.36
7	4.5	275	65	34.32	8.11	8.93
8	5.98	141	32.2	56.62	14.52	17.31
9	3.01	141	32.2	12.9	10.86	17.48
10	3.01	408	32.2	8.45	3.75	6.07
11	5.98	408	32.2	20.74	5.6	5.99
12	5.98	408	97.7	21.86	6.12	6
13	2	275	65	5	9.09	8.97
14	4.5	50	65	91.49	33.42	48.66
15	4.5	275	65	34.74	8.17	8.68
16	3.01	141	32.2	12.4	10.82	17.46
17	5.98	141	32.2	53.18	14.28	17.29
18	3.01	408	32.2	7.84	3.75	6.06
19	5.98	408	32.2	20.26	5.65	5.99
20	3.01	141	97.7	10.6	10.81	17.49

Minitab program Response surface CCD was used to get optimum condition. The result from CCD program were pH, contact time, and weight or concentration of biosorbent for Pb were pH 6.64, contact time 81.1 minute and weight of biosorbent was 50 mg.

Adsorption Capacity of Biosorbent Coffee Husk

Adsorption capacity of biosorbent coffee husk to adsorption of Pb, Cd, and Cr was done at room temperature (isothermal adsorption). Adsorption of Pb, Cd and Cr was done with variation of concentration 1-500 mg/L and for adsorbate Cd and Cr with variation concentration was 1-350 mg/L. Efficiency adsorption Pb, Cd and Cr were 100%-52, 6%, 100-27, 6% dan 100%-5, 9%, respectively. Adsorption capacity were 0.998-297, 67 mg/g, 0.994-99, 8 mg/g, 0.997-75, 695 mg/g.

Table 4: Optimum condition of experiment to adsorption of Pb, Cd dan Cr

Pb	**pH**	**6.6**
	Time (min)	81.1
	Biosorbent (mg/50ml)	50
Cd	pH	5.6
	Time (min)	55.5
	Biosorbent (mg/50ml)	50
Cr	pH	4.4
	Time (min)	96.7
	Biosorbent (mg/50ml)	50

Table 5: Efficiency and adsorption capacity of biosorbent coffee husk

Concentration of adsorbate (mg/L)			**Efficiency adsorption (%)**			**Adsorption capacity Qe (mg/g)**		
Pb^{2+}	**Cd^{2+}**	**Cr^{6+}**	**Pb^{2+}**	**Cd^{2+}**	**Cr^{6+}**	**Pb^{2+}**	**Cd^{2+}**	**Cr^{6+}**
1	1	1	100	100	100	0.998	0.994	0.997
2	2	2	100	100	100	1.99	1.998	1.998
4	4	4	100	100	98.72	3.99	3.98	3.929
10	10	10	100	90.5	98.49	9.98	9.022	9.81
20	20	20	100	79.1	98.44	19.95	15.765	19.61
40	60	60	100	63.8	51.27	39.86	38.225	30.699
60	80	80	100	60.4	47.96	59.82	48.018	38.022
80	100	100	100	54.3	44.08	79.76	61.442	43.927
100	150	200	100	46.6	35.03	99.7	69.339	75.695
150	200	300	100	42.2	21	149.48	83.716	69.361
200	300	350	100	33.3	5.91	199.5	99.799	52.447
300	350		95.5	27.6		297.67	96.555	20.553
350			75			261.89		
400			65.1			259.91		
450			58.2			259.85		
500			52.6			262.49		

Tables 4 and 5 showed capacity adsorption of biosorbent to adsorb of Pb was the highest from Cd and Cr. Adsorption capacity was influence of adsorbate concentration.

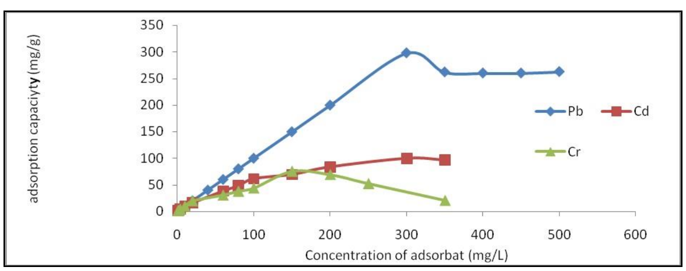

Figure 2: Adsorption capacity with concentration adsorption

Figure 2 showed that increased concentration of adsorbate caused decrease of efficiency of adsorption. The adsorption capacity of Pb, Cd and Cr increased with increase of concentration. After reached the optimum adsorption, the capacity was decreased.

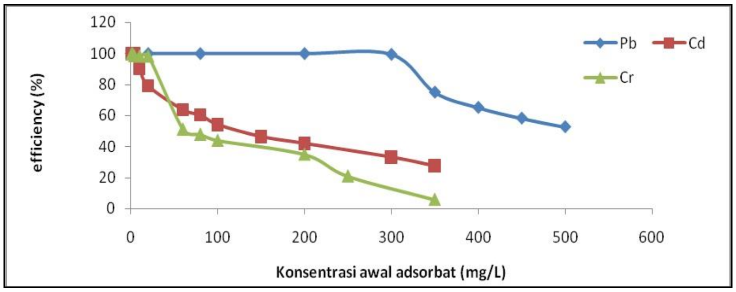

Figure 3: Efficiency adsorption with concentration Pb^{2+}, Cd^{2+}, dan Cr^{6+}

Efficiency adsorption Pb, Cr and Cd with concentration 100-500 mg/L showed decrease of efficiency with increase of concentration. Isothermal adsorption Pb by biosorbent coffee husk was analyzed by 2 model isothermal are model Langmuir dan Freundlich. The result showed trend to Langmuir with 0.9999 dan 0.9631. This indicated that biosorbent was monolayer and homogeny so interaction biosorbent and adsorbate was monolayer (Figure 3).

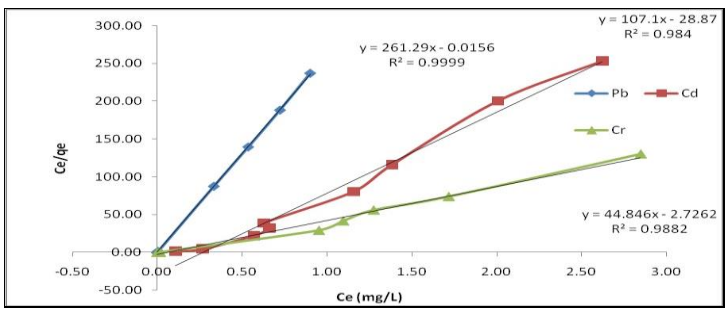

Figure 4: Adsorbate concentration at Langmuir model condition

The Langmuir isotherm was applied to the present study to estimate the adsorption capacity of coffee husk. It is valid for monolayer adsorption onto a surface containing a finite number of identical sites [4]. The linier plots of Ce/Qe vs. Ce for Pb, Cd, Cr show that adsorption follows the langmuit adsorption model. Optimum Adsorption capacity (qm) biosorbent of coffee husk to adsorb of ion Pb, Cd and Cr ions according to Langmuir model was 261.30 mg/g, 108.81 mg/g and 45.38 mg/g. Equilibrium constant for Pb, Cd and Cr ions adsorption were 15363 L/g, 3.55 L/g and 14.18 L/g respectively (Figure 4). This indicated adsorbate affinity Pb to active site of biosorbent is higher than Cr and Pb [19,20].

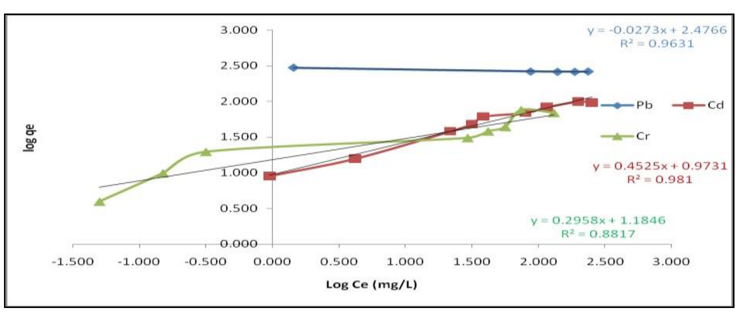

Figure 5: Adsorbate concentration at Freundlich adsorption isothermis

The freundlich adsorption isotherm was also applied for the adsorption of Pb, Cd, Cr onto coffee husk. Linier plot in log Ce vs. log qe show that the adsorption of metal ions onto the coffee husk follow the Freundlich isotherm model. Range of separation for adsorption Pb, Cd dan Cr are 0.00003-0.017, 0.08-0.97 dan 0.009-0.76, respectively. Separation factor are effected by adsorbate concentration, the higher of adsorbate so separation factor will be lower this caused adsorbate can be desortion (Figure 5).

CONCLUSION

The experiment result shows that coffee husk is an excellent alternative for removal of Pb, Cd, Cr from aqueous solution. The biosorption was dependent on pH, adsorbent dose, contact time and initial metal concentration. Both Langmuir and freundlick isotherm were followed by the adsorption of metal ion. Coffee husk have potential to use as biosorbent to adsorb metal ion. Optimum pH condition of Pb^{2+}, Cd^{2+}, dan Cr^{6+} were 6.6; 5.6; and 4.4. Contact time with range 81.1; 55.5 dan 96.7 menit, and biosorbent concentratuon 50 mg/50 mL. Adsorptionby biosorbent based on model Langmuir, adsorpat monolayer. Optimum adsorpsi capacity (qm) biosorbent coffee husk to adsorb ion Pb, Cd dan Cr are adalah 261.30 mg/g, 108.81 mg/g and 45.38 mg/g.

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