JURNAL REKAYASA PROSES
VOLUME 16, NUMBER 2, 2022, xx–xx

RESEARCH ARTICLE

Study of chromium removal from wastewater using SSF-CW model: comparison between physical adsorption by coal CFA and phytoremediation by vetiver grass (*Vetiveria Zizanioides L*)

Titik Indrawati[1], Sarto[1], Agus Prasetya[1,*]

[1]Department of Chemical Engineering, Universitas Gadjah Mada, Jl. Grafika 2,Yogyakarta, 55281, Indonesia

Received 25 October 2021; revised 9 December 2021; accepted 14 December 2021

OBJECTIVES The study aims to compare the effectiveness of chromium removal from water using adsorption by coal fly ash (CFA) and phytoremediation by vetiver grass (*Vetiveria zizanioides L*) as well as a combination of both CFA and vetiver grass. METHODS The experiment was carried out in four different reactors, having size of 100 cm (length) x 60 cm (wide) x 80 cm (height). One reactor was filled with gravel and CFA, without vetiver grass (RI), while another one was filled with gravel and vetiver grass, without CFA (RIV). The other two reactors were filled with gravel, CFA, and vetiver grass with the mass ratio of gravel/CFA of (25:2) and (25:1), denoted as RII and RIII, respectively. Fifty (50) L of synthetic wastewater containing 14.612 ppm of chromium was filled into the reactors and continuously re-circulated for 15 days. Chromium accumulation in CFA and plants was analyzed on day 15. RESULTS The results of plant development are indicated by the presence of new shoots and roots that grow during phytoremediation processes. In addition, there was an increase in weight and number of vetiver stems indicating the persistency of vetiver grass in such a harsh wastewater condition. The removal of Cr from wastewater in RI, RII, RIII and RIV at days 15 were 81%, 93.2%, 85.8% and 75.7%, respectively. CONCLUSIONS it can be concluded that: (1) vetiver grass (*Vetiveria zizanioides L*) has high potential as phytoremediator plant, (2) Chromium adsorption by CFA plays important role in Cr removal from wastewater, and (3) combination of adsorption by CFA and a phytoremediation by vetiver grass significantly increases the removal of chromium from wastewater.

KEYWORDS adsorption; vetiver grass (*Vetiveria Zizanoides L*); chromium removal; coal CFA (CFA); phytoremediation; sub surface flow constructed wetlands (SSF-CW)

1. INTRODUCTION

Wastewater is the residue from industrial processes, households, laboratories, or offices that have experienced quality degradation due to the presence of hazardous materials. Besides industrial wastewater, laboratory wastewater containing heavy metals such as chromium must be treated before being discharged into the water because of its toxicity. Laboratory wastewater is characterized by its dynamic distribution and content and its long impact. The quality of wastewater is influenced by the volume of wastewater, the content of pollutants, and the frequency of waste disposal. The quantity of laboratory wastewater is considered small, while the content of pollutants is varied and some even contain hazardous waste (Said 2008). The source of laboratory wastewater are chemicals solutions used for experiments or testing such as sulfuric acid (H_2SO_4), potassium dichromate ($K_2Cr_2O_7$), mercury sulphate (Hg_2SO_4), ferro ammonium sulfate (FAS), ferroin, etc. Chromium in laboratory wastewater can be in the form of Cr^{3+} (Cr(III)) and Cr^{6+} (Cr(VI)). The presence of high chromium in laboratory wastewater can cause environmental pollution and have a bad impact on health (Melyta et al. 2019). Cr toxicity is highly dependent on its oxidation form and Cr(VI) is more toxic than Cr(III) for plants, animals, and microorganisms. High Cr(VI) concentrations have significant harmful effects on human health including lung, cancer, kidney, liver, and gastric damage (Sultana et al. 2014).

Wastewater treatment technology can be carried out by biological, chemical, and physical processes, which are based on the characteristics of the compounds contained in wastewater. For waste containing heavy metals such as gold mining processing waste, of course, biological treatment is not the first choice. This is because the existing heavy metals can poison the microorganisms used (Fadlilah et al. 2018). Subsurface Flow Constructed Wetlands (SSF-CW) is a promising alternative wastewater treatment technology that is built and designed based on the involvement of aquatic plants, soil, or other media and microbes. It is a simple and

*Correspondence: aguspras@ugm.ac.id

 DOI 10.22146/jrekpros.69978

easy to control technology for treating heavy metals' contained wastewater (Suswati and Wibisono 2013).

Plant types that can be applied for phytoremediation must have high biomass production, be capable of accumulating contaminants well at the top of the plant beyond the concentration of contaminants found in the soil (hyperaccumulator), and be tolerant to the local environment (Ramdani et al. 2019). Vetiver grass is a prospective plant because it has been extensively used for soil and water conservation and land stability worldwide. Its massive fibrous roots have the opportunity to contact the high levels of metals in wastewater (Srisatit and Sengsai 2003). Today, much attention is directed to the reuse of coal fly ash (CFA). The literature on various aspects of the use of CFA is abundant and hence many possibilities on how to expand the use of the material are presented. As CFA contains SiO_2 and a portion of unburnt carbon, one of the applications is the use of CFA as a low-cost adsorbent for the removal of dyes and heavy metal ions (Adamczuk and Kołodyńska 2015). This study aims to compare the effectiveness of chromium removal from water using adsorption by Coal Fly Ash (CFA) and using phytoremediation by vetiver grass (*Vetiveria zizanioides L*), as well as using a combination of both CFA and vetiver grass. In addition, the combined method of adsorption and phytoremediation in SSF-CW will be a novel approach for heavy metal removal from wastewater.

2. RESEARCH METHODOLOGY

2.1 Materials

Coal fly ash (CFA) that was used as plant media and adsorbent was supplied by the Electrical Power Plant in Bunton, Cilacap, Central Java – Indonesia. Gravel as media was obtained from Gendol River, Sleman, Yogyakarta. Vetiver grass (*Vetiveria zizanioides L*) as a phytoremediation plant was collected from Probitstore Flora nursery, Bogor, West Java.

Gravel were collected from Gendol River, Sleman, Yogyakarta, having of 2.39 g/cm^3 with size of 10.0–30.0 mm. The gravel with diameters of 8 mm and 16 mm are gravelly sand and finely gravel types with porosity values of 0.35–0.38 (Tchobanoglous et al. 2003). The artificial wastewater containing potassium dichromate of 15 mg/L was prepared by mixing potassium dichromate (PA EMSURE® ACS, ISO, Merck) and aquadest obtained from Brataco Chemical, Yogyakarta. Four SSF-CW reactors were prepared for batch operation, by recirculating the wastewater. Each reactor consisted of 3 parts (inlet zone, reaction zone, and outlet plus sampling zone). The reactor was made from glass with having a thickness of 10 mm. Each reactor has dimension of 100 cm (length) x 60 cm (wide) x 80 cm (height). The arrangement of the reactor can be seen in Figure 1.

The SSF-CW reactors were designed to be horizontal type sub sub-surface-flow. All of the SSF-CWs follow the criteria as tabulated in Table 1.

One SSF-CW reactor was filled with gravel and CFA, without vetiver grass (RI), while another one was filled with gravel and vetiver grass without CFA (R-IV). The other two reactors were filled with gravel, CFA, and vetiver grass with the mass ratio of gravel/CFA of (25:2) and (25:1), denoted as RII and RIII, respectively.

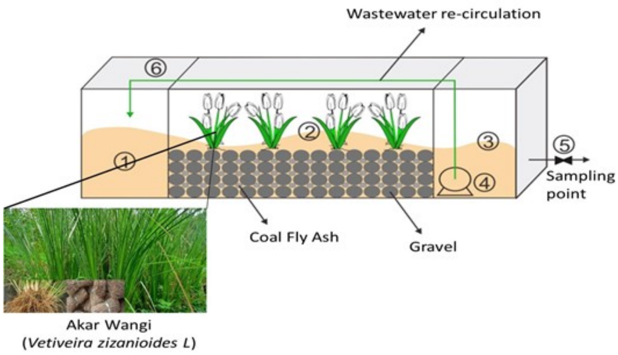

FIGURE 1. Schematic diagram of SSF-CW rig for Cr-removal from wastewater.

TABLE 1. Characteristic of the SSF-CW reactor model.

Parameters	Typical value
Dimensions	100 cm (length) x 60 cm (wide) x 80 cm (height)
Flow rate (m^{3}d^{-1})	4.74
Media (gravel:CFA)	(25:5), (25:2), (25:1), (25:0)
Retention time (day)	15

2.2 Procedures of the experiment

2.2.1 Preparation of media and plants

The size CFA particle used was less than 325 mesh. Elemental composition of the CFA were analyzed using XRF (Rigaku) in Laboratorium Penelitian dan Pengujian Terpadu (LPPT) UGM. The gravel used was 2–3 cm in size and characterized by its specific gravity and size uniformity. One hundred fifty cuttings of vetiver grass (height of 25–30 cm) were placed in the polybags and were grown for 2 months. About 50 to 55 cuttings (150–170 cm in height) were randomly assigned to SSF-CW reactors for the acclimatization process for 30 days. Artificial wastewater was then filled into each reactors following the acclimatization process.

2.2.2 Experimental procedure of SSF-CW

Fifty (50) L of synthetic wastewater containing 14.612 mg/L of chromium was filled into each reactor. The wastewater in the reactor was continuously re-circulated for 15 days. Effluent samples were collected on day 15 for chromium analysis. Chromium accumulation in CFA and plants were also analyzed on day 15. Total chromium amount in wastewater was analyzed according to SNI 06–6989.17–2004 while the CFA, gravel, and plant by mixed acid digestion (Allen, B and B.F. Hajek 2018; Srisatit and Sengsai 2003). Chromium content in plants was analyzed in roots and leaves. The analysis of chromium in wastewater was carried out using Atomic Absorption Spectrophotometer methods(AAS). The efficiency of chromium removal can be determined by comparing the chromium levels before and after the removal in SSF-CW.

$$\%\ \text{efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

Where C_0 is initial concentration Cr, C_t is concentration of Cr after adsorption and phytoremediation

TABLE 2. Chemical composition of CFA (as carbon and major oxide).

Elements	C	Al_2O_3	SiO_2	SO_3	CaO	TiO_2	MnO	Fe_2O_3	NiO	CuO	ZnO	Br	SrO	BaO
Content (%)	59.86	4.07	13.99	1.825	13.70	0.285	859	6.018	0.019	0.0087	0.0072	0.0025	0.0814	0.0572

TABLE 3. Contents of trace elements in the CFA.

Elements	C	Al	Si	S	Ca	Ti	Mn	Fe	Ni	Cu	Zn	Br	Sr	Ba
Content (%)	79.94	1.801	5.429	0.604	8.33	0.146	0.0562	3.571	0.0125	0.0059	0.0049	0.0022	0.0588	0.0451

3. RESULTS AND DISCUSSION

3.1 Characterization of material

The composition of CFA is summarized in Table 2 for carbon and its major oxide, and in Table 3 for its elements. The mean size of the CFA particle was 0.044 mm.

[EPA] Environmental Protection Agency (2000) and the recent Indonesian Government Regulation decided not to categorize CFA as a hazardous substance to preserve its future beneficial use. Common use of CFA currently is as pozzolanic materials in cement mixture, as concrete materials, and in other construction applications. Its application as an adsorbent by converting it into synthetic zeolites is also possible (Adamczuk and Kołodyńska 2015). Fly ash is a finely porous material, containing silica, alumina, and carbon in it, making fly ash potential as an adsorbent (Judy, Ir and Witono, Retti B and M.Sc.App., Miryanti, Y.I.P. 2015). Fly ash can be used as an adsorbent because of its structural similarity to zeolite or is known as zeolite-like material (ZLM). This is because fly ash contains components such as K_2O, Al_2O_3, CaO, and SiO_2 which are commonly involved in the formation of zeolite. The porous structure of zeolite is a property that can be used as a an adsorbent material (Wardani, L., D. 2018). Table 2 shows the major components of CFA are silicate minerals (measured as SiO_2) and calcium (as CaO). It can be observed that CFA also contains quite large amounts of iron (analyzed as Fe_2O_3), aluminium (as Al_2O_3), and sulphur (analyzed as SO_3). According to the American Concrete Institute (1991) (parts 1226.3R-3), the material used in this study is classified as Class C because it contains more than 10% CaO and less than 70% of the three main components (SiO_2, Al_2O_3, and Fe_2O_3). It has pozzolanic properties, but also reacts directly with water to form CSH ($CaO.SiO_2.2H_2O$). Calcium Hydroxide and Ettringite hardens like cement. Gravel as the media in the SSF-CW is a place for plants to grow, a medium for microorganisms to breed, assist in the sedimentation process, and assist in the adsorption of odors from biodegradation gases. While the other role is the place where the chemical transformation process occurs, the storage place for the nutrients needed by plants (Supradata 2005).

3.2 The growth rate of plants

The results of plant development are indicated by the presence of new shoots and roots that grow during the phytoremediation process. In addition, there was an increase in the weight and number of vetiver stems. The initial and final weight of vetiver grass (*Vetiveira zizanioides L*) measured on as non-dry basis, was presented in Table 4. Assuming that the water content in the plants was not significantly different, the weight measurement can indicate the growth of the plants in each reactor (by comparing the final weight with the initial weight). This data has clearly indicated the persistence of the plant to grow in chromium contaminated wastewater and acted as a phytoremediator.

3.3 Analysis of chromium

3.3.1 Accumulation of chromium in plants

Vetiver grass (*Vetiveria zizanoides L*), due to its morphological and physiological characteristics and tolerance to high levels of heavy metals and adverse conditions, has been successfully applied in this experiment. Besides its excellency for the removal of heavy metals from contaminant soil (Dotro et al. 2011), the plant also proved to be able to adsorb Cr directly from the water bodies. The calculation of chromium content in the plant was based on a dry-basis. Table 5 shows the accumulation of chromium in roots and stems from each SSF-CW reactor (measured on a mg/kg dry basis).

Table 5 shows that vetiver grass mostly accumulated chromium in the roots. This indicates that vetiver grass is a hyperaccumulator for chromium. Hyperaccumulator plants are plants which have the ability to adsorb and accumulate a large number of heavy metals. The limit of metal content contained in the biomass so that a plant can be called a hyperaccumulator varies depending on the type of metal. For examples, nickel accumulation as high as 10 mg/kg dry mass (equivalent to 0.001%), and cadmium as high as 100 mg/kg dry mass (equivalent to 0.01%) are considered the hyperaccumulator limits, while the limit for cobalt, copper and lead it is 0.1% (1000 mg/kg dry weight) and for zinc and manganese, it is 1% (10,000 mg/kg dry weight, respectively (Dwityaningsih et al. 2019). Table 5 presents the ability of vetiver grass to accumulate chromium in the order of 10,000 mg/kg to almost 200,000 mg/kg, showing its high potential as a hyperaccumulator plant for chromium.

3.3.2 Accumulation of chromium in CFA

The accumulation of chromium in CFA after 15 days of use in the SSF–CW experiment was shown in Table 6.

TABLE 4. The wet weight of vetiver grass before and after phytoremediation in SSF-CWs.

Plants	SSF–CW reactor			
	I	II	III	IV
Initial Weight (gr)	–	785	762	786
Final Weight (gr)	–	916	817	809
% Increase	–	16.7	7.2	2.9

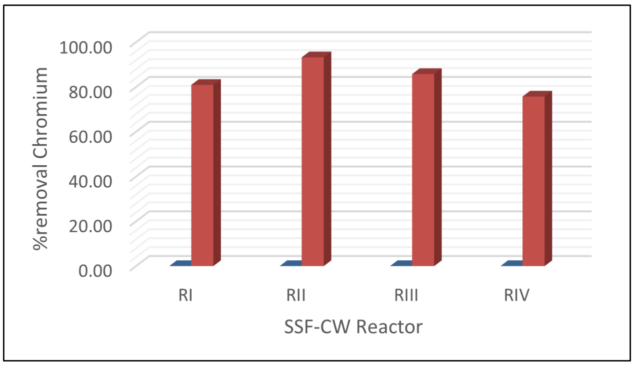

FIGURE 2. Removal of Chromium in wastewater.

The accumulation that occurs in the media is due to Cr adsorption on the active sites of the adsorbent which is proportional to the surface area of the CFA. Interesting results had been found in RI and RIII, where the amount of chromium adsorbed was the lowest and the highest, respectively; while RII lied in between. RI which only contained CFA without vetiver grass was highly less effective in adsorbing chromium compared to that RIII, which contained CFA and vetiver grass. This indicates synergy between vetiver grass and CFA in adsorbing chromium from wastewater.

3.3.3 Analysis of chromium in wastewater

A summary of the removal of chromium on day 15 of SSF-CWs operation is provided in Table 7. It can be seen that RII, which was a combination of adsorption and phytoremediation in the SSF system with a gravel/CFA ration of (25:2) gave the best performance compared to other reactors. This condition indicates that the amount of CFA affects the performance of the SSF-CW in removing chromium. The removal of Chromium in waste water for all SSF-CW can be seen at in Figure 2.

Figure 2 shows that chromium removal by adsorption by CFA is higher than that of phytoremediation by vetiver grass. This is because in adsorption, initially most of the adsorbent active sites have not been occupied. This results in a higher amount of the chromium ions to be adsorbed, but with increasing time the adsorbate will get closer to a certain value, which indicates its saturation condition (Mandalahi et al. 2016). On the other hand, phytoremediation needs more times to remove the pollutant due to its lengthy process involving several steps such as adsorption by roots, phyto-extraction, and translocation to the other parts of the plant. This is following research by Gwenzi et al. (2017) that metal removal by phytoremediation was generally less than that by adsorption, accounting for between 34% and 54.6% for both adsorbents. RII which is a combination of adsorption and phytoremediation with a media ratio (25:2) gave the best efficiency because the amount of CFA was more than other reactors so the adsorption capacity is greater. Its accordance to Srisatit and Sengsai (2003) the efficiency of chromium removal with Surat Thani ecotype containing *Vetiveria zizanoides L* for 0.1 m level, was about 89.29%. The removal of Cr from wastewater in RI, RII, RIII, and RIV at days 15 were 81.%, 93.2%, 85.8%, and 75.7%, respectively.

TABLE 5. Accumulation chromium in plants.

Plants	CW			
	RI	RII	RIII	RIV
Roots (mg/kg)	–	34.126	65.130	192.597
Stem (mg/kg)	–	22.696	23.804	71.832

TABLE 6. The accumulation of chromium in the CFA.

CFA	SSF-CW reactor			
	RI	RII	RIII	RIV
Chromium(mg/kg)	9.143	16.113	82.894	–

TABLE 7. Chromium removal .

SSF-CW Reactor	RI	RII	RIII	RIV
Initial Cr conc. (mg/L)	14.612	14.612	14.612	14.612
Final Cr conc. (mg/L)	2.785	0.987	2.079	3.544

4. CONCLUSIONS

Vetiver grass (*Vetiveria zizanoides L*) has been able to survive in a Cr-contaminated wastewater system, indicated by its increase in weight and the presence of new shoots and roots during the phytoremediation processes. The plant has been proven as a potential phytoremediator for Cr-removal. CFA has played a significant roles in Cr-removal through its adsorption ability. CFA also plays important roles in the growth of the plants. The removal of Cr from wastewater on day 15 in RI, RII, RIII, and RIV was 81%, 93.2%, 85.8%, and 75.7%, respectively. It is obtained that a combination of adsorption by CFA and phytoremediation by vetiver grass in the SSF-CW system gave the best result. This research also found that there is a synergy between vetiver grass and CFA in removing chromium from wastewater, showing the potential of a combined method of adsorption and phytoremediation for heavy metal removal from wastewater.

ACKNOWLEDGMENTS

We thank you to PasTi scholarship 2019 from Direktorat Pendidikan Tingi (Dikti), Pusat Inovasi Agroteknologi (PIAT) UGM, PT. Indonesia Power II PLTU Bunton, and all related participants for supporting of the research.

REFERENCES

Adamczuk A, Kołodyńska D. 2015. Equilibrium, thermodynamic and kinetic studies on removal of chromium, copper, zinc and arsenic from aqueous solutions onto fly ash coated by chitosan. Chemical Engineering Journal. 274:200–212. doi:10.1016/j.cej.2015.03.088.

Allen, B and BF Hajek. 2018. Mineral occurrence in soil environment. https://doi.org/10.2136/sssabookser1.2ed.c5.

American Concrete Institute. 1991. ACI manual of concrete practice. pt. 1. American Concrete Institute. https://www.concrete.org/topicsinconcrete/topicdetail/manualofconcretepractice?search=manualofconcretepractice.

Dotro G, Larsen D, Palazolo P. 2011. Preliminary evaluation of biological and physical–chemical chromium removal mechanisms in gravel media used in constructed wetlands. Water, Air, & Soil Pollution. 215(1-4):507–515. doi:10.1007/s11270-010-0495-9.

Dwityaningsih R, Pramita A, Syarafina S. 2019. Review potensi tanaman obat akar wangi (vetiveria zizanioides) sebagai tanaman hiperakumulator dalam fitoremidiasi pada lahan tercemar logam. Jurnal Pengendalian Pencemaran Lingkungan (JPPL). 1(01):51–56. doi:10.35970/jppl.v1i01.55.

[EPA] Environmental Protection Agency. 2000. Free water surface wetlands. Environmental Protection Agency:1–8. https://www3.epa.gov/npdes/pubs/free_water_surface_wetlands.pdf.

Fadlilah I, Prasetya A, Mulyono P. 2018. Recovery ion Hg2+ dari limbah cair industri penambangan emas rakyat dengan metode presipitasi sulfida dan hidroksida. Jurnal Rekayasa Proses. 12(1):23. doi:10.22146/jrekpros.34496.

Gwenzi W, Mushaike CC, Chaukura N, Bunhu T. 2017. Removal of trace metals from acid mine drainage using a sequential combination of coal ash-based adsorbents and phytoremediation by bunchgrass (vetiver [vetiveria zizanioides l]). Mine Water and the Environment. 36(4):520–531. doi:10.1007/s10230-017-0439-3.

Judy, Ir and Witono, Retti B and MScApp, Miryanti, YIP. 2015. Pengembangan adsorben activated fly ash untuk reduksi ion Cu2+ dan Cr6+ dalam limbah cair industri tekstil:9. https://journal.unpar.ac.id/index.php/rekayasa/issue/view/210.

Mandalahi H, Muis L, Latief M. 2016. Adsorpsi merkuri (II) menggunakan zeolit dari fly ash batubara. Chempublish Journal. 1(1). https://core.ac.uk/download/pdf/229107857.pdf.

Melyta D, Prasetya A, Sarto. 2019. Pengaruh melati air terhadap penyisihan krom dalam limbah cair penyamakan kulit pada sistem subsurface Flow Constructed Wetland. Seminar Nasional Teknik Kimia Soebardjo Brotohardjono XV Program Studi Teknik Kimia UPN "Veteran" Jawa Timur Proceding.

Ramdani F, Prasetya A, Purnomo CW. 2019. Removal of pollutants from chicken slaughterhouse wastewater using constructed wetland system. IOP Conference Series: Earth and Environmental Science. 399:012085. doi:10.1088/1755-1315/399/1/012085.

Said M. 2008. Pengolahan limbah cair hasil pencelupan benang songket dengan metoda filtrasi dan adsorpsi. http://ejurnal.mipa.unsri.ac.id/index.php/jps/article/view/421.

Srisatit T, Sengsai W. 2003. Chromium removal efficiency by vetiveria zizanioides and vetiveria nemoralis in constructed wetlands for tannery post -treatment wastewater. Methodology. https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.510.4685&rep=rep1&type=pdf.

Sultana MY, Akratos CS, Pavlou S, Vayenas DV. 2014. Chromium removal in constructed wetlands: A review. International Biodeterioration & Biodegradation. 96:181–190. doi:10.1016/j.ibiod.2014.08.009.

Supradata. 2005. Pengolahan limbah domestik menggunakan tanaman hias (cyperus alternifolius) dalam sistem lahan basah buatan aliran bawah permukaan (ssf-wetlands). Program Pasca sarjana Universitas Diponegoro:64–67. http://eprints.undip.ac.id/15122/.

Suswati ACSP, Wibisono G. 2013. Pengolahan limbah domestik dengan teknologi taman tanaman air (constructed wetlands). Indonesian Green Technology Journal. 2(2):70–77. https://igtj.ub.ac.id/index.php/igtj/article/view/117.

Tchobanoglous G, Burton FL, Stensel HD, Metcalf & Eddy I, Burton F. 2003. Wastewater engineering: treatment and reuse. McGraw-Hill higher education. McGraw-Hill Education. https://onesearch.id/Record/IOS2847.INLIS000000000014658.

Wardani, L, D K. 2018. Karakterisasi fly ash (abu terbang) batubara sebagai adsorben pada limbah cair yang mengandung logam. https://eprints.uny.ac.id/57987/.