CERAMIC FILTERS AND THEIR APPLICATION FOR CADMIUM REMOVAL FROM PULP INDUSTRY EFFLUENT

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ABSTRACT

The purpose of this paper was to investigate the performance of ceramic filters made from a mixture of natural clay, rice bran, and iron powder in removing cadmium from pulp industry effluent. Some parameters were examined such as acidity, total dissolved solid (TDS), total suspended solid (TSS), electrical conductivity (EC), and cadmium concentration. Results showed that the composition percentage of the ceramic filter, which in this case amounted to 87.5% natural clay, 10% rice bran, and 2.5% iron powder, may decrease cadmium concentration in pulp industry effluent by up to 99.0%. Furthermore, the permeate flux decreased after 30 minutes of filtration time, and subsequently became constant at one hour of contact time. In addition, Scanning Electron Microscope (SEM) micrographs of the ceramic filter surfaces indicate that ceramic filters have a random pore structure and can be categorized as microfiltration filters.

Keywords: Cadmium; Ceramic filters; Permeate flux; Pulp industry

1.   INTRODUCTION

Wastewater from the Kraft pulp industry process (Kamali & Khodaparast, 2014) may contain heavy metal contaminants such as lead and cadmium. Cadmium in pulp industry wastewater needs to be treated prior to being released into the water. In low concentrations, cadmium is a non-essential extremely toxic trace element in rivers, lakes and ponds (Guner, 2010). However, cadmium can be dispersed into the environment through industrial processes such as metal plating, alloy manufacturing, nickel-cadmium batteries, plant foods, pesticides, and paint pigments. Pulp industry wastewater may contain heavy metal contaminants such as lead and cadmium, which are derived from the pulping process. Therefore, cadmium has been reported to be a potent carcinogen and teratogen (Sharma, 2008).

The Ministry of Environment of the Republic of Indonesia Regulation Number 03/2010 stipulates that cadmium concentration in excess of 0.1 mg.L^{-1} is not allowed to be discharged into bodies of water. In addition, the World Health Organization (WHO) restricts the maximum concentration of cadmium (II) in drinking water to 0.003 mg.L^{-1}. At present, available options for pulp effluent treatment include chemical oxidation, adsorption, sedimentation, and membrane filtration. (Pokhrel & Viraraghavan, 2004).

Ceramic membranes have several advantages such as good mechanical, chemical, and thermal properties (Yang & Tsai, 2008; Jana et al., 2010). Therefore, ceramic membranes are used for

nutrient processing, biotechnology, and pharmaceutical products (Yang & Tsai, 2008). Nevertheless, some disadvantages of ceramic membranes are their high production cost, high membrane weight, and the fact that they are difficult to clean due to the fouling susceptibility. Numerous methods have been proposed for cadmium removal from wastewaters such as ion exchange resins, solvent extraction, membrane technologies, precipitation, adsorption, electrochemical treatment, chemical precipitation, and biosorption (Yilmaz et al., 2012; Jha et al., 2012). Heavy metal reduction may also be performed using microorganisms (bioremediation) (Boopathy, 2000), or plants (phytoremediation) (Ali et al., 2013) to mitigate the effects of heavy metal ions in the environment. However, such techniques are relatively expensive because of intensive energy consumption.

Filtration studies using porous tubular filter supports performed for the treatment of solutions containing dye and cadmium were investigated by Ezziane et al. (2010). The 99.99% rejection rate of cadmium ions was obtained in a treatment time of two hours. In another study, Vasudepan & Lakshmi (2011) used the electrolysis method to study cadmium removal from the wastewater. They found that cadmium concentration could be decreased by approximately 97.8% and 96.9%, respectively, using alternating current and direct current for electrocoagulation. In another study, Boparai et al. (2011) concludes that nano zero valent iron (nZVI) can be used as an efficient adsorbent for removing cadmium from contaminated water sources. Cadmium adsorption was also investigated by Hydari et al. (2012) using activated carbon, chitosan biosorbent, and mixed (composite) as an adsorbent. The results obtained at optimum operating conditions brings about 100% removal of cadmium. Further, Saljoughi & Mousavi (2012) use polysulfone-based nanofiltration for cadmium removal, and reduced cadmium concentration from wastewater by 98%.

The application of low-cost ceramic filters in wastewater treatment continues to interest researchers. For instance, Han et al. (2009) show that ceramic filters made of sludge and fly ash ceramic particles are safe for wastewater treatment. Hasan et al. (2011) further report that ceramic filters made of 80% clay soil and 20% rice bran would be applicable for use in membrane bioreactor facilities without clogging after one year of operation. Another study using local clays impregnated with silver compounds shows that clays that contain traces of crystalline albite or crystalline pyroxene have better sorption of silver species, and the mineralogy of the source materials was found to have the most significant influence on the strength of ceramic filters (Craver et al., 2014). The low-cost and locally produced tubular composite membranes from natural aluminosilicates (clay, bentonite, feldspar, quartz, alumina) were studied by Almandoz et al. (2015). The results show that such composite membranes were suitable for microfiltration process and able to remove 100% insoluble residue and 87–99% of bacteria.

The use of ceramic membrane in wastewater treatment is actually limited because of the higher cost of such membranes (Saffaja et al., 2004). In addition, the cost of ceramic membranes is ten times greater than the cost of polymer membranes (Jana et.al., 2010). For that reason, it is necessary to find a low-cost material for ceramic membranes. The present work aims to investigate an alternative treatment of pulp industry wastewater using ceramic filters. The materials used for ceramic filter fabrication in the current work are natural clay and rice bran, which are easily available and inexpensive. Fabricated ceramic filters can be used to improve the quality of effluent from pulp and paper processing, mainly in neutralizing the pH and lowering levels of cadmium in the effluent. The research was focused on the development of ceramic filters, characterization of the porosity and surface area, and performance evaluation of the ceramic filters for cadmium pulp industrial wastewater treatment.

2. EXPERIMENTAL

2.1. Ceramic Filters

Ceramic filters used in this study were designed as porous tubes made of a mixture of natural clay, rice bran, and iron powder. The average weight of each ceramic filter is about 300g. Two types of ceramic filter were fabricated for the current work. Ceramic filters with a composition of 77.5% natural clay, 20% rice bran, and 2.5% iron powder are stated as Filter A. Meanwhile, ceramic filters with a composition of 87.5% natural clay, 10% rice bran, and 2.5% iron powder are reffered to as Filter B. Two filter compositions were chosen due to their better mechanical strength and crack-free properties. Natural clay, rice bran (particle size of 500 μm), and iron powder (particle size of 500 μm) were homogenized with 30% clean water, molded, dried at room temperature and sintered at 900°C for 12 hours at a local ceramic manufacture. The composition of natural clay from South Sumatra, Indonesia, was shown in Table 1 (South Sumatra Energy and Mineral Resource, 2005).

Table 1 South Sumatra natural clay properties

No.	Compound	Concentration (wt%)
1.	SiO_2	65.35
2.	Fe_2O_3	6.65
3.	NH_2CO_3	14.13
4.	CaO	3.13
5.	MgO	0.29
6.	Na_2O	6.52
7.	K_2O	2.69
8.	TiO	0.30
9	H_2O	0.94

2.2. Sample and Analysis

The pulp mill effluent sample used in experiment was collected from one of pulp mill in South Sumatra. The samples were analyzed according to the Indonesian standards of wastewater. Some parameters examined are pH, TSS, TDS, EC, and cadmium content. Process variables studied were pressure differences (ΔP), filter composition, and feed flow rate. In addition, a Scanning Electron Microscope (JEOL 330 Japan) was used to determine ceramic filter surface. The Quantachrom Nova A-600 porosimeter used for pores distribution examination and Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA-6800) for cadmium determination. Ceramic filters design: inner diameter of 5 cm, the outer diameter is 7 cm, and 25 cm length. It is placed in a polyethylene filter cartridge with an inner diameter of 8.5 cm, outer diameter of 9 cm, and 25 cm length.

2.3. Experimental Set-up

The equipment used in the experiment include a polyethylene tank with a capacity of 250L, stirrer, centrifugal pumps, pressure gauge, and flow-meter. The system was also equipped with a sand filter, spoons filter (5 μm of pore size), and activated carbon filters. Wastewater samples were coagulated using 200 mg.L^{-1} of Poly Aluminum Chloride. They were stirred at 100 RPM for one minute and then 60 RPM for 10 minutes before they were fed into a storage tank. The filtrate was collected in a storage tank with a capacity of 250L and pumped into sand filter, sediment filter, activated carbon filter, and ceramic filter, respectively. The permeate was collected in a 1000 mL beaker glass and measured after 15, 30, 45, and 60 minutes of filtration time. Permeate flux was calculated as follows:

$$J_v = \frac{V}{A} \times t \qquad (1)$$

where V is the permeate volume, A is area of ceramic filter and t is the filtration period. Figure 1 shows the experimental setup of the present work.
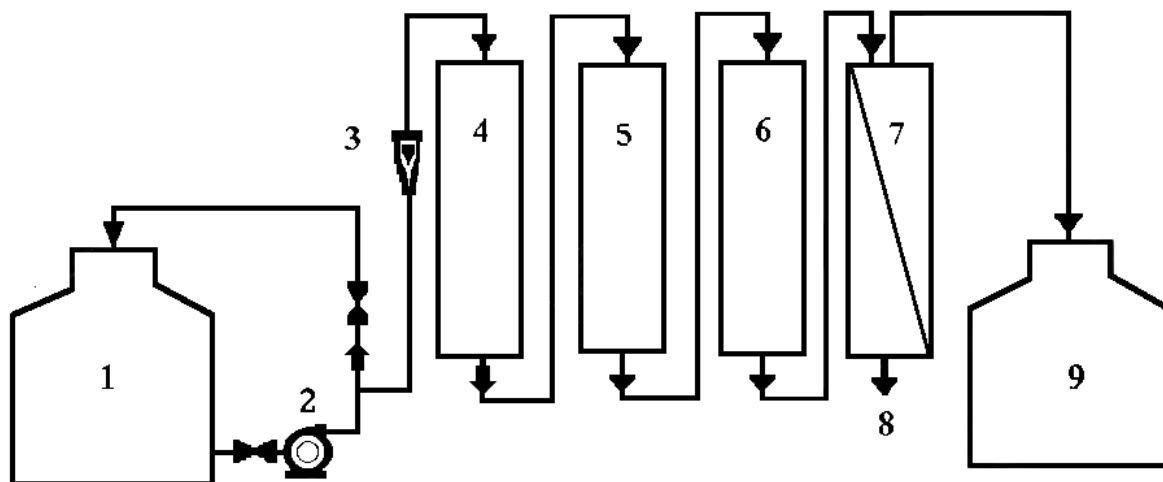

Figure 1 Experimental set-up (1. Feed tank; 2. Centrifugal Pump; 3. Flowmeter; 4. Spoons filter column; 5. Sand filter column; 6. Activated carbon filter; 7. Ceramic Filter; 8. Retentate; 9. Permeate Tank)

3.   RESULTS AND DISCUSSION

Table 2 displays the sample analysis. It is seen that cadmium, COD, TSS, and pH were above the Indonesian standard for pulp industry wastewater.

Table 2 Sample analysis

Parameters	Values	Indonesian Standard
Cd (mg.L^{-1})	0.65	0.1
Fe (mg.L^{-1})	0.64	10
Pb (mg.L^{-1})	0.21	1
COD (mg.L^{-1})	215	100
TDS (mg.L^{-1})	567	-
EC (µS.cm^{-1})	1107	-
TSS (mg.L^{-1})	162	150
pH	9.84	6-9
Turbidity (NTU)	135	-

3.1.   Effect of Contact Time on Permeate Flux

The influence of contact time on the flux at different pressures (ΔP) is shown in Figure 2. All ceramic filters showed a flux decline after 30 minutes of filtration time and remained constant for one hour. The permeate flux declined due to the build-up of solute on the filter surface, which was caused by several factors such as concentration polarization, adsorption, and plugging of the pores. The concentration polarization will affect the flux of microfiltration and ultrafiltration membranes mainly for high operating pressure. The filter fouling may be caused by higher values of TDS and TSS in feed with prolonged operating time together with adsorption of cadmium on filter pores. As a consequence, the permeate flux of the

microfiltration process decreases with time, which will significantly reduce the filtration performance (Zhang et al, 2005). Cadmium ion adsorption by clay, which depends on the ceramic filter characteristics, concentration of solute, and pH, reduce the cadmium in the feed solution.

Clays consist of negatively charged aluminosilicate layers kept together by cations and they have the ability to adsorb water between the layers, resulting in strong repulsive forces and clay expansion. Clay swelling depends on the molecular packing of intercalated water, charge locus, charge density, and the type of counterion (Hensen & Smit, 2002). Adsorption of cadmium may occur at different sites on the aluminosilicate structure of clay over a wide range of concentrations (Bergaya et al., 2006) or by electrostatic attraction. In addition, increases in temperatures will reduce the water retention capacity, and thus decrease the clay swelling capacity (Anderson et al., 2010). However, the effect of clay swelling of the flux needs further investigation since the contact time is too short. Increasing the contact time will increase the fouling risk of ceramic filters caused by high time does not affect the removal of cadmium since the cadmium concentration is constant suspended solid particle from the raw water. As shown in Table 4, increases in the contact after one hour of contact time.
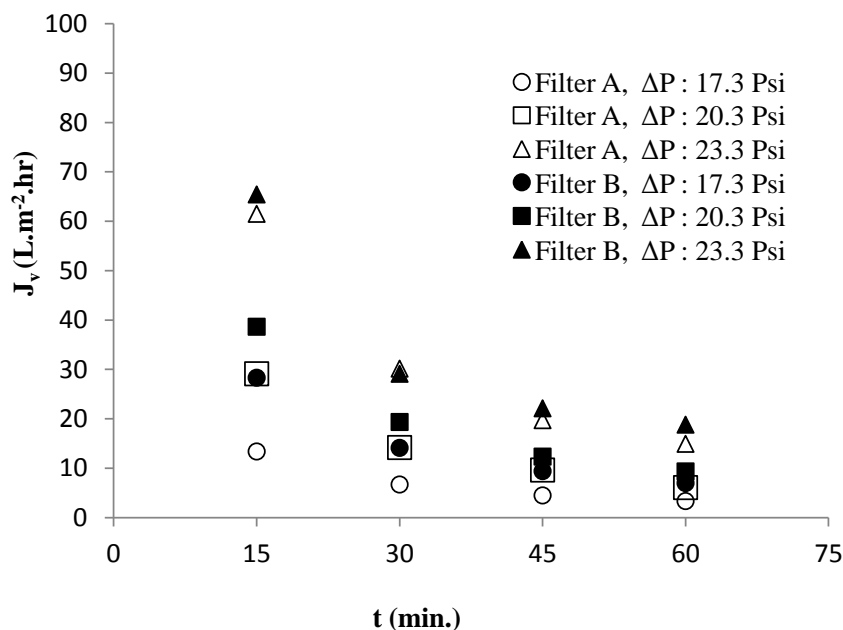

Figure 2 Permeate fluxes

3.2. Permeate Analysis

Permeate analysis can be seen in Table 3. It is shown that TDS, EC, pH, and cadmium concentrations of permeate meet the Indonesian standard for pulp industrial wastewater. Filter A was able to reduce the cadmium concentration by up to 99.53%, and Filter B by up to 99.90%. All permeates also showed good turbidity with pH in the range of 6.59 and 7.46. This means the effluent is safe to discharge into the environment. It also indicates effective absorption of cadmium on the ceramic filter surfaces.

Table 3 Permeate Analysis

ΔP (psi)	Time (min.)	Filter A				Filter B			
		TDS (mg.L^{-1})	EC (μS.cm^{-1})	Cd (mg.L^{-1})	pH	TDS (mg.L^{-1})	EC (μS.cm^{-1})	Cd (mg.L^{-1})	pH
17.3	15	490	982	0.005	6.72	472	945	0.003	7.46
	30	494	988	0.005	6.84	469	943	< 0.0015	6.62
	45	494	989	0.003	6.83	468	943	< 0.0015	6.62
	60	492	986	0.002	7.46	469	949	< 0.0015	6.62
20.3	15	490	980	0.005	7.32	477	954	0.002	6.60
	30	490	981	0.005	7.42	478	958	< 0.0015	6.59
	45	490	981	0.003	7.20	477	949	< 0.0015	7.32
	60	491	982	0.002	6.60	477	955	< 0.0015	7.20
23.3	15	488	970	0.005	6.59	462	925	< 0.0015	6.93
	30	489	977	0.002	7.32	475	950	< 0.0015	6.74
	45	489	979	< 0.0015	7.20	479	959	< 0.0015	6.74
	60	488	977	< 0.0015	6.93	478	957	< 0.0015	6.95

Table 4 illustrates the cadmium removal efficiency of Filter A and Filter B. Filter A was able to reduce the cadmium concentration by up to 99.53%, and Filter B by up to 99.90%. It has shown that Filter B is more effective in the removal of cadmium from pulp industry effluent at a pressure difference of 20.3 Psi and one hour of filtration time. This is due to characteristics of the filter such as the porosity and surface area of Filter B, which is larger than Filter A. Filter B is also able to reduce the levels of TDS and TSS in feed, making a good permeate in terms of turbidity. Besides, these two types of ceramic filters can neutralize the pH of permeate.

Table 4 Pulp Industry wastewater treatment using ceramic filters

Parameters	Ceramic Filter A	Removal (%)	Ceramic Filter B	Removal (%)
Cd (mg.L^{-1})	0.003	99.53	0.0015	99.00
TDS (mg.L^{-1})	498	12.17	472	16.75
EC (μS.cm^{-1})	986	10.93	970	12.38
TSS (mg.L^{-1})	21.4	86.79	17.8	89.01
pH	7.14	27.44	6.98	29.07
Turbidity (NTU)	7.12	94.65	2.56	98.08

The filter characteristics are presented in Table 5. The amount of rice bran affects the porosity of the filters. An increase in the rice bran percentage of the filter composition will increase the filter's porosity. Average pore diameters for both filters range from between 1 and 10 μm. It is suggested that rice bran should be oxidized at high a temperature to realize a random pore in the ceramic filters. This will lead to an increase of the pore formation in the ceramic filters.

Table 5 Filter characteristics

Ceramic Filter	Rice bran (%)	Average Pore Diameter (μm)	Surface area (m^{2}g)	Porosity (%)
A	20	7.84	12.01	41.96
B	10	1.09	14.63	43.95

Pores play an important role in the heavy metal adsorption of membranes or filter surfaces. Increasing the addition of rice bran as a pore forming agent in the ceramic filter composition results in lower mechanical strength since the porosity obtained is higher (Yang & Tsai, 2008). Consequently, it can decrease the heavy metal concentration from wastewater using the adsorption mechanism. A simple and rapid method to determine the filter surface is to use a Scanning Electron Microscope as shown in Figures 3 and 4.
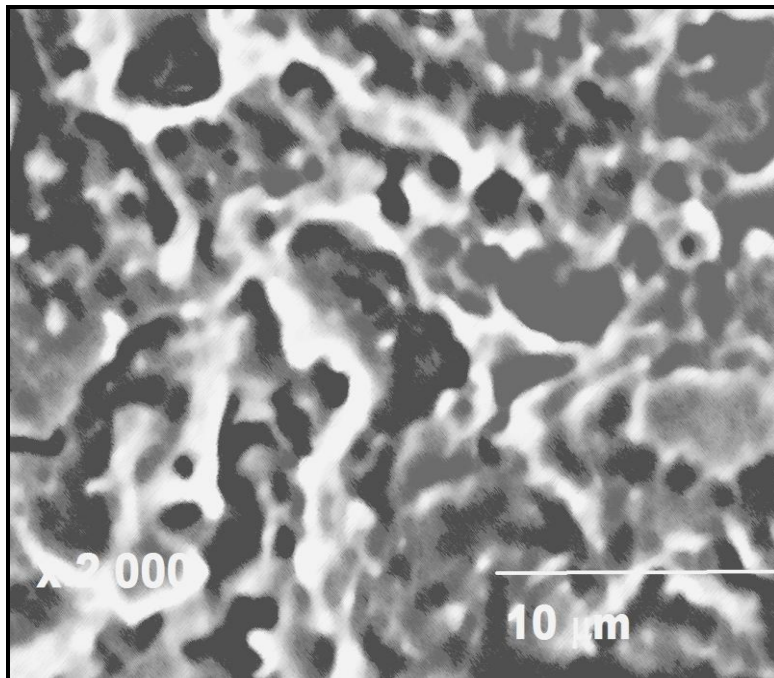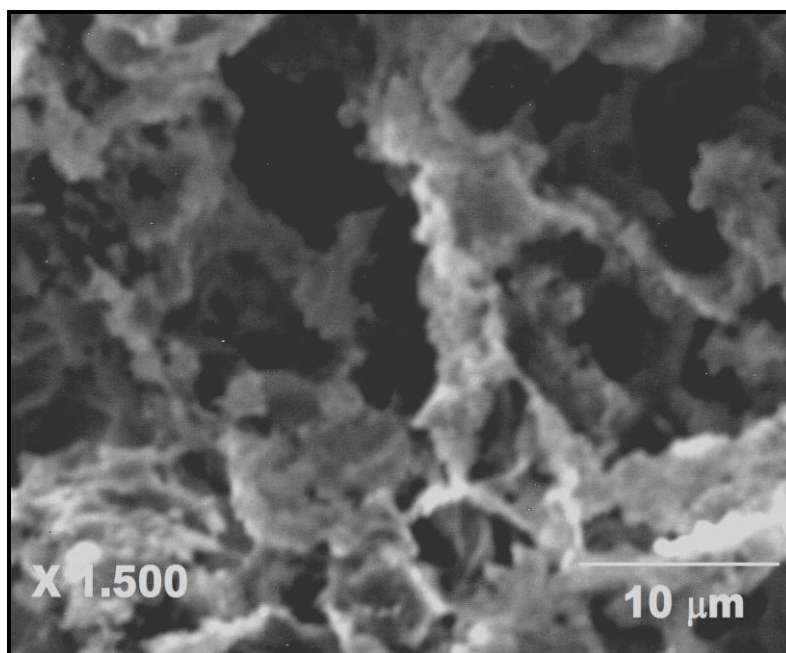

Figure 3 SEM micrograph of Filter A

Figure 4 SEM micrograph of Filter B

4. CONCLUSION

Ceramic filters made from 87.5% natural clay, 10% of rice bran, and 2.5% iron powder may reduce cadmium from pulp industry effluent by up to 99.0%. The permeate flux declined after 30 minutes of contact time and remained constant for one hour. The ceramic filters can be categorized as a microfiltration filter, and they can be used in the treatment of wastewater containing cadmium.

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