Pb removal in pulp and paper industry leachate wastewater using activated carbon-ceramic composite adsorbent

T Aprianti1*, S Miskah1, R Moeksin1, S Sisnayati2 and S Nasir1

1Department of Chemical Engineering, Sriwijaya University, South Sumatera, Indonesia
2Department of Chemical Engineering, Tamansiswa University, South Sumatera, Indonesia

*Corresponding Email : tineaprianti@unsri.ac.id

Abstract. The leachate wastewater from pulp and paper industry is known containing various types of heavy metals, the contamination of heavy metals contained in industrial wastewater which is released to water body will accumulate and eventually pollute the environment. The improper wastewater disposal by industries does not only greatly reduce marine vegetation and animal life but also contributes to the destruction of aquatic ecosystem. It is necessary to do the wastewater treatment to eliminate or at least to reduce the heavy metal content to the legal standard quality. One of the most commonly method used for wastewater treatment is adsorption, this study uses the adsorbent made from the mixture of clay and activated carbon formed into ceramic balls with the size of ± 0.5 cm in diameter. The ratios of clay and activated carbon are 6:1, 6:2, 6:3, 6:4 and 6:5. The pulp and paper wastewater treatment method is conducted by contacting wastewater containing Pb with the adsorbent in a column made of glass of 2 inches diameter and 50 cm length, contact time variations are 30, 45, 60, 75, 90, 105, 120, 135, 150, 165, 180, 195, 210, and 240 min. The most favorable result is 92.45%, the adsorbent is able to reduce the Pb concentration from 0.53 mg/L to 0.04 mg/L respectively at 180 minutes contact time with adsorbent ratio of 6:5.

1. Introduction
In any industrial activities, the wastewater must not be directly discharged into the environment due to its hazardous content, therefore it must be processed in advance in order to improve its quality [1]. On the contrary, there are still many industries that dispose their wastewater into the environment through rivers, lakes or directly to the sea without proper treatment [1]. The disposal of wastewater directly into the environment is the main cause of water pollution [2], [3].

Water can be seriously contaminated by various inorganic components [4], including various types of dangerous heavy metals which are widely used for various purposes so that they are produced continuously on an industrial scale [2], [5], [6]. All industries which produce wastewater containing heavy metal must get strict supervision so they will not endanger the workers and the surrounding environment [6], [7]. One of industries that produces wastewater containing heavy metals is pulp and paper industry [8].

Pb is a kind of heavy metal compound that can be accumulated in water bodies as a result of human or industrial activities [9]. Water bodies that have been polluted by a large amount of Pb compounds
or ions which exceed the proper concentration can cause the death of aquatic biota. Excessive amount of Pb$^{2+}$ in plants can interfere and inhibit various physiological processes [10].

1.1. Adsorption

One effort to process wastewater containing Pb is by the adsorption process. Adsorption is chosen because it is relatively a simple method and can use inexpensive natural material adsorbents from the remains of unused biomass [3]. In this study, activated carbon is used as one of adsorbent material in powdered form along with clay which also in powdered form. Powdered activated carbon (PAC) is a good adsorbent material due to its adsorption power. The followings are the reasons of using activated carbon as an adsorbent [4]:

- Has special micro pores.
- Has special biological characteristics.
- High density and good pore structures.
- The surface area is about 300 m$^2$/gram.

Adsorption is a surface phenomenon due to the accumulation on a solid-liquid surface boundary. Adequacy can occur due to the attraction. There are 2 types of adsorption [11-13]:

- Physical or Van der Waals adsorption
- Chemical adsorption

Adsorption in this case is a non-specific and non-selective, because its adsorption force occurs due to the hydrogen coordination bond. If the adsorbate and the adsorbent surface are bound to the Van der Waals force alone, it is called physical or Van der Waals adsorption. The adsorbed molecule is weakly bound to the surface and the adsorption heat is low. If the adsorbate and the surface of the adsorbent react chemically it is called chemical adsorption. The heat value of adsorption is equivalent to a chemical reaction due to the formation of chemical bonds that are formed or broken during the adsorption process.

Adsorption process occurs when solid surfaces in contact with a solution, the adsorbed material tends to accumulate and build layers of solute molecules on the surface due to the negative charges that pull the positive charges to get attached to the adsorbent’s surface. Chemical adsorption produces layer formation of monomolecular adsorbate on the surface through charges from the valencies of molecules on the surface [14]. Physical adsorption is caused by molecular condensation in capillaries from adsorbate. In general, elements with larger molecular weight will be adsorbed more easily [15]. A rapid formation of an equilibrium concentration of the adsorbent's surface followed by slow diffusion into carbon particles.

The adsorption rate is overall controlled by the diffusion speed of the solute molecules in the capillary pores of carbon particles. That speed is inversely proportional to the square diameter of the particle, the solute concentration increases along with increasing temperature and is inversely proportional to the increase in molecular weight of the solute [16]. Adsorption techniques have proven successful in removing heavy metals [17].

1.2. Clay

Clay is being considered as an alternative to low cost adsorbents [4]. Studies show that clay’s adsorption capability is caused by negative charges on silicate minerals which are neutralized by adsorption of positively charged cations such as cationic dyes, heavy metals, etc. Another major reason for the high adsorption capacity of clay is its wide surface starting from 800 m$^2$/gr [16].
1.3. Powdered Activated Carbon (PAC)

PAC has become the most widely used adsorbent because of its high capacity for heavy metal adsorption [17-19]. PAC is commonly used as an adsorbent for wastewater treatment, but its light structure makes it easily washed out in the wastewater flow and got carried away with the effluent [20]. However, due to the difficulties and costs involved in regeneration, combining clay and PAC as the adsorbent materials will be a good method for wastewater treatment process, because clay will bind PAC and make it heavier but it will not reduce its adsorption capacity since clay is also a good adsorbent material. In order to make clay and PAC are strongly bound to each other, they can be molded into any shapes, such as spheres or oval and then calcined into ceramics [7]. The purpose of this study is to evaluate the efficiency of the adsorption capacity PAC-ceramic adsorbent in adsorbing Pb contained in the pulp and paper industry wastewater.

2. Material and Method

The adsorption equipment used consisting of adsorption columns made of glass 2 in diameter with 50 cm height, centrifugal pump, flowmeter, flow regulator, pipes, iron frame, feed tank and effluent collection tank. The adsorbent requires molder equipment, mixer, furnace, and an oven. The materials used are powdered activated carbon (PAC), powdered clay, NaOH p.a and aquadest. Ceramic adsorbent materials comprise a mixture of powdered clay and PAC with dry weight ratios of 6:1, 6:2, 6:3, 6:4 and 6:5. The powdered clay and PAC are mixed evenly in a mixer, add about a little amount of aquadest to the mixture until it becomes a very thick slurry, mold the slurry mixture into the form of spheres with the diameter of ± 0.5 cm using the molder. Calcine the spheres in an oven with a high temperature of ± 1000°C for 10 hours, afterwards leave the spheres for 1 hour to cool them down.

For activation process, the ceramic adsorbent is immersed in the NaOH solution for 1 (one) hour to fill in the negative charge to the adsorbent’s surface [21], after that wash the adsorbent with aquadest two times and dry it in the oven at 150°C for 1 (one) hour.

The leachate wastewater used is taken from the pulp and paper industry leachate discharge pipeline in Muara Enim regency, South Sumatra. Based on the laboratory analysis results, the initial concentrations of Pb contained in pulp and paper wastewater is 0.53 mg/L. The treatment of adsorption process is started to be counted as soon as the wastewater is contacted with the adsorbent in the adsorption column by flowing the wastewater from the top of the column. The contact time variations are 30, 45, 60, 75, 90, 105, 120, 135, 150, 165, 180, 195, 210, and 240 min. The amount for each treatment is 600 mL of wastewater and 700 gr of adsorbent. The parameters to be studied are the concentration of Pb in wastewater before and after treatment at each contact time. Analysis used in this research is Atomic Absorption Spectrometer (AAS) to measure the concentration of Pb contained in wastewater. The data to be collected are the analysis of Pb concentration measured from feed and discharge wastewater of the adsorption column. The collected data will be displayed in graphical form.

The equation used for calculating the adsorption capacity is:

\[
q_e = \frac{[C_a] - [C_b]}{W} V
\]  

(1)

and the percentage of adsorption capacity is measured by equation:

\[
%q_e = \frac{[C_a] - [C_b]}{[C_a]} \times 100\%
\]  

(2)

where \(q_e\) is the adsorption capacity (mg/L), \(%q_e\) is the adsorption percentage, \(C_a\) is the initial concentration and \(C_b\) is the equilibrium concentration of Pb in the samples solution (mg/L), \(V\) is the volume of the samples solution (L) and \(W\) is the weight of the adsorbent (gr) [7].
3. Results and Discussions

Table 1. Adsorption capacity at 120 min contact time

| Contact Time (min) | Adsorbent Ratio | Equilibrium Concentration (mg/L) | Adsorption Capacity (mg/g) x10^{-3} |
|--------------------|----------------|----------------------------------|-----------------------------------|
| 120                | 6:1            | 0.36                             | 0.146                             |
|                    | 6:2            | 0.24                             | 0.249                             |
|                    | 6:3            | 0.19                             | 0.291                             |
|                    | 6:4            | 0.15                             | 0.326                             |
|                    | 6:5            | 0.11                             | 0.360                             |

Figure 1. Adsorption capacity of various adsorbent ratios at 120 min contact time

We can see in figure 1 that the adsorption capacity increases with the increase of PAC mass within the adsorbent ratios. The most favorable percentage result of adsorption capacity is 92.45% occurred at 6:5 where the Pb concentration reduces from 0.53 mg/L to 0.11 mg/L respectively. This proves that the properties and the characteristics of porous PAC give a great adsorption impact in adsorbing Pb. Therefore, we can conclude that the more PAC mass in the adsorbent material the higher adsorption capacity [7].

Table 2. Adsorption capacity of 6:5 adsorbent ratio

| Ratio  | Contact Time (min) | Equilibrium Concentration (mg/L) | Adsorption Capacity (mg/g) x10^{-3} |
|--------|--------------------|----------------------------------|-----------------------------------|
| 0:0    | 0                  | 0                                | 0                                 |
| 0:15   | 0.42               | 0.094                            |
| 0:30   | 0.39               | 0.120                            |
| 0:45   | 0.35               | 0.154                            |
| 0:60   | 0.30               | 0.197                            |
| 0:75   | 0.26               | 0.230                            |
| 0:90   | 0.24               | 0.249                            |
| 0:105  | 0.18               | 0.300                            |
Table 1. Adsorption capacity of 6:5 adsorbent ratio with various contact time

| Time (min) | Adsorption capacity (mg/gr) x 10^-3 |
|------------|-----------------------------------|
| 135        | 0.09                              |
| 150        | 0.08                              |
| 165        | 0.06                              |
| 180        | 0.04                              |
| 195        | 0.04                              |
| 240        | 0.04                              |

Figure 2. Adsorption capacity of 6:5 adsorbent ratio with various contact time

From figure 2 we can see that the adsorption capacity increases along with the contact time. The most favorable result of adsorption capacity occurred at 180 min with 0.42 x 10^-3 mg/gr where the Pb concentration reduces from 0.53 mg/L to 0.04 mg/L respectively, and adsorption capacity remains constant from 180 until 240 min contact time. We can see in figure 1 that the concentration of Pb decreases with the increase of contact time until it reaches its saturation point at 180 min contact time, proving that the length of contact time gives a serious affect the adsorption, therefore we can conclude that the longer contact time the more ions are attached to the adsorbent’s surface [16], [22], [23].

4. Conclusions

- PAC-ceramic composite adsorbent is able to reduce the Pb concentration contained in leachate wastewater of pulp and paper industry with most favorable result of 92.45% at 180 min contact time with 6:5 ratio of clay and PAC.
- PAC-ceramic adsorbent composite adsorbent can be an alternative for leachate wastewater treatment of pulp and paper industry.
- The ratio of adsorbent material gives a crucial impact on the adsorption process, the adsorbent that contains more activated carbon will have better adsorption capacity compared to the adsorbent with less activated carbon.

References

[1] Lu A, Zhong S, Chen J, Shi J, Tang J and Lu X 2006 Removal of Cr(VI) and Cr(III) from aqueous solutions and industrial wastewaters by natural clino-pyrrhotite *Environmental Science and Technol.*, vol 40, no 9 pp 3064–3069
[2] Sheoran A S and Sheoran V 2006 Heavy metal removal mechanism of acid mine drainage in
heavy metal-ized powdered activated carbon nated with anionic surfactants –

ature Chemical Acta, ons from wastewaters: A review

IOP Conf. Series: Earth and Environmental Science 298 (2019) 012011 doi:10.1088/1755-1315/298/1/012011

[3] Wardhana W A, Dampak Pencemaran Lingkungan 1st ed (Yogyakarta: Andi Offset)

[4] Babel S and Kurniawan T A 2003 Low-cost adsorbents for heavy metals uptake from contaminated water: a review J. Hazardous Materials vol 97, no 1 pp 219–243

[5] Feng D, Aldrich C and Tan H 2000 Treatment of acid mine water by use of heavy metal precipitation and ion exchange Minerals Engineering vol 13, no 6 pp 623–642

[6] Lacour S, Bollinger J, Serpand B et al Removal of heavy metals in industrial wastewaters by ion-exchanger grafted textiles ion-exchanger grafted textiles Analytica Chimica Acta vol 428, pp 121-132

[7] Aprianti T, Afrah B D and Agustina T E 2017 Acid Mine Drainage Treatment Using Activated Carbon Ceramic Adsorbent in Adsorption Column Int. J. on Advanced Science, Engineering and Information Technol. vol 7, no 4 pp 1241-1247

[8] Mahale S and Goswami-giri A S 2015 Environmental Friendly Approach in Paper Making using Natural Organic Waste vol 4, no 14 pp 489–493

[9] Sheng G et al 2009 Adsorption of Pb(II) on diatomite as affected via aqueous solution chemistry and temperature Colloids and Surfaces A: Physicochemical and Engineering Aspects vol 339, no 1–3 pp 159–166

[10] Fu F and Wang Q 2011 Removal of heavy metal ions from wastewaters: A review J. Environmental Management vol 92, no 3 pp 407–418

[11] Tsai W T, Chang C Y, M. C. M C, Chien S F, Sun H F and Hsieh M F 2001 Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl2 activation,” Chemicalsphere vol 45, no 1 pp 51–58

[12] Rajeshwarisivaraj S, Sivakumar P, Senthilkumar S and Subburam V 2001 Carbon from Cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution Bioresource Technol. vol 80, no 3 pp 233–235

[13] Dias J M, Alvim-Ferraz M C M, Almeida M F, Rivera-Utrilla J and Sánchez-Polo M 2007 Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review J. Environmental Management vol 85, no 4 pp 833–846

[14] Gupta V K, Gupta B, Rastogi A, Agarwal S and Nayak A 2011 A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye—Acid Blue 113 J. Hazardous Materials vol 186, no 1 pp 891–901

[15] Newcombe G, Drikas M and Hayer R 1997 Influence of characterised natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption of 2-methyisoborneol Water Research vol 31, no 5 pp 1065–1073

[16] Sari A and Tuzen M 2014 Cd(II) adsorption from aqueous solution by raw and modified kaolinite Applied Clay Science vol 88, pp 63-72

[17] Jusoh A, Su Shiung L, Ali N and Noor M J M M 2007 A simulation study of the removal efficiency of granular activated carbon on cadmium and lead Desalination vol 206, no 1–3 pp 9–16

[18] Mohan D and Chander S 2001 Single component and multi-component adsorption of metal ions by activated carbons Colloids and Surfaces A: Physicochemical and Engineering Aspects vol 177, no 2–3 pp 183–196

[19] Ahn C K, Park D, Woo S H and Park J M 2009 Removal of cationic heavy metal from aqueous solution by activated carbon impregnated with anionic surfactants J. Hazardous Materials vol 164, no 2 pp 1130–1136

[20] Li W, Gong X, Li X, Zhang D and Gong H 2012 Removal of Cr(VI) from low-temperature micro-polluted surface water by tannic acid immobilized powdered activated carbon Bioresource Technol. vol 113, pp 106–113

[21] Hameed B H, Din A T M and Ahmad A L 2007 Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies J. Hazardous Materials vol 141, no
Acknowledgments

Authors would like to acknowledge encouragement from colleagues, assistance from laboratory staff and financial support from Sriwijaya University.