Effects of initial concentration, adsorbent mass, pH and temperature to personal care products waste removal with activated carbon as adsorbent

H R Priyantini¹, L Riadi¹, C Effendi¹, F Effendi¹ and A Mitayani²

¹Department of Chemical Engineering, University of Surabaya, Raya Kalirungkut, Surabaya, 60293, Indonesia
²Research Center for Electronics and Telecommunication (P2ET), Indonesian Institute of Sciences (LIPI), Sangkuriang, Bandung, 40135, Indonesia

E-mail:

Abstract. Before being discharged into the water, waste from the personal care products (PCP) industry needs to be treated using the adsorption process. In this study, activated carbon is chosen as adsorbent because of its organophilic property, abundance, and continuous system. The experiment was carried out in batches using 3 variables of COD concentrations in PCP wastes in 250 ppm, 225 ppm, and 200 ppm with the adsorbent mass amount of 0.3 g/l, 0.35 g/l, and 0.4 g/l. In this experiment, the effects of initial COD concentration, adsorbent mass, pH, and temperature on the adsorption process, equilibrium models and mass transfer coefficients of adsorption will be analyzed. Equilibrium models of Distribution Coefficient, Freundlich, and Langmuir Model, were implemented in this experiment. From results of the study, the equilibrium system of PCP waste and activated carbon using Langmuir Equilibrium achieved a removal value of 69.03% at concentration of 200 ppm and the adsorbent mass of 0.4 g/l. To determine the mass transfer coefficient, an external adsorption model was used. The coefficient value of mass transfer coefficient (kc) with the trial method is 3.78x10⁻⁸ m/min. Using numerical method with MATLAB, the result is 7.6222x10⁻⁸ m/min, while using the analytical approach, the result is 7.413x10⁻⁸ m/min.

1. Introduction

The demand of Indonesian market for personal care products (PCP) increases consistently every year at around 10-15% [1]. The higher the PCP products from industry and the community’s consumption, the higher the waste will be formed, such as organic waste, pharmaceutical waste and nano-waste namely engineered nanomaterial (ENM). This waste flows to the environment from making process, wrapping, distributing, to personal care product consumption. This waste is also called pharmaceutical and personal care product (PPCP) waste.

There are several methods to reduce PPCP liquid waste level if after secondary treatment, the waste characteristic values still do not meet quality standards and one of them is with tertiary treatment. Quality standard for pharmaceutical liquid waste chemical oxygen demand (COD) level according to East Java Provincial Government Regulation Number 72 Year 2013 [2] is 75 mg/L.
Adsorption is commonly selected for tertiary treatment. Adsorption for liquid waste treatment becomes popular because it is more efficient and more stable compared to biological method that also yields large amount of sludge [3]. Meanwhile, adsorption process is very efficient, easy to design and operate, relatively affordable and not affected by toxicity like biological treatment [4]. Furthermore, removal percentage of organic waste is estimated quite high, around 70-80% [5].

The material often used for conventional adsorption is activated carbon. Activated carbon is commonly used for adsorption because of its large surface area and it does not need adsorbent preparation. However, because of its large surface area, activated carbon regeneration needs a high cost technique. The common regeneration method is thermal regeneration, but it can remove 5-10% carbon because carbon structure is damaged [6].

The research commonly used to investigate the PCP waste adsorption process is generally performed using synthetic waste with synthetic compound concentration parameter. Because of the large amount of component in PCP waste, the parameter used to investigate the PCP waste adsorption process is COD. COD is the amount of oxygen (mg O₂) needed to oxidize organic substances in 1 liter of water sample. So far, there is no research activity that investigates PCP waste adsorption process with COD as the main parameter, so that further research is needed to figure out the PCP waste adsorption characteristic by those two types of adsorbent in order to obtain operation condition and adsorbent type which fits PCP waste treatment the most. The objective of the study is to evaluate the best operation conditions, such as initial concentration of waste, adsorbent mass, pH and temperature for PCP removal using activated carbon as adsorbent.

2. Research method
The system process of this research is described in figure 1. The process consists of 7 steps which is initiated by PPCP waste characterization and ended with adsorption modelling. The modelling is based on finding the most optimum parameter to obtain maximum percentage of removal.

2.1. PCP waste characterization
Waste characterization included initial total suspended solid (TSS) level test, initial 5-day biological oxygen demand (BOD₅) and initial COD. This procedure determined whether waste needed pretreatment before adsorption process or not, referring to East Java Provincial Government Regulation Number 72 Year 2013 [2] concerning pharmaceutical waste. Initial TSS level test used gravimetry method. Initial BOD₅ level test used reagents: phosphate buffer, MgSO₄, CaCl₂, FeCl₃, 6H₂O and KI obtained from BDH. Initial COD test used K₂Cr₂O₇ and AgSO₄ reagents obtained from e-Merck. Activated carbon for this experiment was obtained from Merck.

2.2. Maximum COD percent removal determination at various initial COD concentration of wastewater
The diluting waste at various concentration was carried out in order to figure out maximum COD percentage of removal which could be reached. The same adsorbent mass was used for all variables, that is, 0.15 gr. Experiment data were sampled at 0, 1, 3, 5, 10, 15, 20, 30, 40, 60, 80, 100 and 120-th minute and waste volume used in this experiment was 500 ml. Adsorption equilibrium data were obtained after 24 hours since the adsorption process started. Variables used in this experiment were: 250 ppm, 225 ppm and 200 ppm.
2.3. Optimum adsorbent mass determination
After obtaining the initial concentration for maximum percentage of removal in previous step, the adsorbent mass for this experiment was varied until the maximum percentage of removal was reached. Experiment data were sampled at 0, 13, 5, 10, 15, 20, 30, 40, 60, 80, 100 and 120-th minute and waste volume used in this experiment was 500 ml. Adsorption equilibrium data were obtained after 24 hours since the adsorption process started. Variables used in this experiment were: 0.15 gr, 0.175 gr and 0.2 gr.

2.4. Optimum pH determination
With the previous initial concentration that made up the maximum percentage of removal, initial pH was measured. Then, pH was adjusted until reaching acidic pH (pH=4) and basic pH (pH=11). The adsorption process was performed using previous adsorbent mass which resulted in maximum percent removal. The adsorption results from the maximum percentage of removal in acidic pH, neutral pH, and basic pH were then compared. Experiment data were sampled at 0, 13, 5, 10, 15, 20, 30, 40, 60, 80, 100 and 120-th minute and waste volume used in this experiment was 500 ml.

2.5. Optimum temperature determination
With the previous initial concentration, adsorbent mass and pH that made up maximum percent removal, temperature was measured and then varied to obtain the optimum temperature that resulted in the maximum removal percentage. Experiment data were sampled at 0, 13, 5, 10, 15, 20, 30, 40, 60, 80, 100 and 120-th minute and waste volume used in this experiment was 500 ml. Variables used in this experiment were: 30°C, 35°C, 40°C, 45°C and 50°C.

3. Results and discussions
This research discusses PCP waste adsorption which is effluent secondary treatment, using activated carbon. Table 1 shows PCP waste characteristic data before entering adsorption process compared to the quality standards from government [2] concerning pharmaceutical waste.

| Parameter | Quality Standards [8] | Characteristic Used in Experiment |
|-----------|------------------------|----------------------------------|
| COD       | 150 mg/L               | 860 mg/L                         |
| BOD$_5$   | 75 mg/L                | 72 mg/L                          |
| TSS       | 75 mg/L                | 8 mg/L                           |
| pH        | 6-9                    | 7.9                               |

Activated carbon used in experiment is powder type activated carbon from Merck with surface area of 800 m$^2$/gr.

3.1. Initial COD concentration effect
Three pollutant concentration variables (250 ppm, 225 ppm and 200 ppm) were used to understand the pollutant concentration effect on the adsorption process in certain adsorbent mass values. This pollutant concentration range was selected based on pollutant concentration for tertiary treatment in industry which has to be the lowest pollutant concentration. The ideal adsorption process was performed in thin solution. Initially, wastewater was diluted with distilled water because PCP waste has COD concentration of 860 ppm. Activated carbon mass used here was 0.15 gr. Experiment data were sampled at 0, 13, 5, 10, 15, 20, 30, 40, 60, 80, 100 and 120-th minute. Figure 2 shows COD value change versus time with adsorbent mass of 0.15 gr in various initial concentration.
Figure 2. Profile of COD concentration versus time with adsorbent mass = 0.15 gr in various initial concentration.

Figure 3. Profile of COD concentration versus time with initial COD concentration = 200 ppm in various initial adsorbent mass.

Table 2. COD percent removal data in various initial COD concentration

| COD<sub>0</sub> [mg/L] | 246.9 | 222.7 | 211.9 |
|-----------------------|-------|-------|-------|
| COD<sub>2-hour</sub>  | 179.559 | 128.363 | 114.889 |
| COD<sub>eq</sub> [mg/L] | 166.087 | 128.363 | 104.111 |
| percent removal       | 32.738% | 42.354% | 50.867% |

Table 3. COD percent removal data in various adsorbent mass

| COD<sub>0</sub> [mg/L] | 214.5897 | 214.5897 | 211.9 |
|-----------------------|----------|----------|-------|
| Adsorbent mass [gr]   | 0.2      | 0.175    | 0.15  |
| COD<sub>2-hour</sub>  | 66.3867 | 93.3327 | 114.889 |
| COD<sub>eq</sub> [mg/L] | 66.3867 | 85.2489 | 104.111 |
| percent removal       | 69.0634% | 60.2735% | 50.867% |

Table 2 shows the COD percentage of removal data in various initial concentration (246.9 ppm, 222.7 ppm and 211.9 ppm). Meanwhile, for COD concentration of 250 ppm, after 2 hours of adsorption process, COD concentration becomes 179.559 ppm, where this result does not yet meet the quality standards from government [2].

In the lower concentration, the number of particle bonds among waste particles is lower, hence the adsorption of waste particles to activated carbon becomes more optimum. Furthermore, adsorption process is ideally performed in gas and thin solution, so that if the solution concentration is lower, adsorption process is more optimum [7]. Therefore, for next adsorption process, initial COD concentration of 211.9 ppm is applied.

3.2. Adsorbent mass effect

In varied adsorbent mass experiment, three variables of adsorbent mass were used: 0.15 gr, 0.175 gr and 0.2 gr. Figure 3 shows COD value change versus time in initial COD concentration of 200 ppm with various adsorbent mass.

On Table 3, it can be seen that adsorption process optimum mass is obtained at mass of 0.2 gr, where the greater the adsorbent mass, the greater the active side for adsorbent adherence. Quality standard from government is met for all mass and in the next process, the adsorbent mass of 0.2 gr is used.
3.3. Isotherm and adsorption kinetics

From varied initial COD concentration and adsorbent mass experiment, isotherm for this experiment can be estimated from plotting curves as comparison among Langmuir, Freundlich and distribution coefficient isotherm.

![Figure 4. PCP waste adsorption process with activated carbon as adsorbent. (a) Langmuir isotherm plot; (b) Freundlich isotherm plot; (c) Distribution coefficient isotherm plot.]

| ISOTHERM             | PARAMETER               | R²   |
|----------------------|-------------------------|------|
| Langmuir             | \( K_L = -0.028 \, \text{L/mg} \) | 0.973|
|                      | \( C_{\mu,\text{max}} = 217.391 \, \text{mg/g} \) |      |
| Freundlich           | \( K_F = 2424.062 \, \text{mg/g} \) | 0.703|
|                      | \( n = -2.384 \)       |      |
| Distribution Coefficient | \( k_d = 0.295 \, \text{g/L} \) | -1.051|

In figure 4, it can be seen that the most suitable equilibrium for this research is Langmuir isotherm. As seen in table 4, Langmuir equilibrium has value of R² = 0.973. The value is the closest number to 1 if compared to R² values from Freundlich and distribution coefficient equilibrium. This fact shows that PCP waste adsorption process using activated carbon follows monolayer adsorption model as described in equation (1).

\[
\mu_{\text{eq}} = \frac{C_{\mu,\text{max}} K_L C_{\text{eq}}}{1 + K_L C_{\text{eq}}} \tag{1}
\]

Analytical approach COD is obtained by using equation (2).

\[
\int_{C_{\mu,\text{eq}}}^{C} \frac{dC}{C - C_{\text{eq}}} = \frac{k_c \times A \times t}{V} \tag{2}
\]

Analytical approach is an approach with exponential method resulting in steep declining line then flattening at some point, while experiment data are declining with sloping trend. Therefore, trial method is carried out to find COD value from modelling that approximates experiment value more precisely. COD trial value approximates experiment data better than analytical approach.

In PCP waste adsorption experiment using activated carbon, various \( k_c \) (mass transfer coefficient) values ranging from 5.175x10⁻⁸ to 11.57x10⁻⁸ with various adsorbent mass and initial concentration of PCP waste were used. Average \( k_c \) value obtained with analytical approach is 7.70x10⁻⁸. Meanwhile, average \( k_c \) from trial method is 3.78x10⁻⁸. Because the values are close to one another, it can be concluded that \( k_c \) value is not affected by adsorbent mass and initial concentration of PCP waste.

3.4. Effects of pH

In varied pH adsorption process experiment, three variables of various pH were used, that is, pH=4, pH=7.5 and pH=11. pH=4 is used for setting up acidic situation in adsorption process, while pH=11 is used for setting up basic situation in adsorption process. From there, a match between adsorbent and adsorbate in acidic, neutral and basic pH are evaluated. Neutral pH for this waste is 7.5. In this varied pH experiment, fixed initial concentration of 200 ppm and adsorbent mass of 0.2 gr are used. pH value
that gives the biggest decrement of COD is 4 (acidic pH) which also means that pH value of 4 results in the biggest percentage of removal of 74.086%. This proves that acidic pH is more suitable for activated carbon. Theoretically, CA possesses point of zero charge (PZC) in pH=5.4. When the pH of solution is below PZC, CA will suffer from protonation, so that positive charge will also decrease. Therefore, CA will adsorb more anionic compounds. The original pH of the solution tends to be basic, that is, is 7.5, thus, to increase the percentage of removal, the pH of the solution should be acidized to less than 5.4.

3.5. Effects of temperature
In this experiment, adsorption process with 5 varied temperatures: 30, 35, 40, 45 and 50°C was performed. The best temperature for the adsorption process was at 50°C. It was supported by the value of $k_c$ (equilibrium constant between concentration in liquid and solid state) as can be seen in equation (3). Table 5 shows the effect of temperature and $k_c$. $C_{u,eq}$ denotes adsorbate concentration in adsorbent and $C_{eq}$ denotes adsorbate concentration in solution when those reach equilibrium.

$$k_c = \frac{C_{u,eq}}{C_{eq}} \quad (3)$$

| $T$ [K] | $1/T$ [1/K] | $\ln k_c$ |
|---------|-------------|-----------|
| 303     | 0.0033      | 0.824889  |
| 308     | 0.003247    | 1.385905  |
| 313     | 0.003195    | 1.546015  |
| 318     | 0.003145    | 1.849222  |
| 323     | 0.003096    | 1.946211  |

4. Conclusions
In constant activated carbon mass, the biggest percentage of removal value is obtained in the lowest COD initial concentration of 211.9 ppm. In the fixed PCP waste concentration, the biggest percentage of removal value is obtained in the highest varied mass, that is, is 0.2 gr. The highest percentage of removal is reached when COD initial concentration is 200 ppm, adsorbent mass is 0.2 gr, pH of solution is 4 and temperature is 50°C where percentage of removal value obtained is 73.69%. Mass transfer coefficient value ($k_c$) with trial method is $3.78 \times 10^{-8}$ m/min. With computer-aided simulation, it is $7.6222 \times 10^{-8}$ m/min, while with analytical approach, it is $7.413 \times 10^{-8}$ m/min.

Reference
[1] U.S. Department of Commerce 2016 Personal Care & Cosmetics Products Cosmetics, (Indonesia: Toiletries and Skincare Market Overviews)
[2] East Java Provincial Government 2013 East Java Provincial Government Regulation Number 72 Year 2013 Concerning Quality Standards of Wastewater for Industry and/or Other Commercial Activities
[3] Bellir K Bouziane I Sadok Boutamine Z Lehocine M Bencheikh and Meniai A H 2012 Sorption Study of a Basic Dye “Genetian Violet” from Aqueous Solutions Using Activated Bentonite (Energy Procedia 18) pp 924 – 933
[4] Ahmaruzzaman Md 2008 Adsorption of Phenolic Compounds on Low-Cost Adsorbents: A Review (Adv. in Colloid and Interface Sci. 143) pp 48-67
[5] Shon H K Phuntsho S Vigneswaran S Kandasamy J 2011 Physico-Chemical Processes for Organic Removal from Wastewater Effluent (Encyclopedia of Life Support System: Water and Wastewater Treatment Technologies)
[6] Sufnarski M D 1999 The Regeneration of Granular Activated Carbon Using Hydrothermal Technology (Texas University at Austin, Dept. Of Engineering.)
[7] Fatimah I 2014 Adsorption and Catalysis Using Clay-Based Material (Jakarta: Graha Ilmu)