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Removal of Lead (II) Ions from Aqueous Solution Using Desiccated Coconut Waste as Low-Cost Adsorbent

Abdul Rahman Abdul Rahim[a], Nurul Ekmi Rabat[b], Khairiraihanna Johari[a,*], Norasikin Saman[c], Hanapi Mat[c]

[a]Department of Chemical Engineering, Faculty of Engineering, Universiti Teknologi PETRONAS, 32610, Bandar Seri Iskandar, Perak, Malaysia.
[b]Centre for Contaminant Control, Institute of Contaminant Management, Universiti Teknologi PETRONAS, 32610, Bandar Seri Iskandar, Perak, Malaysia.
[c]Advanced Materials and Process Engineering Laboratory, School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.
khairiraihana.j@utp.edu.my

Waste from coconut milk processing industry namely desiccated coconut waste (DCW) was used to remove Pb (II) due to Pb (II) hazardous effect in the environment. The main objective of this study is to study and develop the adsorption capability of the DCW adsorbent. The chemical and physical properties of the DCW adsorbent were depicted by the FT-IR spectra and the elemental CHNS analysis. The maximum Pb (II) adsorption capacity (Q) toward DCW adsorbent was 50.33 mg/g at pH solution of 6 with the rate of 0.004 mg/min. In addition, the Pb (II) equilibrium data were best fitted to the Langmuir isotherm model, whereas the kinetic data obeyed the pseudo-second-order kinetic model. In the regeneration study, DCW adsorbent has remained stable up to two adsorption cycles. Thus, these satisfactory results revealed that the use of DCW as an alternative low-cost adsorbent for the removal Pb (II) from aqueous solution is feasible.

1. Introduction

Recently, lead, Pb (II) concentration in sources for drinking water increases to a concerning level due to various industrial activities such as textile dying, ceramic and glass industry, battery manufacturing and petroleum refining industry (Azouaou et al., 2013). It was reported that the industrial wastewater contained lead up to a concentration of 200 – 500 mg/L (Arbabi et al., 2015) where the maximum allowable limit for Pb (II) in water is only 0.015 mg/L. Pb (II) ion is one of the most toxic heavy metals which are non-biodegradable (Patterer et al., 2017) and highly persistent in the nature (Lavecchia et al., 2016). Exposure to Pb (II) ion can occur through inhalation of Pb (II)-contaminated air or Pb (II)-contaminated food source (Dixit et al., 2015). World Health Organization (2016) reported that exposure of Pb (II) in children can cause distorted and stunted intelligence development. In addition to that, in case of higher magnitude of exposure, Pb (II) ion can cause body convulsion, comatose condition or fatality.

Adsorption process is one of the removal techniques that has been widely applied in removing heavy metals because the process is very feasible, cost effective and easy to be operated (Ayucitra et al., 2017). Typically, adsorbents namely activated carbon (La Motta et al., 2016), silica (Saman et al., 2013), alumina (Mahmoud et al., 2010), zeolite (Qiu et al., 2018) and bentonite (Md Ariff et al., 2018) are utilized in adsorption process. However, these adsorbents are expensive (Patterer et al., 2017) because the sources are not renewable (Saman et al., 2015) and complex preparation method is required before it can be used in the process. This leads to various studies conducted on adsorbent alternative that are low cost that can offer the same adsorptive capability as the commercialized adsorbent. Agriculture wastes (AWs) is considered as the best source for low cost adsorbent because the source is abundantly available, a by-product of other industry and it only require minimal treatment before can be utilized for adsorption process. AWs such as coconut waste (Johari et al., 2013), coconut coir pith (Saman et al., 2015), oil palm endocarp (Marrugo et al., 2015), rice husk (Dada et al., 2012), sawdust (Ghasemi and Gholami, 2014) and spent coffee grounds (Ayucitra et al., 2017) have been

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utilized in adsorption study in removing heavy metals. Johari et al. (2013) reported that AWs can adsorb the heavy metals due to the presence of functional group such as carboxyl, ketone, alkane and alkene, on the surface of the waste which provided the adsorbent with sufficient surface affinity.
Among all of the AWs adsorbent, coconut waste such as coconut husk, fibre, shell and coir pith have been widely studied for heavy metal removal application. However, there are limited studies available on utilization of desiccated coconut waste (DCW) for the same application. DCW is a by-product from moisture extraction process in coconut milk processing industry (Johari et al., 2013). DCW is a potential low-cost adsorbent due to abundant availability of the source as it has no commercial value or industrial use and it can be obtained at minimal or at a cheaper cost. Therefore, in this study, DCW is used as potential precursor in removing Pb (II) from its aqueous phase. Several parameters such as effect of solution pH, effect of initial Pb (II) concentration, effect of agitation time are studied in order to evaluate the adsorption performance of DCW as adsorbent.

2. Methodology

2.1 Materials and chemicals

DCW was collected from a local market in Perak, Malaysia. Analytical grade sodium hydroxide (NaOH, 99.99 %) and nitric acid (HNO_3, 65 %) were purchased from Merck (Germany). Lead (II) nitrate salt ($Pb(NO_3)_2$, 99.99 %) was purchased from Fisher Scientific (USA).

2.2 Preparation of DCW adsorbent

Raw DCW was washed with distilled water for a few times and sundried. The dried DCW was then ground to a size of 150 – 300 µm using the laboratory grinder. The DCW was washed again with distilled water to remove dirt and contaminants from the grinding process. DCW was oven – dried at a temperature of 105 °C for about 2 d before it was stored in desiccator before further use.

2.3 Characterization of DCW

Fourier-transform infrared (FT-IR) spectrophotometer was used to determine the existence of functional groups on the surface of the DCW where the measurement was conducted in the region range of 450 – 4,000 cm^{-1} according to KBr disk method. CHNS Analysis was used to measure the elemental carbon, hydrogen, nitrogen and sulfur composition on the surface of the DCW adsorbent which was measured according to DCW's dynamic flash combustion.

2.4 Pb (II) ion adsorption measurement

Adsorption experiment was carried out under batch adsorption process using the same method employed by Johari et al. (2013). 25 mL of Pb (II) solution of desired concentration was placed into a 100 mL conical flask. Diluted solution of HNO_3 and NaOH solution were used to regulate the pH of the solution. 25 mg of DCW adsorbent were added into the solution and the mixture was then agitated on a mechanical shaker of 200 rpm at room temperature (30 °C) for 1 d which was an adequate time to ensure equilibrium has achieved. The mixture was then filtered using a nylon filter syringe and the filtrate is collected. The concentration of the Pb (II) solution was determined by using the atomic absorption spectrophotometer (AAS), Hitachi Model (Japan). Adsorption capacity of the Pb (II), Q (mg/g) onto DCW adsorbents was calculated according to Eq(1):

$$Q = (C_i - C_f)\left(\frac{V}{m}\right) \quad (1)$$

C_i and C_f are the initial and final concentration of the heavy metals (mg/L), V is the volume of the heavy metals solutions (L), and m is the mass of the DCW adsorbent used (g). Several parameters such as pH of Pb (II) solution (2 – 6), initial Pb (II) concentration (25 – 200 mg/L) and agitation time (1 – 1,440 min) were conducted in order to study the performance of DCW adsorption towards the Pb (II) removal.

2.5 Regeneration of spent DCW adsorbent

The DCW adsorbent from the previous adsorption measurement study was used for another adsorption-desorption cycle. The spent DCW was washed and agitated in diluted HNO_3 solution for 1 d and subjected again to Pb (II) adsorption process. HNO_3 was used in washing the spent adsorbent because HNO_3 is one of the best desorption agents in desorbing Pb (II) ion (Lata et al., 2015). Adsorption capacities of the DCW for each cycle was compared to determine the regenerative properties of the DCW adsorbent.

3. Results and discussion

3.1 Characterization of DCW adsorbent

The surface functional group of DCW adsorbent was characterized using FTIR analysis and the spectra is shown in Figure 1. The peak between 2,950 – 2,800 cm^{-1} indicates stretching of C-H group while peak between 1,780 – 1,670 cm^{-1} shows the stretching of C=O group. The peak at ~ 1,465 cm^{-1} and ~ 1,375 cm^{-1} are assigned to the bending of C-H group. The peak around 1,100 cm^{-1} represented the bending of C-C group and in the range of 840 - 790 cm^{-1} representing bending of C-H. The presence of these functional groups provided sufficient negative charge to attract Pb (II) ion to the active sites for adsorption to happen. Based on CHNS analysis, it was observed that DCW has the highest percentage of carbon (C, 50.18 %), followed by hydrogen (H, 8.09 %), nitrogen (N, 3.41 %) and sulphur (S, 0.33 %). High carbon percentage indicated that DCW is a good precursor as porous adsorbent. Substantial amount of hydrogen, nitrogen and sulphur offers the advantages of maintaining the functional group that are responsible for adsorption capacity of the adsorbent. Similar results were reported by Johari et al. (2013) where the percentage of elemental carbon is higher (58.7 %). The carbon percentage in another part of the coconut waste such as coir pith and coconut fibre were observed in a similar range between 40.68 - 50.29 % (de Sousa et al., 2010).

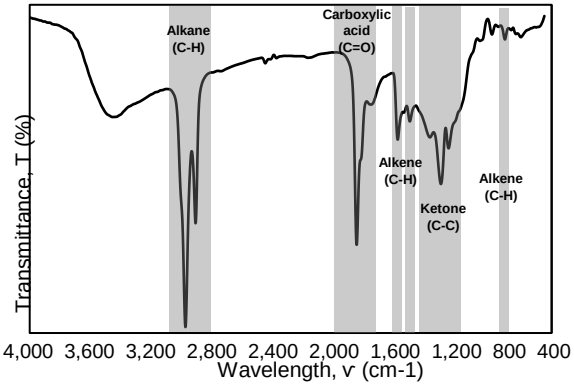

Figure 1: FT-IR spectra of DCW adsorbent

3.2 Effect of solution pH

The study on effect of pH on the DCW adsorption capacity was conducted at pH 2, pH 4 and pH 6. It was found out that the adsorption capacity increases with increase in solution pH as shown in Figure 2. Lowest adsorption capacity was recorded at pH 2 (Q = 6.740 mg/g) and the highest at pH 6 (Q = 44.020 mg/g). At lower pH condition, the Pb (II) solution contain high amount of H^+ ion due to its acidic condition. In large amount, H^+ ion created repulsion with Pb^{2+} ion which impeded the binding of Pb^{2+} ion to the actives sites on the pores of DCW surface, resulting in lower adsorption capacity. Several researchers reported these similar trends in which that at lower pH, low adsorption capacity was observed and higher adsorption capacity was observed at higher pH of Pb (II) solution (Ghasemi and Gholami, 2014). It can be concluded that adsorption of Pb (II) using DCW was the best at pH 6 condition. The adsorption study was not carried out at pH higher than pH 6 due to precipitation of the Pb (II) solution with NaOH.

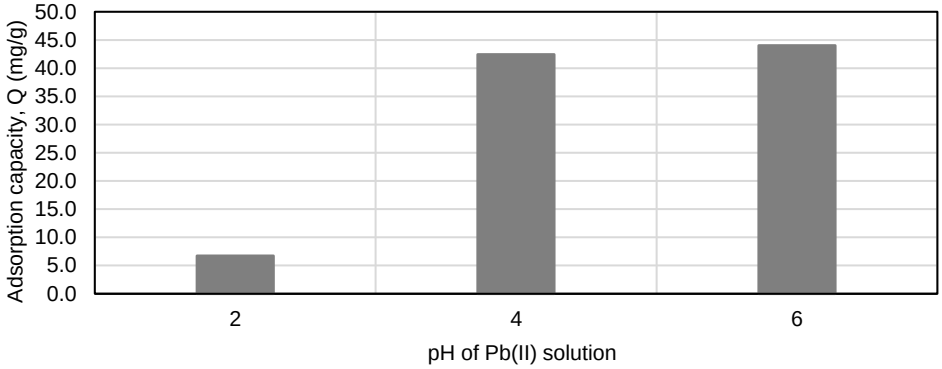

Figure 2: Effect of pH on adsorption of DCW (Experimental conditions: initial concentration of Pb (II) = 50 mg/L; agitation time = 1 day; DCW mass = 25 mg; temperature = 30 °C; and agitation speed = 200 rpm)

3.3 Effect of initial concentration

In addition, based on the study on the effect of initial Pb (II) concentration, Figure 3 showed that the adsorption capacity, Q increases with increase in initial concentration from 20 mg/L (Q=11.80 mg/L) to 125 mg/L (Q=50.330 mg/L). Other studies on Pb (II) removal using other low cost adsorbent namely green algae Spirogyra (Q=140 mg/g) (Gupta and Rastogi, 2008), Myrtaceae sawdust (Q=10 mg/g) (Ghasemi and Gholami, 2014) and spent ground coffee (Q=8.66 mg/g) (Ayucitra et al., 2017) conform well with the obtained value. The increase trend indicated that as the initial concentration is higher, it will have resulted in higher adsorption capacity until saturation condition. Johari et al. (2013) conducted a study using DCW adsorbent in Hg (II) removal also reported similar trend (Q = 500 mg/g) for the effect of initial concentration.

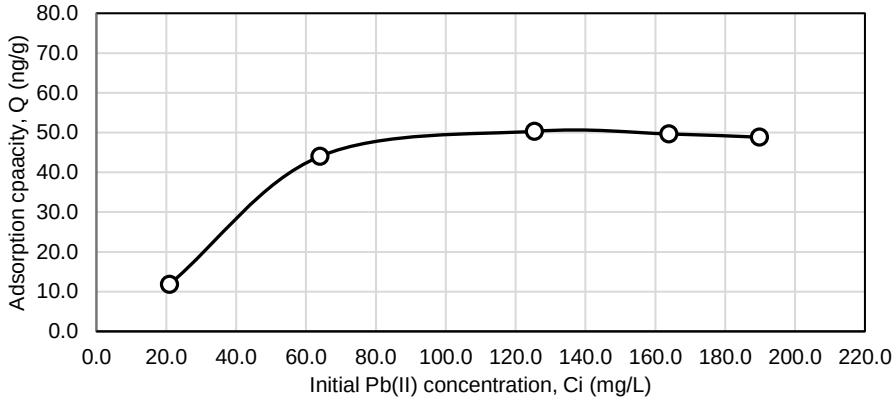

Figure 3: Effect of initial concentration on adsorption of DCW (Experimental conditions: agitation time = 1 d; DCW mass = 25 mg; temperature = 30 °C; solution pH = pH 6; and agitation speed = 200 rpm)

3.4 Effect of agitation time

Figure 4 shows time dependence of Pb (II) adsorption onto DCW adsorbent. The initial adsorption rate was very rapid from 1 min to 180 min at 0.004 mg/min. After that, the adsorption rate started to achieve equilibrium at 1,440 min. This result obtained was similar to the study by Johari et al. (2013), where the DCW adsorbent was found to achieve the equilibrium after 1 d of Hg (II) adsorption process.

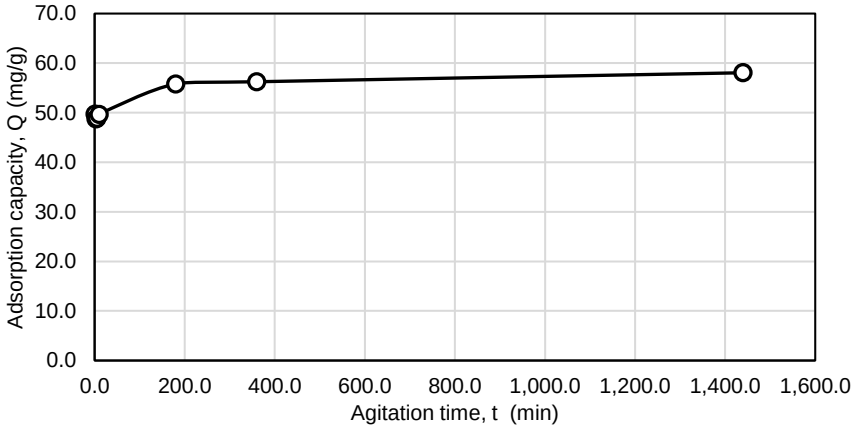

Figure 4: Effect of agitation time on adsorption of DCW (Experimental conditions: Pb (II) concentration = 50 mg/L; DCW mass = 25 mg; temperature = 30 °C; solution pH = pH 6; and agitation speed = 200 rpm)

3.5 Isotherm model fitting studies

Experimental data obtained were further analyse using several existing isotherm models such as Langmuir, Freundlich and Temkin. Table 1 showed the experimental data fit the best into Langmuir isotherm with R^2 value = 0.969 near to 1. Fitting into Langmuir isotherm indicated that the adsorption process of Pb (II) ion into DCW is a monolayer adsorption. The maximum monolayer capacity of DCW, Q_m = 55.865 mg/g. The R_L value determined whether the type of isotherm was favourable or not, where it is favourable if $0< R_L <1$,

unfavourable for $R_L > 1$, linear if $R_L = 1$ and irreversible if $R_L = 0$. Based on calculation, R_L value depicted in Table 1 lies in the range of 0 and 1 which indicates the isotherm was favourable.

3.6 Kinetic model fitting studies

In addition, experimental data obtained were also analyse using existing kinetic model which are pseudo-first order (PFO), pseudo-second order (PSO) and Elovich. Table 1 showed the data fit the best into pseudo-second order (PSO) kinetic model with R^2 value of 0.999. Besides that, another comparison that can be made was the experimental Q value from the PSO kinetic model. The calculated Q value from the model conform well with the Q value obtained from experiment in which Q_{theory} = 58.140 mg/g and Q_{exp} = 58.050 mg/g. Fitting into PSO proposed that the adsorption process of Pb (II) ion into DCW adsorbent is governed by chemical adsorption or chemisorption.

Table 1: Isotherm model and kinetic model parameters

	Model	Linearized equations	Parameter
Isotherm model	Langmuir	$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$	Q_m(mg/g) = 55.865; B (L/mg) = 0.065; R_L = 0.0779; R^2 =0.969
	Freundlich	$\ln Q_e = \ln k_f + \frac{1}{n} \ln C_e$	n=2.628; k_f (mg/g) =147.6; R^2= 0.595
	Temkin	$Q_e = B\ \ln K_T + B \ln C_e$	B (J/mol) = 10.407; k_t(L/mg) = 1.208; b_t (kJ/mol) = 238.187; R^2=0.651
Kinetic model	Pseudo-first order	$\ln(Q_e - Q_t) = \ln Q_e - k_1 t$	Q_{theory} (mg/g)= 8.430; K_1 (1/min)= 0.004; R^2=0.97
	Pseudo-second order	$\frac{t}{Q_t} = \frac{1}{k_2 {Q_e}^2} + \frac{1}{Q_e} t$	Q_{exp}(mg/g) = 58.05; Q_{theory} (mg/g) = 58.14; K_2 (mg/min) = 0.004 ; R^2=0.999
	Elovich	$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta}\ lnt$	α (mg/g.min) = 1.34 x 10^{15}; β (g/mg) = 0.735; R^2 = 0.687

3.7 Regeneration of spent DCW adsorbent

The spent DCW adsorbent was subjected to another adsorption – desorption cycle. Based on Figure 5, it was indicated that the adsorption capacity of DCW decreases from cycle 1 (58.05 mg/g) to cycle 2 (44.60 mg/g). This account for 23 % reduction of DCW adsorption capacity. The reduction is probably because of Pb (II) are not fully desorbed during the desorption process which lead to the pore still being accommodated by Pb (II) ion. As less sites were available, less Pb (II) ion were adsorbed on the next cycle of adsorption which lead to decrease in adsorption capacity in the next cycle. A similar study also reported that based on the adsorption-desorption process of DCW on Hg (II), the adsorption capacity that were obtained for several cycles were almost constant (Johari et al., 2013). This proves that DCW is a good adsorbent material and has a potential to be as a low-cost adsorbent in adsorbing heavy metal ion.

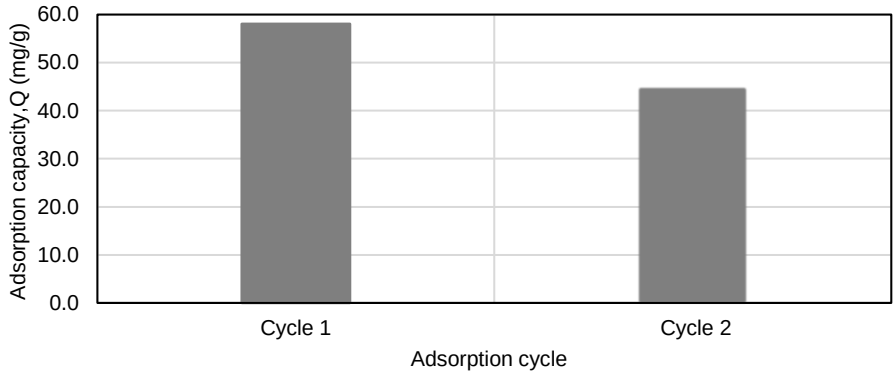

Figure 5: The Pb (II) adsorption - desorption cycle using 0.1 M HNO_3

4. Conclusion

The results obtained from the studies shows that DCW has a good potential as raw material for its application in removing Pb (II) from its aqueous phase. Characterization of adsorbent shows that DCW has sufficient affinity towards Pb (II) ion with good elemental percentage of carbon (50.18 %). The increase in initial Pb (II) concentration and increase in agitation time resulted in increase of amount of Pb (II) adsorbed. The maximum adsorption capacity of DCW was 55.86 mg/g, obtained at T = 30 °C and pH = 6. The data fitted well into Langmuir

isotherm and pseudo – second order kinetic model indicating it is a chemical adsorption process that involve monolayer adsorption. Regeneration studies concluded that it has great regenerability properties making DCW a good candidate for low-cost adsorbent.

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