

Adsorption of Pb (II) Heavy Metals from Wastewater Using Modified Rice Husk as Adsorbent

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Abstract

Pb (II) heavy metal from wastewater as by-product of industrial activity often causes problem to environment. In order to minimize the amount of Pb (II), wastewater was treated in various ways, including adsorption process using adsorbent. Rice husks that containing lignin, cellulose, and hemicellulose are one of potential candidates to be utilized as adsorbent. The purpose of this research is to modify rice husk by using sodium hydroxide and citric acid and to know adsorption capacity and adsorption efficiency of modified rice husk adsorbent on Pb (II) metal uptake from wastewater. To identify substituted groups, analysis samples by using Fourier Transform Infrared was performed and to determine adsorbed amount of Pb (II) into adsorbent an Atomic Adsorption Spectroscopy Method was conducted. The result showed that optimum adsorption capacity and adsorption efficiency was 5.08 mg/g and 84.52%, respectively. These results were obtained on 60 ppm of Pb (II) adsorbate concentration and 0.8 M citric acid concentration for 150 minutes of contact time.

Key words: Pb (II), adsorption, sodium hydroxide, citric acid, rice husk

Introduction

Wastewater from industrial activity often causes problems for the environment. Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (Gupta et al., 2001). The presence of heavy metal ions is a major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries and storage batteries industries, (Kadirvelu et al., 2001). Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption, and coprecipitation/adsorption. Studies on the treatment of effluent bearing heavy metal have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent (Sharma et al., 2011). Despite its extensive use in water and wastewater treatment industries, activated carbon remains an expensive material. Therefore, the adsorption method with an inexpensive adsorbent of agricultural solid waste could be an alternative method to reduce pollution due to cheaper and effective adsorbents (Grassi et al., 2012).

Rice husk has a wide range of pore size that plays a very important role in the process of adsorption. With proper activation process, pores size can be enlarged and adapted to the size of molecules of liquid waste of heavy metal so that adsorbate can be absorbed easily into pore of adsorbent. So far, some researchers have used other biomaterials to absorb heavy metals including coffee waste (Rossner et al., 2009), paddy straw (Kumar et al.,

2006), tea waste (Amarasinghe et al., 2007) and other adsorbents (Bhattacharya et al., 2008). A low-cost adsorbent such as rice husks can be chemically activated with an oxidator to increase the adsorption capacity of heavy metals. Adsorption capacity can be increased through interaction with the metal oxidator in solution (Marshall et al., 1999, 2000, 2001). The processing of solid waste material with some acids such as citric acid, tartaric acid and phosphoric acid at a rather high temperature can increase the adsorption of heavy metal ions (Marshall et al., 1999, 2000, 2001). With this activation, some acid groups can occur and form ester groups (Marshall et al., 2001).

Chemical activation of rice husk with citric acid can enhance the adsorption capacity of heavy metals liquid waste. The process can increase the amount of carbonyl group and enlarge the surface area of the adsorbent, and create more negative groups on the surface of rice husk. In addition to further increase the ion exchange capacity, in this research previous established method was modified slightly by adding sodium hydroxide as a co-activator before activation by main activator of citric acid. This research aims is to study the ability of modified rice husks to adsorb lead (II) metal ions toward adsorption capacity and adsorption efficiency by varying the initial concentration of adsorbate and the effect of activation with citric acid.

Materials and Methods

Equipment and Materials

The equipments and tools used in this study were hot plate, glassware, oven dryer, ball mill, desiccator, digital scales, Atomic Absorption Spectrometry (AAS) type AA 6300 (Shimadzu), FTIR IR Prestige 21 (Shimadzu) and sieve shaker. On the other hand materials used were rice husks with particle size of 18-35 mesh, sodium hydroxide, citric acid, a solution of $Pb(NO_3)_2$ and distilled water.

Research Procedure

First, rice husk washed several times with distilled water to remove dust and dirt. Then, rice husks was soaked in hot water for 1 hr, then dried under sun for 4 hours and later dried again in oven dryer at 120 °C for 1 hour. Dried results were then milled using a ball mill and sieved on the size of 18-35 mesh. Finally, rice husks were dried again at 120 °C for 3 hours and then stored in a desiccator. A few grams of rice husk were dissolved into a solution of NaOH 0.5 M. This was done to remove the silicates in rice husks that later allowing adsorption processes run better. During activation process, NaOH will enter into the cellulose structure and reacts with silicate contained in rice husk to form sodium silicate. The addition of NaOH during activation will form a few new sites on the surface of the adsorbent so that will increase adsorption capacity. The mixture of rice husk and NaOH is then stirred at 80 rpm for 60 min at room temperature. The mixed NaOH and rice husk then washed by distilled water repeatedly until a pH of ± 7 . Then dried at 50 °C for 2 hours.

1 gram of netralized rice husk then was mixed with 100 ml of 0.5 M citric acid for 2 hours at 80 rpm, then dried for 3 hours at 50 °C. The same procedure was repeated for others concentration of citric acid. Modified rice husks was then washed with distilled water to remove the excess of citric acid until a pH of ± 7 , followed by re-drying at 50 °C for 24 hours (Marshall et al., 2000). 1 gr of activated rice husks was mixed with 100 ml of $Pb(NO_3)_2$ 20 ppm at speed of 80 rpm for different time (0 to 150 minutes) at room temperature. After the adsorption process was completed, sample solution was taken to be analyzed by AAS. The above treatment was repeated for concentrations of 40, 60, and 80 ppm.

Testing of lead content in the sample is in accordance with SNI 06-2517-1991. It was performed at a wavelength of 283.3 nm. FTIR analysis of samples before and after modification was performed at infrared wavelength range of 400 to 4000 cm^{-1} . KBr was

used as the background in analysis of powder samples. A total of 5% by weight of the sample was homogenized with 95% of KBr.

Results and Discussion

Determination of Equilibrium Adsorption Time Pb (II) on the Preliminary Test

In order to know the effect of equilibrium time on adsorption of lead ion that was adsorbed by activated rice husks, preliminary tests were conducted by varying contact time. Figure 1 shows that the optimum contact time was at 150 minutes with adsorption capacity of 5.15 mg/g. After contact time of 150 minutes, adsorption capacity did not increase significantly like below of 150 minutes. This condition indicates that the adsorption capacity has been reached the equilibrium point. The longer contact time, the more adsorbed metal ions Pb (II) that will increase until reach equilibrium phase. The same result was also found by Makinde et al., (2007). In our research, with increase of contact time between adsorbent and adsorbate causes the pore inside adsorbent is filled with more adsorbate, so the more difficult for other remain adsorbates to find free space available inside. This led to the quantity of adsorbate that was adsorbed by the adsorbent will increase relatively low or even become static at equilibrium phase as observed at Figure 1 below.

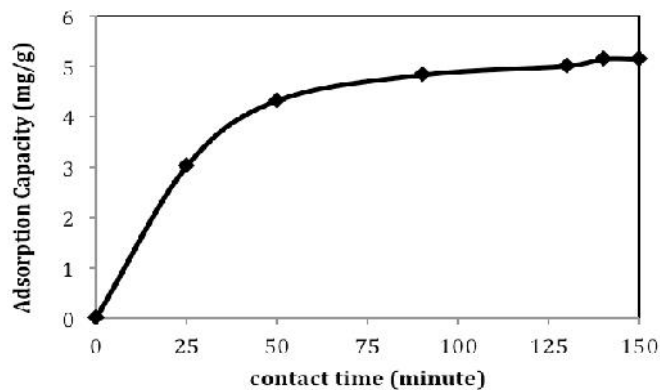


Figure 1. The relationship between contact time and adsorption capacity on lead concentrations of 80 mg/L using adsorbent after activation with concentrations of 0.8 M citric acid

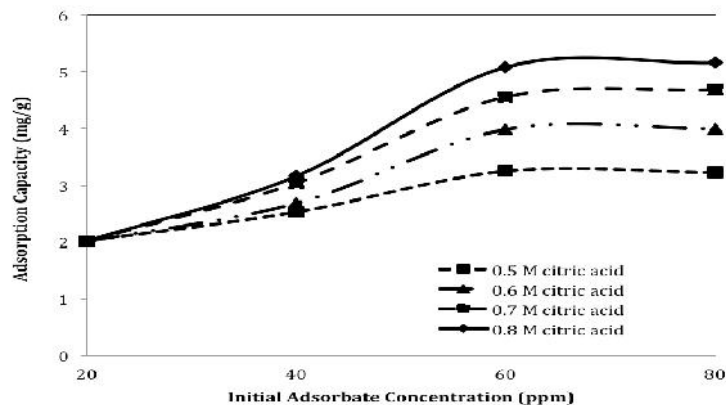


Figure 2. Effect initial concentration of Pb (II) adsorbate and concentration of citric acid on adsorption capacity

Effect of Initial Concentration of Adsorbate against Absorption Capacity

From Figure 2 it can be seen that at a concentration of 0.8 M citric acid, adsorption capacity reach a significant increase of adsorbate concentration of 40 mg/L to 60 mg/L. It was also observed that the optimum of initial adsorbate concentration is 60 mg/L in which provide

the highest adsorption capacity. For adsorption efficiency, similar behaviour was also observed. The lowest adsorption efficiency was observed at 0.5 M citric acid concentration and the largest adsorption efficiency of 84.52% was found at 0.8 M citric acid concentration and at adsorbate concentration of Pb (II) 60 mg/L.

Effect of Citric Acid Concentration on Adsorption Capacity

From Figure 3 it can be seen that at respective concentrations of Pb (II) an increase of adsorption capacity increase slightly for each concentration of citric acid. The lowest adsorption capacity was obtained at 0.5 M citric acid concentration and the highest adsorption capacity was obtained at 0.8 M citric acid concentration. Similar to adsorption capacity, the increase of citric acid concentration also affected the adsorption efficiency of activated rice husk. The highest capacity efficiency was observed when rice husk was activated with 0.8 M citric acid concentration at initial concentration of Pb (II) 60 mg/L. However, when adsorbent was activated with others citric acid concentration, adsorption capacity also increased but not significantly.

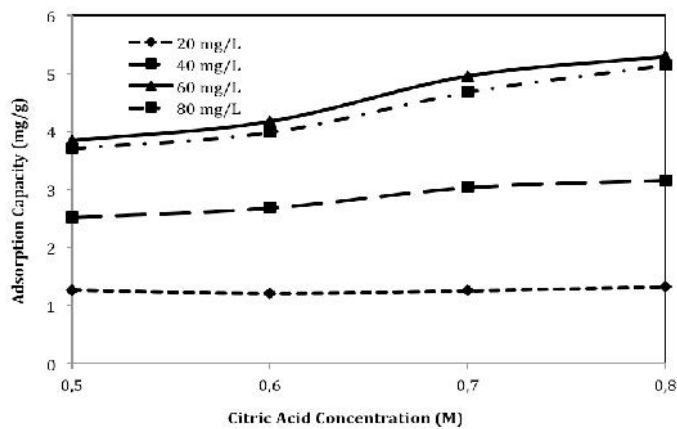


Figure 3. The effect of citric acid concentration (M) and adsorbate concentration toward adsorption capacity (mg/g) at contact time of 150 minutes

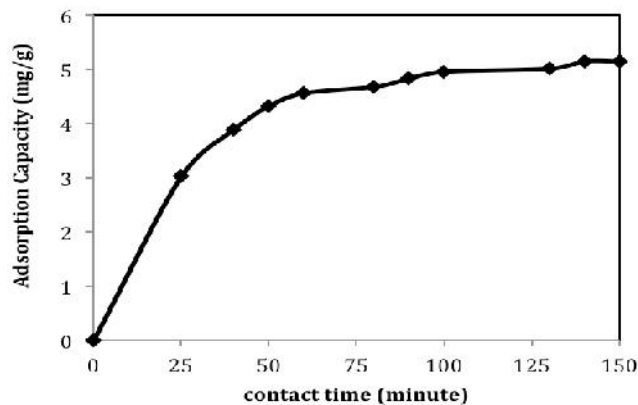


Figure 4. The effect of contact time (minutes) on the adsorption capacity (mg/g) at a concentration of Pb (II) 60 mg/L and 0.8 M citric acid concentration

Relationships of Contact Time on Optimum Conditions toward Adsorption Capacity

In order to study the effect of contact time on adsorption capacity, we conducted research at optimum of adsorbate concentration (60 mg/L) and citric acid concentration (0.8 M). The result showed that the length of contact time affected the adsorption capacity in which the

longer of contact time then the Pb^{2+} ions that adsorbed by activated rice husk will also increase. Figure 4 explains that contact time was inversely exponential with adsorption capacity. Based on Figure 4, it can be seen that the largest adsorption capacity was obtained after adsorption process was conducted for 140 and 150 minutes. However, the different adsorption capacity was small after adsorption took around 130 until 140 minutes, this is because the adsorption capacity tend to be saturated with longer time of 140 minutes to 150 minutes.

Effect of Citric Acid Addition on Functional Group of Adsorbent

The effect of citric acid addition on modification of rice husks especially functional group can be determined by using Fourier Transform Infrared (FTIR). Graph of infrared spectra are shown in Figure 5. It was observed that the adsorbent has a hydroxyl bond as observed by changing of wavelength absorption at 3244 cm^{-1} . Carbonyl group is present due to the influence of citric acid activation. On activation of adsorbent with 0.5 M citric acid concentration, carboxyl groups have been present in wavelength absorption of 1087 cm^{-1} which indicate a CO group, and in 1718 cm^{-1} that indicates the group of $C = O$. This also applies to the activation of citric acid concentration of 0.6, 0.7 and 0.8 M, where there appeared the greatest absorption, namely at activation by using 0.8 M citric acid concentration. At citric acid concentration of 0.5 M it was observed that carboxyl group spectra has a small (narrow) catchment area (peak), along with increasing concentrations of citric acid it seem that the peak area became wider. It can be seen from Figure 5 that after activation with 0.8 M citric acid concentrations, the absorption area was much wider, This is indicates that a growing number of carbonyl groups was formed with the increasing concentration of citric acid.

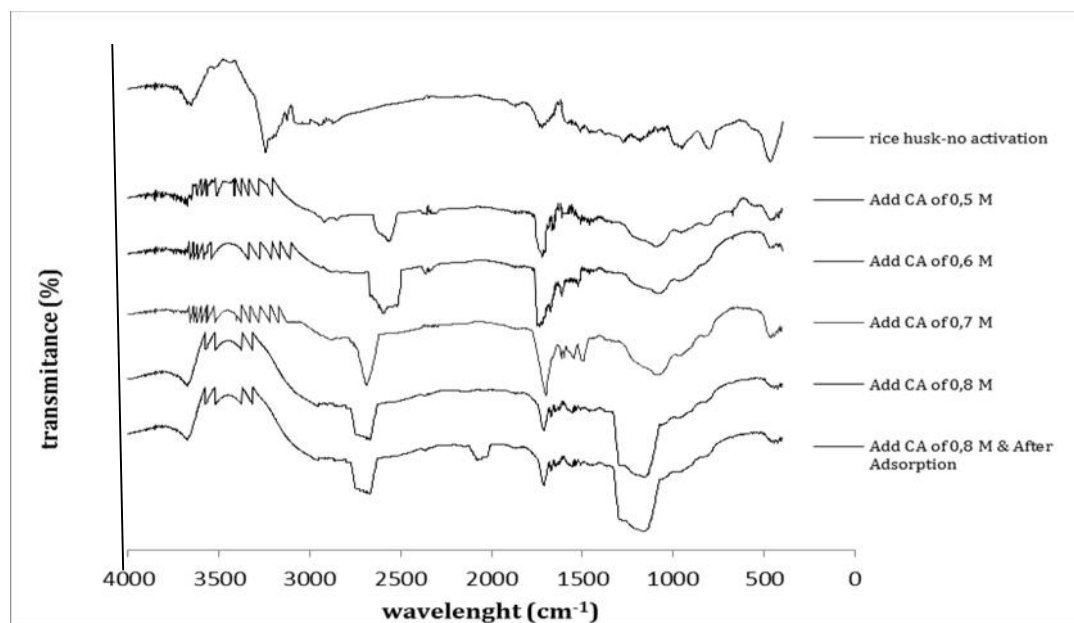


Figure 5. The wavelength of infrared spectra on activated adsorbent (CA = citric acid)

At a wavelength of 2567 cm^{-1} , there was an absorption spectra that refers to OH group of carboxylic acids, namely after activation with 0.5 M citric acid concentration. This OH group of was due to the effect of activation by citric acid. On activation of citric acid from concentration of 0.5 M to 0.8 M, it was observed that a shift in absorption spectra from right to left (to larger wavelength), that is also influenced by the concentration of citric acid. Therefore, it can be concluded that the addition of citric acid as activator to modify rice husk give an effect to the adsorbent that is by substituting a carbonyl group on the hydroxyl group.

Conclusions

In this study we found that the adsorption process of lead (II) metal ions onto activated rice husks reached the highest adsorption capacity and adsorption efficiency by 5.08 mg/g and 84.52%, respectively. These adsorption processes were performed at initial lead (II) concentration of 60 mg/L and 0.8 M citric acid concentration with contact time of 150 minutes. The adsorption process was influenced significantly by addition of citric acid as main activator and the addition of small amount of sodium hydroxide in the preliminary treatment as co-activator. With the increase of citric acid concentration, the adsorption capacity would also increase significantly. The present of carboxyl group was due to the influence of citric acid activation. On activation of the adsorbent with a only small concentration of citric acid provided an appear of carboxyl groups in the absorption wavelength spectra of 1087 cm^{-1} which indicate a CO group and at 1718 cm^{-1} indicates the group C = O.

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