A preliminary study for removal of heavy metals from acidic synthetic wastewater by using pressmud-rice husk mixtures

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Abstract. The study was carried out to evaluate the effect of combining pressmud and rice husk in the removal efficiencies of heavy metals in acidic synthetic wastewater. The ratios of pressmud to rice husk were varied at different percentages of weight ratio (0%, 20%, 40%, 60% 80% and 100%) and removal of heavy metals concentrations was observed. The result showed that the removal efficiency was increased with the addition of pressmud by up to almost 100%. Pressmud alone was able to remove 95% to 100% of heavy metals while rice husk alone managed to remove only 10% to 20% of heavy metals. The study also demonstrated that pressmud behaved as a natural acid neutralizer. Hence, the initial pH of the synthetically prepared acidic wastewater which was below 2 also was increased to pH ranging from 6 to 8.

1. Introduction

Industrial wastewater with a low pH is considered as an acidic wastewater, a common problem for many industries. Increasingly stringent environmental regulations require that pH, among other contaminants, be controlled to certain levels before they are discharged into a natural body of water or municipal sewer system. Other than that, the existence of contaminated-industrial wastewater with hazardous heavy metals such as Cd, Cr, Cu, Ni, As, Pb and Zn is also a big concern among the chemical-intensive industries.

Heavy metals are easily adsorbed by living organisms because of their high solubility in the aquatic environment. Once they enter the food chain, the consumption of large concentrations of heavy metals may start to accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders (Barakat, 2010). Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment as it will constitute a great risk for the aquatic ecosystem, while the direct discharge into the sewerage system may have a negative effect affecting the subsequent biological wastewater treatment (Balintova et al., 2012).

Generally, the removal of heavy metals from aqueous solutions has commonly been carried out through several processes: chemical precipitation, solvent extraction, ion exchange, reverse osmosis or adsorption. Among these processes, adsorption is considered to be the most facile and effective...
method (Wang et al., 2014). Adsorption with a suitable adsorbent can be a simple but effective technique for removing heavy metals from wastewater.

Pressmud is actually compressed waste produced from the filtration of sugarcane juice before crystallization process of sugar. It is usually disposed or sold as immature compost to farmers. Furthermore, pressmud is a source of nutrients for soil and can improve the ability of the soil to hold the water holding capacity. It is a good source of biogas since it contains approximately 5–15% of sugar (Gupta et al., 2010). There is also a study to investigate the potential use of 0.5M H$_2$SO$_4$ treated pressmud as cyanide ion sorbent from aqueous solution (Gupta et al., 2012). The potential of pressmud as chelating agent has been studied to be used to reduce the leachability of heavy metals in landfill leachate by mixing with laterite soil (Maheera et al., 2013).

One of the most widely available agricultural waste in Malaysia is rice husk. Rice husk is the agricultural crop residue generated during dehusking process at rice mills. Numerous applications have been proposed for rice husk utilization from which silica production and energy generation are among the most scrutinized (Bazargan et al., 2015). Unmodified rice husk has been reported for their ability to bind metal ions (Kumar & Bandyopadhyay, 2005). The use of rice husk provides a less costly adsorbent than activated carbon as it is cheap and easily available.

This research is a preliminary study to investigate the potential conversion of waste materials that are produced in large quantity into low-cost adsorbent for the removal of several types of heavy metals such as chromium, iron, manganese, nickel, lead and zinc from acidic synthetic wastewater. This research highlights the ‘reuse’ of the 3R Concept where the elements of the discarded item are used again. The used of rice husk and pressmud, where the pressmud is the compressed sugar industry waste while rice husk is the by-product from rice industry which does not have substantial commercial value can solve the disposal problem of rice husk and pressmud. Both materials have caused environmental problems concerning their disposal. Besides that, the mixture of rice husk-pressmud can remove heavy metals from the wastewater preventing them from entering water stream.

2. Materials and Methods

2.1 Preparation of pressmud
Pressmud was collected from a sugar mill, Malaysian Sugar Manufacturing (MSM) Sdn. Bhd, Seberang Perai, Penang. The pressmud was air-dried at a shady place outdoor for one week. Then, it was sieved through 500μm sieve to remove large and coarse pebbles. The pressmud was later dried in the oven at 60ºC for 24 hours to remove moisture until the weight is constant and stored in air-tied bottle.

2.2 Preparation of rice husk
Raw rice husk was obtained from a local rice mill, Leong Guan Sdn. Bhd, Kepala Batas, Penang. The rice husk was washed and soaked in distilled water for 3 days. It was washed with distilled water until it was odorless. The washing process was continued until the water was colorless, air-dried at room temperature and then dried in the oven at 105ºC for 24 hours to remove moisture until the weight was constant (Lim et al., 2010). The dried rice husk was grounded and sieved to desired particle sizes in the range of 125 - 250μm (Nhapi, I., et al., 2011) and then stored in air-tied bottles.

2.3 Preparation of acidic synthetic wastewater
Metal solutions (chromium, iron, lead, manganese, nickel and zinc) of 1000mg/L in nitric acid from Fisher Scientific, UK were purchased. Each metal solution was diluted with deionized water to obtain similar initial concentrations of acidic synthetic wastewater containing each type of heavy metal at below 10mg/L and later confirmed with ICP Optical Emission Spectrometer Model Varian 715-ES. The pH of the synthetic wastewater was measured using HACH sensION+ PH3 pH meter before and after the experiment.
2.4 Initial Concentration of Heavy Metals in Acidic Synthetic Wastewater
Several heavy metals were chosen in this study. These heavy metals were usually encountered in leachates from landfills. In this study, the initial concentrations of heavy metals for Cr, Fe, Mn, Ni, Pb and Zn with their concentrations were 2.07 mg/L, 2.28 mg/L, 2.13 mg/L, 2.18 mg/L, 2.12 mg/L and 2.17 mg/L respectively determined by using ICP-OES.

2.5 Initial pH of Acidic Synthetic Wastewater
The synthetic wastewater was prepared with metal solutions of 1000mg/L in nitric acid from Fisher Scientific resulting the prepared synthetic wastewater to be acidic. The initial pH values of the acidic synthetic wastewater were low at between 1.04 and 1.45. The higher the initial concentration of heavy metals, the lower the pH value of the synthetic wastewater. The process of heavy metals removal seemed to occur in acidic condition.

2.6 Batch equilibrium test
A 5±0.02 g adsorbent of pressmud-rice husk mixture at different ratio was weighed and poured into 250mL conical flasks respectively. The adsorbent was designated as 1) pressmud alone (RH 0); 2) pressmud 80% while rice husk 20% (RH 20); 3) pressmud 60% while rice husk 40% (RH 40); 4) pressmud 40% while rice husk 60% (RH 60); 5) pressmud 20% while rice husk 80% (RH 80) and 6) rice husk alone (RH 100). The adsorbent were equilibrated with 100 ml of the prepared acidic synthetic wastewater containing heavy metals (Cr, Fe, Mn, Ni, Pb and Zn) in 250mL conical flasks. The conical flasks were agitated using horizontal shaker at a speed of 180 rpm for 24 hours at room temperature (Annadurai et al., 2002; Gupta et al., 2012).

After reaching the equilibrium, the sorbent-solution was centrifuged at 4000 rpm for 20 minutes to separate the liquid and solid form. The supernatant was filtered with No.601 Whatman filter paper and collected in small plastic bottles. The samples were preserved to a pH < 2 with ultrapure HNO₃ according to U.S. EPA Method 200.7 (USEPA, 1994). The samples were stored at 4°C in refrigerator before analyzed by ICP-OES Model Varian 715-ES. The concentration of heavy metals left in the solution was used to calculate the amounts of heavy metals absorbed by the pressmud-rice husk mixtures.

The percentage removal of heavy metals from the initial solution concentration Cₒ, was calculated from the following equation.

\[
\text{Percentage removal} = \frac{(C_o - C_e)}{C_o} \times 100
\]

where \( C_o \) = initial concentration of heavy metals in the solution (mg/L)
\( C_e \) = concentration of heavy metals left in the solution (mg/L)

3. Results and Discussion

3.1 pH Measurement of Rice husk-pressmud Mixtures

| Table 1. pH of rice husk-pressmud mixtures |
|------------------------------------------------|
| Rice husk-pressmud composition | pH | 125-250µm |
|----------------------------------|----|-----------|
| RH 100                          | 6.40 |          |
| RH 80                           | 7.29 |          |
| RH 60                           | 7.41 |          |
| RH 40                           | 7.85 |          |
| RH 20                           | 8.21 |          |
| RH 0                            | 8.04 |          |
pH of the rice husk, pressmud and rice husk-pressmud mixtures was measured with pH meter to determine the original pH of the adsorbent. Table 1 showed the pH of rice husk-pressmud mixture. From the result, the pH value of pure pressmud (RH0) was approximately 8.04. Pressmud was a bit alkaline. Unmodified but washed rice husk (RH 100) was a bit acidic which showed pH value of 6.40. As the composition of pressmud increased in the mixtures, the pH of the mixtures also increased but was limited to around pH 8.

3.2 Final pH Measurement of Acidic Synthetic Wastewater
After the batch equilibrium test, the pH value of the acidic synthetic wastewater was measured again. The pH value of acidic synthetic wastewater added with pressmud increased and became neutral. The acidic synthetic wastewater added with 80% pressmud (RH20), 60% pressmud (RH 40), 40% pressmud (RH 60) and 20% pressmud (RH 80) also become neutral with the pH ranged between 7.29 - 7.85. The synthetic water added with only rice husk remained acidic as pH of the solution did not change. These showed that pressmud can act as buffer to neutralize acidic synthetic wastewater as pressmud had high bicarbonate content about 1069mg/L (Maheera et al., 2013).

3.3 Removal of Heavy Metals
The removal efficiency of six heavy metals namely Cr, Cu, Mn, Ni, Pb and Zn were determined with the initial concentrations of acidic synthetic wastewater which were 2.07mg/L, 2.28mg/L, 2.13mg/L, 2.18mg/L, 2.12mg/L and 2.17mg/L to stimulate trace amount of heavy metals with pH value in the range of 1.04 to 1.45 respectively. The removal efficiencies of Cr, Cu, Mn, Ni, Pb and Zn are illustrated in Figure 1-6 as shown below.

3.3.1 Removal of Cr
Figure 1 showed that the removal efficiency of rice husk and pressmud alone was between 33.0-39.2%. The removal efficiency of Cr for mixtures of pressmud and rice husk had increased till 44.2-71.8%. Figure 1 clearly showed that rice husk alone could remove less than 40% of chromium at low concentration.

According to analysis of variance (ANOVA), composition of pressmud and rice husk in the mixtures had significant impacts on the removal efficiency of Cr (p < 0.05). Pressmud alone had removal efficiency between 30-50%. The combination of pressmud with rice husk clearly improved the removal efficiency of Cr. Pressmud became sticky when it was wet (Maheera et al., 2013). When pressmud was mixed with rice husk, the sticky mixture acted as a pore opener to adsorb Cr. The mixture of rice husk-pressmud had higher removal efficiency than unmodified rice husk and pressmud. The highest removal efficiency achieved at RH 80 which was approximately 72%. Generally, the removal rate of Cr increased from RH 0 to RH 80 proved that higher composition of rice husk was more effective to remove Cr. Rice husk alone, RH 100, showed the lowest removal efficiency because rice husk could not perform well under unfavorable condition as the pH of acidic synthetic wastewater was low at the range of 1.04-1.45. The optimum pH for the adsorption of Cr by rice husk ash was at pH 4 (Anand et al., 2014) while rice husk activated carbon was at pH 2 (Ahmed et al., 2012). When there was no pressmud at RH 100 or only little pressmud at RH 80 to act as buffer, the removal efficiency was low.
Figure 1. Removal efficiency of Cr by different composition of rice husk-pressmud

3.3.2 Removal of Fe
The removal efficiency of Fe was determined with an initial concentration of acidic synthetic wastewater at 2.28mg/L to stimulate a trace amount of Fe with pH value in the range of 1.04 to 1.45 respectively. The removal efficiency of Fe was illustrated in Figure 2 as shown below. According to Figure 2, pressmud alone and pressmud-rice husk mixture could remove 100% of Fe from RH 0 till RH 80, while the removal efficiency dropped at RH 100. Due to the acidic condition, sorption process of rice husk was interrupted since there was no pressmud in RH 100 to neutralize the excessive H⁻ or H₃O⁺ ions in the acidic synthetic wastewater. There was significant correlation between composition ratio of pressmud-rice husk and the removal efficiency since p < 0.05 based on ANOVA.

Figure 2. Removal efficiency of Fe by different composition of rice husk-pressmud

3.3.3 Removal of Mn
The removal efficiency of Mn was determined with an initial concentration of acidic synthetic wastewater at 2.13mg/L. The removal efficiency of Mn was illustrated in Figure 3. Figure 3 showed that as rice husk ratio was increased, the removal efficiency of Mn decreased. Rice husk alone (RH100) showed the lowest removal efficiency as it was not able to absorb Mn under acidic condition where the pH solution was at 1.04. Composition ratio of pressmud-rice husk had a significant effect on Mn removal since p < 0.05 according to ANOVA. For the removal of Mn, pressmud alone seemed to have the highest removal efficiency. Addition of rice husk to pressmud did not improve removal efficiency of Mn. Pressmud alone already removed more Mn than unmodified rice husk.
3.3.4 Removal of Ni
The removal efficiency of Ni was determined with three samples at initial concentrations of synthetic wastewater of 2.18mg/L. The removal efficiency of Ni was illustrated in Figure 4 as shown below. Based on Figure 4, the removal efficiency of RH 0, RH 20 and RH 40 were between 69.12-73.73% respectively. The removal trend decreased from RH 60 to RH 100. Thus, Figure 4 showed the pressmud-rice husk mixtures were more effective than pure rice husk and pure pressmud. Combination of pressmud and rice husk increased the performance in removing Ni. Composition ratio of pressmud-rice husk had no significant effect on Ni removal since p > 0.05 based on ANOVA. These might be due to the property of pressmud to allow Ni ions to adhere on it and also the ability of pressmud to act as a buffer for the acidic synthetic wastewater so that rice husk could perform well for the adsorption of Ni.

3.3.5 Removal of Pb
The removal efficiency of Pb was determined with three samples at initial concentrations of synthetic wastewater of 2.12mg/L. The removal efficiency of Pb was illustrated in Figure 5. The figure showed the similar removal efficiency trend from RH 0 to RH 80 except for RH 100. Figure 5 also showed that pressmud alone and pressmud-rice husk mixtures were very effective to remove trace amount of Pb from aqueous solution. The removal efficiency was between 99-100%. Pressmud alone was a good sorbent for Pb. After the addition of pressmud to rice husk, the removal efficiency was not much
affected and remained high as rice husk alone had been reported as a good adsorbent for Pb ions (Lata & Samadder, 2014).

RH 100, pure rice husk had very low efficiency in Pb removal which was only 27.75% as acidic condition is not suitable for sorption of Pb. According to Wong et al. (2003), the uptake of Pb by tartaric acid of modified rice husk increased when the pH increased from 2 to 3. Since the prepared acidic synthetic wastewater was around pH 2, the removal efficiency of Pb was very low with the absence of pressmud or insufficient amount of pressmud to act as buffer. This was because at low pH, the surface of the sorbent was surrounded by hydronium ions which prevented the metal ions from approaching the binding sites on the sorbent (Wong et al., 2003). Based on ANOVA, there was significant correlation between composition ratio of pressmud-rice husk and the Pb removal since p < 0.05.

![Figure 5. Removal efficiency of Pb by different composition of rice husk-pressmud](image)

3.3.6 Removal of Zn

The removal efficiency of Zn was illustrated in Figure 6 as shown below. It was clearly shown in Figure 6 that pressmud alone and pressmud-rice husk mixtures removed 100% of Zn, while rice husk alone had only removed 4.15% of Zn from the acidic synthetic wastewater. Pressmud alone was a good adsorbent in eliminating the trace amount of Zn. Based on ANOVA, composition ratio of pressmud-rice husk had significant effect on the Zn removal since p < 0.05.

![Figure 6. Removal efficiency of Zn by different composition of rice husk-pressmud](image)
4. Conclusion
Pressmud alone had high removal efficiency of up to 90% to remove trace amount of iron, lead and zinc. Rice husk alone had very low efficiency in the removal of heavy metals due to the acidic condition of the acidic synthetic wastewater. By mixing pressmud with rice husk, the removal trend of iron, lead and zinc did not have much difference. However, when pressmud was mixed with rice husk, the removal efficiency of chromium and nickel increased since it acted as a buffer in the acidic synthetic wastewater due to its high bicarbonate content to enhance the sorption of metal ions to the sorbent. There was a decrease in the removal efficiency of manganese as pressmud was added to the rice husk. But, rice husk alone (RH 100) consistently showed low efficiency for removing all of heavy metals as it could not perform well in acidic condition. The composition of rice husk and pressmud mixtures greatly affected the removal efficiency of heavy metals as it improved the chemical characteristics of the mixture in reducing the heavy metals in the solution and also increased the initial pH of synthetically prepared acidic wastewater from below 2 to as high as 8.

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