



Adsorptive Removal of Mercury by Zeolites And Montmorillonite

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Article Info:

Received: 05 - 07 - 2018

Accepted: 07 - 01 - 2019

Keywords:

Mercury, adsorption, zeolite, clay, thiourea

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Abstract: *The environmental pollution by the drainage containing heavy metals such as Hg is a serious problem in mining activities in Indonesia. We examined the effect of coexisting thiourea on the adsorptive removal of Hg by zeolites and montmorillonite. To a 100 mL of 10 mg/L (0.05 mM) HgCl₂ solution in the absence and presence of 0.5 mM thiourea, different amounts of zeolite (A4, P or mordenite) or montmorillonite was added, shaken for 24 h, centrifuged, and supernatant Hg²⁺ concentration was measured. In the absence of thiourea, the ratio of the negative charges in the adsorbents to the positive charges in Hg²⁺, Ads/Hg ratio, needed to attain >80% Hg²⁺ removal were >70 for mordenite, >1625 for P, >600 for A4, and montmorillonite showed no Hg²⁺ adsorption. In contrast, in the presence of thiourea, nearly 100% removal was attained at lower Ads/Hg ratios: the ratios were 1 for montmorillonite, <10 for P and <18 for A4; the presence of thiourea had little effect for mordenite. These results indicate that Hg²⁺-thiourea complex has extremely high adsorption affinity for negative charges of montmorillonite, A4 and P, and the complex can fully penetrate into the interlayer space of montmorillonite. However, with increasing the Ads/Hg ratio, the Hg²⁺ removal percentage for montmorillonite, A4 and P decreased. Therefore, for the effective removal of Hg²⁺ in the presence of thiourea, the choice of adsorbents and the dose of the adsorbents should be carefully determined.*

How to cite (CSE Style 8th Edition):

Abdillah AM, Abidin Z, Widiatmaka, Johan E, Matsue N. 2019. Adsorptive removal of mercury by zeolites and montmorillonite. JPSL 9(3): 797-801. <http://dx.doi.org/10.29244/jpsl.9.3.797-801>.

INTRODUCTION

In Indonesia, the drainage generated from mining areas sometimes contains heavy metals such as Cd, Co, Pb, Cr and Hg. Heavy metal accumulation in soils is of concern in agricultural production due to the adverse effects on food safety and marketability, crop growth, and the activity of soil organisms (Nagajyoti et al. 2010; Simbolon et al. 2014). For example, in Hg mining districts in Indonesia, soils become heavily polluted by Hg due to the extensive nature of mining and refining activities, and environmental contamination caused by Hg is also a serious worldwide problem (Wang et al. 2012 ; Paundanan et al. 2015).

The most commonly used techniques for removing heavy metals from aqueous solutions include adsorption by such as clays, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials (Kurniawan et al. 2006). Many studies on the adsorption of heavy metals on various materials have been conducted by many researchers around the world with an aim of finding the most effective and cheap

ways of removing heavy metals from the environment. Clays and zeolites are effective adsorbents for toxic metal cations. For example, zeolites like mordenite and clinoptilolite have high selectivity for Cs^+ in aqueous solutions (Johan et al. 2015), and high cation exchange capacities of clays and zeolites make them a suitable candidate for removing heavy metals (Tripathi et al. 2015). In view of cost, many types of natural and cheap clays and zeolites are found in Indonesia (Ministry of Energy and Mineral Resources of the Republic of Indonesia 2015). Recent market price of natural montmorillonite is found to be 20 times lower as compared to activated carbons.

In this study, our targeted heavy metal species was Hg, because most commonly found heavy metal species in Indonesian mining drainage is Hg. As adsorbents, we used zeolites and montmorillonite having high cation exchange capacities, because Hg usually exists as Hg^{2+} in aqueous solutions. However, the adsorptivity of Hg^{2+} onto clays and zeolites is not so high when compared to that of other heavy metal cations. For example, the selectivity of the series of heavy metal cations by zeolites was determined as follows: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Hg}^{2+}$ (Babel and Kurniawan 2003).

On one hand, the adsorptivity of Ag^+ onto montmorillonite is reported to increase in the presence of thiourea (Pleysier and Juo, 1980), and chemical properties of Ag^+ and Hg^{2+} are known to be similar each other. Therefore, objectives of this study were to investigate the adsorption behavior of Hg^{2+} onto zeolites and montmorillonite, and to examine the effect of the coexistent thiourea on the adsorption behavior of Hg^{2+} .

MATERIALS AND METHODS

Natural mordenite was purchased from Nitto Hunka, co. jp, and synthetic Linde type A zeolite (A4) from Wako Pure Chemicals, co. jp. Na-P1 type zeolite (P) was synthesized in this study from a coal fly ash by mixing 10 g of the coal fly ash with 80 mL of 2 M NaOH, followed by heating at 100°C for 24 h. Montmorillonite was obtained from The Clay Science Society of Japan. The samples were repeatedly washed with 1 M NaCl, washed with water, air-dried, and used. All of the chemical reagents used were purchased from Nacalai co. jp.

Different amounts of the sample was each added to a 100 mL of 10 mg/L (0.05 mM) HgCl_2 solution in the absence or presence of thiourea, and shaken for 24 h. After centrifugation, Hg^{2+} concentration in the supernatant was determined by an atomic absorption spectrophotometer (Hitachi Z-5000) and pH of the supernatant was measured. When thiourea was added, the concentration of thiourea in the Hg^{2+} solution was 0.5 mM to give a thiourea/Hg molar ratio of 10.

RESULTS AND DISCUSSION

Initial pH of the HgCl_2 solution was 4.0 in the absence of thiourea and 5.35 in the presence of thiourea, and final pH in the Hg^{2+} adsorption experiments ranged from 5.54 to 10.59. The observed increase in pH is due to the desorption of a small amounts of Na^+ from the zeolites and montmorillonite and subsequent adsorption of H^+ to zeolites and montmorillonite. Our preliminary experiments confirmed that the concentration of Hg^{2+} in the solutions used in this study did not change up to pH of 10.75, which indicated no precipitation of Hg^{2+} occurred in the solution phase at the pH range in the Hg^{2+} adsorption experiments.

The Hg^{2+} adsorption percentages as a function of Ads/Hg ratio for A4, P, mordenite and montmorillonite are shown in Fig. 1. Cation exchange capacity was 6.0 mmol/g for A4, 3.3 mmol/g for P, 2.7 mmol/g for mordenite, and 1.2 mmol/g for montmorillonite. Therefore, for example, when 0.1 g of the sample was added in the adsorption experiments, the Ads/Hg ratio was 60 for A4, 33 for P, 27 for mordenite, and 12 for montmorillonite.

Fig. 1 shows that with increasing the Ads/Hg ratio, the Hg²⁺ adsorption percentage increased for the three zeolites, and montmorillonite did not adsorb Hg²⁺ at all; within the three zeolites, mordenite showed the highest Hg²⁺ adsorptivity. However, even for mordenite, the Ads/Hg ratio of more than 80 (dose of 0.3 g/100 mL) was needed to remove more than 80% of Hg²⁺; the ratio was more than 1625 (5.0 g) for P, and more than 600 (1.0 g) for A4.

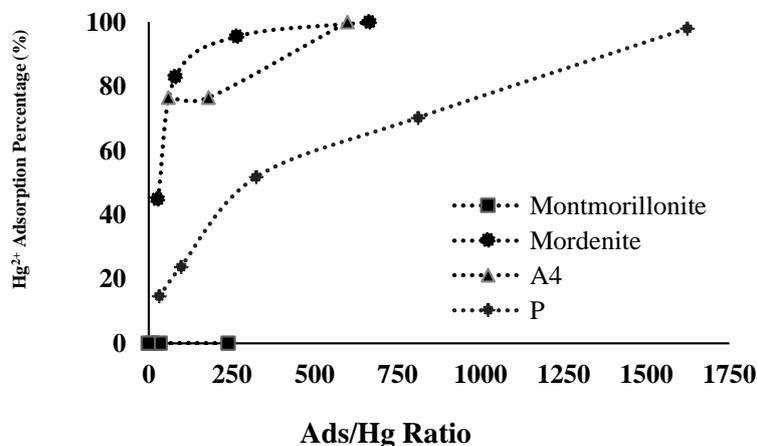


Figure 1. Hg²⁺ adsorption percentage for A4, P, mordenite and montmorillonite as a function of Ads/Hg ratio in the absence of thiourea.

The values of the dose of the adsorbents are, however, too high for the purpose of environmental decontamination, and similar high adsorbents doses are reported such as in the adsorption of 10 mg/L Hg²⁺ with dose of 100g/L of A4 (Attari et al. 2017). These high doses of the adsorbents needed to adsorb Hg are consistent with the results of low Hg²⁺ adsorptivity onto zeolites previously mentioned (Babel and Kurniawan, 2003).

Then, to increase the adsorption selectivity of Hg²⁺ toward zeolites and montmorillonite, we added thiourea to the Hg²⁺ solution in the adsorption experiments. Because the adsorption selectivity of Ag⁺ onto montmorillonite is reported to drastically increase by the formation of Ag⁺-thiourea complex (Pleysier and Creamers, 1975), the similar effect is also expected for Hg²⁺ having similar chemical properties, such as precipitation formation, to Ag⁺.

Fig. 2 shows the Hg²⁺ adsorption percentages for A4, P, mordenite and montmorillonite as a function of the Ads/Hg ratio. The Hg²⁺ removal percentage for montmorillonite was nearly 100% at the Ads/Hg ratio of 1.2 (dose of 0.01 g). This means that all of Hg²⁺ in the solution were adsorbed onto montmorillonite, and almost all of the negative charge sites of montmorillonite including interlayer region were occupied by Hg²⁺-thiourea complex. Because no adsorption of Hg²⁺ onto montmorillonite was observed in the absence of thiourea (Fig. 1), this result indicates extremely high adsorption selectivity of Hg²⁺-thiourea complex to montmorillonite.

Similar phenomena were observed for A4 and P, where nearly 100% of adsorption was observed for A4 at the Ads/Hg ratios of less than 18, and more than 95% of adsorption for P at the ratios of less than 10. The Hg²⁺ adsorption percentage for mordenite was little affected by the coexistence of thiourea. The above results for montmorillonite, A4 and P indicate that the Hg²⁺-thiourea complex has high adsorption selectivity to the negative charges of the adsorbents, not only to the negative charges on the outer surface of their crystals but also to those in their inner surfaces: interlayer space of montmorillonite and inside of A4 and P. The reason for the small effect of the addition of thiourea for mordenite was not clear, and further study is needed.

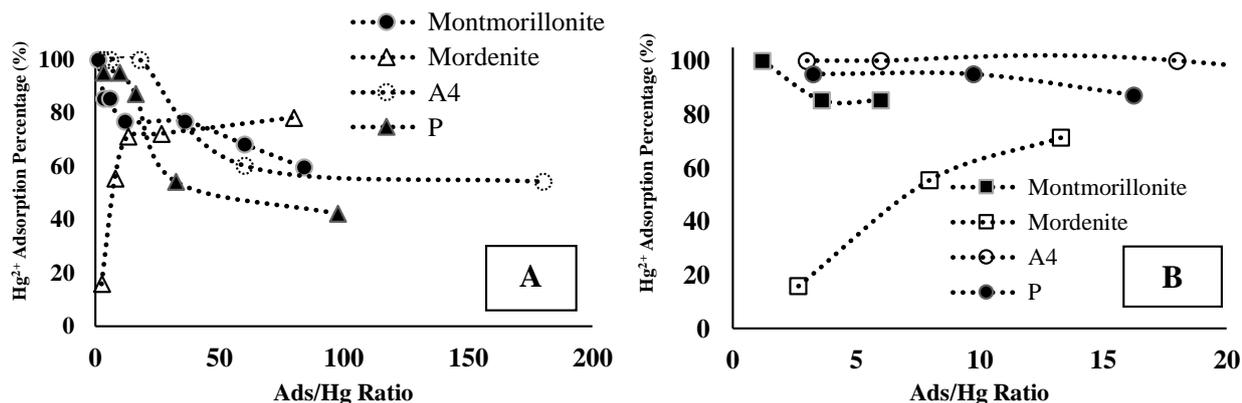


Figure 2. (A) Hg²⁺ adsorption percentage for A4, P, mordenite and montmorillonite as a function of Ads/Hg ratio in the presence of thiourea at a thiourea/Hg ratio of 10, and (B) those at lower Ads/Hg ratios.

Fig. 2 also shows that with increasing the Ads/Hg ratio to higher values, the Hg²⁺ adsorption percentage decreased for montmorillonite, A4 and P. In general, in the adsorption of an adsorbate to an adsorbent, the amount of adsorption of the adsorbate increases with increasing the ratio of adsorbent/adsorbate (Botoman et al. 2017), but the above results contradict to this general observation. One possible explanation for the decrease of Hg²⁺ at higher Ads/Hg ratio may be that most of thiourea was adsorbed to montmorillonite, A4 or P, and the formation of Hg²⁺-thiourea became insufficient, leading to the decrease in the amount of adsorption of Hg²⁺. However, further study is also needed for this phenomena, in addition to the little effect of thiourea addition on the Hg²⁺ adsorptivity of mordenite mentioned above.

CONCLUSION

We have shown for the first time that the addition of thiourea to Hg²⁺ solutions markedly increased the adsorptivity of Hg²⁺ to A4, P and montmorillonite; only a small amount of the adsorbents were needed to remove most of the Hg²⁺. For the effective removal of Hg²⁺ in the presence of thiourea, the choice of adsorbent species and the dose of the adsorbents should be carefully determined, because the excess use of the adsorbents is not cost-effective, and also decreases the Hg²⁺ removal efficiency.

ACKNOWLEDGEMENTS

The authors thank to SUIJI-JP MS (Six University Initiative Japan Indonesia Joint Program Master) Bogor Agricultural University and Ehime University, Indonesia and also thank to Asami Kumon, Lester Botoman, and Tandaditya Ariefandra for their contribution in laboratory work.

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