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Heavy Metal Retention on Agricultural Soil

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It is known fact that heavy metal cannot be degraded chemically and it tends to accumulate and remain in the soil or water that can cause significant effect on environmental. Heavy metal in water may cause on the disturbance of aquatic life and the consumer; similarly, for soil or agricultural soil it may cause the fertility of the plant cultivated on the soil and may cause certain effect on health of the plant consumer. Therefore, it is important to know the ability and capacity of soil or agricultural soil in retaining heavy metals. Hence, in this paper a study on the adsorption of heavy metals on various types of soils to represent major component of agriculture soil is studied. The studies are involved the measurement of excess adsorption of heavy metals on selected soils and interpretation of adsorption isotherm of binary adsorption using commonly available adsorption isotherm theories. The excess adsorption isotherm was measured by conventional liquid phase adsorption measurement technique. The adsorption isotherm was interpreted by analysis of excess adsorption isotherm with monolayer pseudo ideal adsorption theory. In this work is different from most commonly reported adsorption in the literature. Here the adsorption isotherm analyzed based on binary adsorption whereas in most of literature only single adsorption are reported, and also there is no assumption that adsorption isotherm is directly equal to excess adsorption isotherm. The results presented here are excess adsorption isotherm and adsorption isotherm for binary and monolayer adsorption of copper onto clay. Result also shows the adsorption capacity of copper ions on clay.

Keywords: Excess adsorption isotherm, pseudo ideal monolayer adsorption, binary adsorption, heavy metal pollution

I. INTRODUCTION

Heavy metal contaminant entered onto soil or water through both natural and anthropogenic processes. Sources of heavy metals are mainly from anthropogenic wastes such as industrial activities, agricultural activities and domestic disposal (Arabzai & Honma, 2014; Sangiumsak & Punrattansin, 2014). In agriculture, the usage of pesticides such as herbicide, insecticide and fungicide are widely since last century. All these pesticides may contain toxic chemicals and also heavy metals (Aikpokpodion *et al.* 2010; Zhou *et al.* 2011). Heavy metals were accumulated in soil or mobilized to groundwater or water pathway which are depending on the strength of chemical form between the particular heavy metal and soil; due to soil possesses the ability to bind with heavy metal in various forms such

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as surface complex formation and precipitation (Bhakta & Munekage, 2013). The mechanism of heavy metal ions on soil surfaces which generally involves the loss of a metal ion from an aqueous to a contiguous solid phase is often unknown; it is always relate to adsorption, surface precipitation and fixation processes (Bradl, 2004). Even soil is a major reservoir for retaining heavy metal but heavy metal cannot be degraded (Ihaddadene, 2016); and the rate of generation via man-made cycles are more rapid relative to the natural. Accumulation of heavy metals in soil will increase the concentration in district which may cause the fertility of the plant cultivated on the soil and insecure agricultural production that cause certain effect on health of the plant consumer (Al-Qahtani, 2016; Zhou *et al.* 2011).

In other situation, considered that low levels of heavy metals found in present-day soil and with the continuous inputs from anthropogenic activities will cause exceeding the limit of the ability and capacity of soil in retaining heavy metals; and further it influenced the retention and the released of heavy metals from the soil which will be carried by runoff during rainfall to the stream and sea, then settle down into the seabed. Finally, it will pollute the aquatic ecosystem and cause on the disturbance of aquatic life (Govind & Madhuri, 2014; Jaishankar *et al.* 2014). Therefore, it is important to enhance the knowledge of retention of heavy metal in soil. Due to the retention of heavy metal in soil was related with its adsorption in soil and also the capacity of soil to hold or bind with the heavy metal. Measurement and models of adsorption isotherm have been reported in literatures, but the adsorption isotherms were directly interpreted from measured excess adsorption isotherm; and the adsorption isotherm were analyzed only as single adsorption but not binary adsorption (Arabzai & Honma, 2014; Jiang *et al.* 2010; Ghasemi-Fasaei *et al.* 2012; Budianta, 2011; Müllerová *et al.* 2003). Only few analysis of excess adsorption isotherm reported but is relevant to organic solvent mixture (Bono *et al.* 2016; Bono *et al.* 2014; Bono *et al.* 2008).

Soil is the most abundant adsorbent in earth. Thus, the aim of this study was involved the measurement of excess adsorption of heavy metals on selected soil and interpretation of adsorption isotherm of binary adsorption using pseudo ideal monolayer adsorption theory. Adsorption was conducted using copper as adsorbate and clay as adsorbent. Copper was represented as heavy metal on fungicide whereas clay was selected to represent part of the soil composition as the major compositions of common agricultural soil are clay and sand.

II. MATERIALS AND METHODS

The research works involved measurement of excess isotherm, analysis and interpretation of adsorption isotherm. The experimental work was carried out using a conventional technique of excess adsorption isotherm measurement with some modification (Bono et al. 2014; Bono et al. 2007). Copper ions as copper nitrate trihydrate (Cu(NO3)2.3H2O) was purchased from Sigma-Aldrich, whereas clay (kaolin, Al2Si2O5(OH)4) from R & M Chemicals. The concentrations of Cu2+ solutions were prepared in the range of 10-6000 mg/kg. These studies concentrations were at below and until above the range of natural copper concentration in soil. The quantities of adsorbent and Cu2+ solution were set to a weight ratio of 1:50. All samples were prepared in 3 replicates. The samples were kept in a 250 mL sealed conical flask and placed in incubator shaker at 30oC and 100 rpm for 24 h, for achieving the equilibrium.

The samples were then centrifuged, and the concentrations of the solutions were determined using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). For the purpose of analysis and interpretation of adsorption isotherm, the following equations were used. The numerical value of excess adsorption isotherm of Cu2+ was determined using Equation 1:

$$\Gamma_1 = \frac{W_0(x_{10}-x_1)}{W_s} \tag{1}$$

Number of moles for component 1 and 2 of adsorbed phase (mol/g): Where, x_{10} is the initial concentration of Cu^{2+}, x_1 is concentration of Cu^{2+} in equilibrium, W_o is the weight of solution and W_s is weight of adsorbent. Whereas, Equation 2, 3, 4, 5 and 6 which derived from the combination of materials balance of adsorption system and idealized equilibrium adsorption equation were used to explain the pseudo-ideal monolayer adsorption theory (Bono *et al.* 2014; Farhadpour & Bono, 1988). Pseudo-ideal equation:

$$\frac{x_1 x_2}{\Gamma_1} = \frac{1}{N_s}\left[x_1 + \frac{1}{K-1}\right] \tag{2}$$

Concentration for component 1 and 2 of adsorbed phase (mole fraction):

$$x_1^s = \frac{Kx_1}{1+(K-1)x_1} \tag{3}$$

$$x_2^s = 1 - x_1^s \tag{4}$$

$$n_1^s = N_s \frac{Kx_1}{1+(K-1)x_1} \tag{5}$$

$$n_2^s = N_s - n_1^s \tag{6}$$

Where, K is the equilibrium constant, N_s is the total mole of adsorbed (adsorption saturation value), x_2 is the equilibrium concentration, x_1^s and x_2^s are the respective concentration of component 1 in adsorbed phase; n_1^s and n_2^s are the respective moles of component 1 and 2 adsorbed.

III. RESULTS AND DISCUSSIONS

Assessment of excess isotherm, analysis and interpretation of adsorption isotherm were described based on the collected data. Figure 1 shows the excess adsorption isotherm of binary adsorption of Cu^{2+} onto clay experimentally. Measurement of this excess isotherm was conducted at low region of sorbate Cu^{2+} concentration (10-6,000 mg/kg). In the range of these concentrations, adsorption was indicated a preference for one component (Cu^{2+}) from the solution. But it is necessary to understand that previously it was assumed the change in concentration was only measure on solute (Cu^{2+}) had been adsorbed whereas the solvent (water) was not involved in the adsorption process (Kippling,1965). This concept may valid for system which solute has very limited solubility in the solvent but not for completely miscible system. Thus, it is important to recognize each component of the mixture that maybe involved in the adsorption. In this study, both concentration of solute and solution were accounted in the adsorption system. Based on the experimental result, it is expected that the excess isotherm is a U-shaped type according to the classification of composite isotherms (Song *et al.* 2013). For a U-shaped isotherm, the binary adsorption was perfect and the adsorbent surface is homogenous due to the shape of a surface excess isotherm is influenced by the nature of absorbent surface and also the bulk solution properties. Hence, the excess adsorption isotherm of Cu^{2+} onto clay obtained is monolayer type.

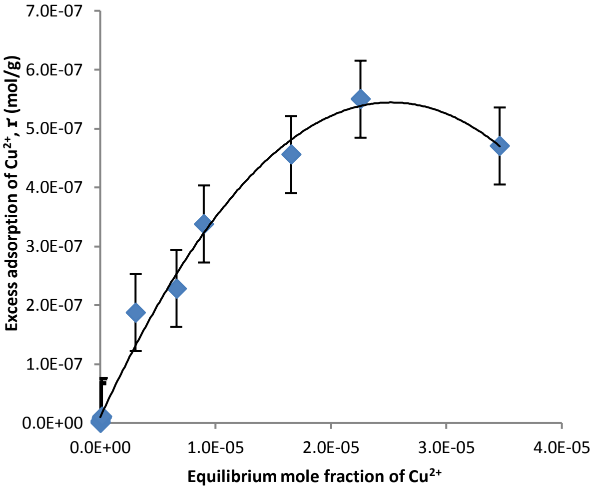

Figure 1. Excess adsorption isotherm of Cu^{2+} onto clay at 30°C.

The analysis of adsorption system using Equation 2 has shown conformity to pseudo-ideal monolayer adsorption theory. The plot of versus produced a straight line. The data satisfactory fitted to Langmuir relation indicating that the adsorption involved as monolayer type and also as conformity to Pseudo-ideal monolayer adsorption theory. The slope and intercept of the plot were used to yield the equilibrium constant, $K = 2.16 \times 10^5$ and capacity adsorption, $N_s = 5.57 \times 10^{-4}$ mmol/g. The capacity adsorption value of Cu^{2+} in clay is very small, which means only 3.54×10^{-2} mg/g of Cu^{2+} can be hold in 1 gram of clay. It has been reported that the range of natural copper contents in soils are between 2 to 250ppm and on average 30ppm (Vlček & Pohanka, 2018). Therefore, if the concentration of Cu^{2+} in clay is exceeded the limit, then the further adsorption of Cu^{2+} is depends on the organic matters that present in clay (Violante *et al.* 2003). Otherwise, the unadsorbed Cu^{2+} will runoff or pollute the related area. The individual adsorption isotherm obtained from Equation 5 shows no point inflexion in the curve which corresponds to U-shaped composite isotherm.[19] It also indicated a selective adsorption occurs which only a type of adsorbate was adsorbed in the adsorption system. Whereas, the concentration for Cu^{2+} in adsorbed phase was calculated using Equation 3 produced the plot in Figure 2 showed that the adsorption of the Cu^{2+} onto clay is favorable. Therefore, clay is able to hold Cu^{2+} with condition not exceed the capacity limit.

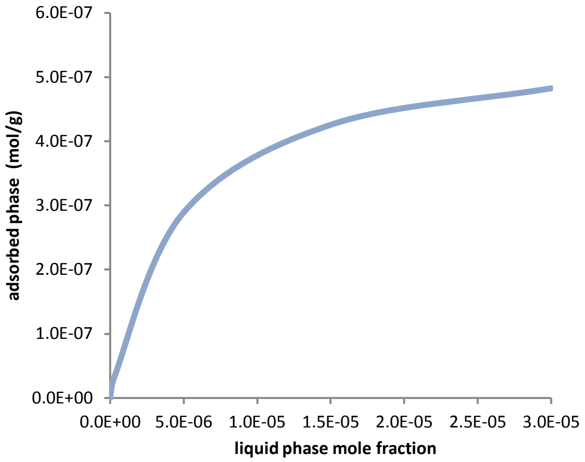

Figure 2. Adsorbed phase concentration for Cu^{2+} on clay in equilibrium

IV. SUMMARY

Adsorption isotherm of Cu^{2+} onto clay was confirmed as monolayer type. This finding can also be applied to other bivalent heavy metal ions such as Zn^{2+} and Pb^{2+}. Similar studies can also carry out on other agricultural soils so that the knowledge of excess adsorption isotherm can be further enhanced.

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