THE INFLUENCE OF MINERALOGICAL COMPOSITION ON THE ADSORPTION CAPACITY OF HEAVY METALS SOLUTION BY JAVA NATURAL CLAY, INDONESIA

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Abstract

The adsorption capacity of four clay samples (Boyolali-BYL, Sleman-SLM, Gunungkidul-GK, and Pacitan-PCT) from Java, Indonesia, for copper (Cu) lead (Pb), zinc (Zn) and cadmium (Cd) solution was investigated by using batch equilibrium test. The adsorption data were presented using an isotherm curve, and adjusted to the Langmuir equation model, which produced the maximum adsorption capacity of the clay samples. The physical, chemical, and mineralogical analysis showed that the BYL and PCT samples have higher montmorillonite content, cation exchange capacity (CEC), and specific surface area (SSA) compared to SLM and GK clay samples. The batch equilibrium test revealed that the clay samples with higher montmorillonite content produced higher heavy metal adsorption capacity due to the higher cation exchange capacity (CEC), and specific surface area (SSA). The batch equilibrium test also show that the adsorption order for the metals cations followed the selectivity order $Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+}$. The Langmuir model resulted in the adsorption processes, offering maximum adsorption capacities from 196.08 to 769.23 mg/g for Cu, 217.39 to 416.67 mg/g for Pb, 106.38 to 114.94 mg/g for Zn and 104.17 to 113.24 mg/g for Cd of four clay samples studied. The highest adsorption capacity was achieved for the BYL sample. The lowest was the GK sample, in which the order of the maximum adsorption capacity of clay samples was BYL > PCT > SLM > GK sample. This research indicated that the proportion of montmorillonite content in the clay samples affected the maximum adsorption capacity of the heavy metal in the solution.

Keywords: Adsorption, Batch test, Clay, Heavy metals, Java

Introduction

Nowadays, the presence of lead (Pb), copper (Cu), zinc (Zn), and cadmium (Cd), which are a heavy metals contaminant group that has toxic properties to humans and are usually found in waste [1,2]. Natural clay has physical and chemical properties to be able to adsorb heavy metals [3]. Several studies on natural clays' ability to adsorb heavy metals have been carried out using the batch equilibrium test, which is the simple but effective method [4, 5, 6, 7]. The batch equilibrium test is a practical and quick test to predict the maximum amount of contaminants that can be adsorbed by a material and a representation of the experiment that can destroy all material structures; for example, the surface of the clay, which is an adsorbent medium. The batch equilibrium test is also carried out to measure the distribution coefficient (K). A measurement of this K value is essential because it is an indication of contaminant retention by solids. Several studies have been conducted only for geological of natural clay deposit and mineralogy in Java, Indonesia [8, 9, 10, 11]. However, the comprehensive research for the mineralogical composition of these natural clay influenced the heavy metals' adsorption need to be investigated. The study of heavy metal adsorption in natural clay is an

important aspect, as stated by several previous studies [12, 13, 3]. This understanding of the adsorption will deliver knowledge for the use of natural clay for environmental remediation purposes.

This research aims to study characteristics and adsorption capacity on clay samples obtained from several locations in Java, Indonesia, and quantify the value of heavy metal adsorption. In this research, the batch equilibrium test was performed to obtain adsorption parameters, including maximum adsorption capacity (Q_{max}) and adsorption constant, by calculating the Langmuir equation model determination. The Langmuir model is widely used because of its mathematical simplicity and also easily interpretable constant which related to the highest possible adsorption [14]
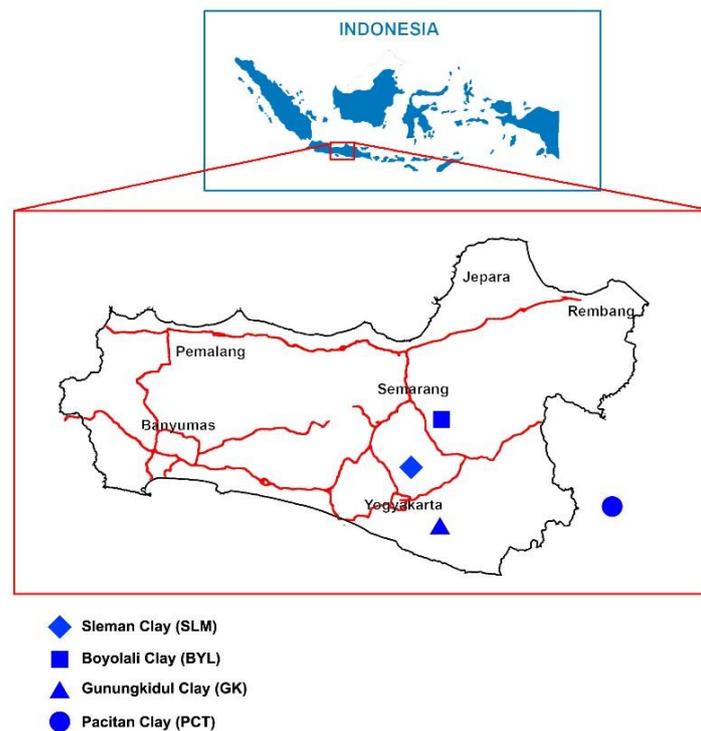
Figure 1. Sampling locations of clay in Java, Indonesia

Materials and methods

Clay Samples

The clay samples in this study were obtained from four locations in Java, Indonesia, with different geological backgrounds. They were the clays of Boyolali (BYL), Gunungkidul (GK), Sleman (SLM), and Pacitan (PCT). The sampling location can be seen in Figure 1, and the geological information on the clay samples can be seen in Table 1 based on other studies [15, 16, 17, 18].

Table 1. Geological Information of Clay Samples

Clay Sample	Geological Formation	Clay Genesis
Boyolali (BYL)	Kerek Formation	Volcanic glass alteration
Sleman (SLM)	Old Andesite Formation	Andesite intrusion alteration
Gunungkidul (GK)	Semilir Formation	Volcanic glass alteration
Pacitan (PCT)	Punung Formation	Volcanic glass alteration

Some of the main properties of clay samples were analyzed using the following procedure. The grain size was analyzed using the wet sieving and hydrometer method. The clay sample's pH was measured using a glass electrode, with a ratio of 1:5 for clay and water samples. The cation exchange capacity (CEC) of clay samples was analyzed by the $BaCl_2$ method [19]. The specific surface area (SSA) of clay samples was measured by Brunauer–Emmett–Teller (BET) method. The mineralogical content and types of clay minerals were analyzed using X-Ray Diffraction (XRD) technique. The XRD was operated using a Philips PW1710 diffractometer with Ni-filtered CuKα radiation at randomly oriented samples. The quantitative assessment value of the mineral phases' presence was obtained from the XRD data, adopting the intensity of specific reflections and standard external variety of minerals [20].

Batch Equilibrium Test

The heavy metal adsorption experiment on clay samples was carried out using the batch equilibrium test. In this experiment, the adsorption performance of Pb, Cu, Zn, and Cd was investigated in the clay samples used in this study that was done by preparing 10 grams of clay sample, which was placed in a 500-ml measuring cup. The desired eight heavy metal concentration solutions 5.0, 2.5, 1.25, 0.63, 0.32, 0.16, 0.08 and 0.04 mmol/l were prepared in this experiment at constant temperatures (25°C). Then, 250 ml of a solution containing $Cu(NO_3)_2$, $Cd(NO_3)_4$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$ has been added into the cup. The clay sample was dried, and then the batch test is carried out. The clay samples and heavy metal solution were stirred for 12 hours at room temperature and then were left without stirring for 24 hours. The agitation rates tested were 200 rpm, and the pH of the solution was kept on 6.5. The mixture was filtered with a 0.45 µm filter. The filtered solution was then analyzed for Pb, Cu, Zn, and Cd concentration with the measurement of inductively coupled plasma atomic emission spectroscopy (ICP AES). All analyzes were carried out by making duplicates three times.

The maximum adsorption capacity (Q_{max}) of the Langmuir isotherm equation for adsorption was calculated using the Equation [21]:

$$Q = Q_{max} \frac{K.C}{1 + K.C} \tag{1}$$

where,

Q = adsorbed amount (mg/g)
Q_{max} = maximum adsorption capacity (mg/g)
K = adsorption constant (l/mg)
C = initial metal concentration (mg/l)

Result and Discussion

Physical, Chemical, and Mineralogy of Clay Samples

Several properties of clay samples are given in Table 2. The BYL and PCT samples had higher CEC and SSA values compared to the SLM and GK samples. This phenomenon occurred may be attributed to the montmorillonite-typed mineral had three layers, which were a repetition of one layer of alumina and two layers of silica.

Table 2. Several Properties of Clay Samples

Properties	BYL	SLM	GK	PCT
Sand (%)	12.3	22.3	19.9	17.9
Silt-Clay (%)	87.7	77.7	80.1	82.1
pH	7.2	7.3	7.1	7.4
Specific Surface Area (SSA) (m^2/g)	98	39.5	32	87
Specific Gravity	2.73	2.65	2.63	2.74
Cation Exchange Capacity (CEC) (meq/100 g)	71	45	35	65

Generally, CEC and SSA values of four clay samples show that relatively intermediate compared with other natural clay that has been studied by another researcher [22, 23, 24]. Another study state that the CEC and SSA value of pure montmorillonite mineral up to 150 meq/100 g and >100 m^2/g [22] [25]. This difference may be due to differences in the percentage of clay minerals, and the existence of other mineral impurities like quartz. Also, this may cause for reducing the value of CEC and SSA, as found by other studies [26, 27, 28]
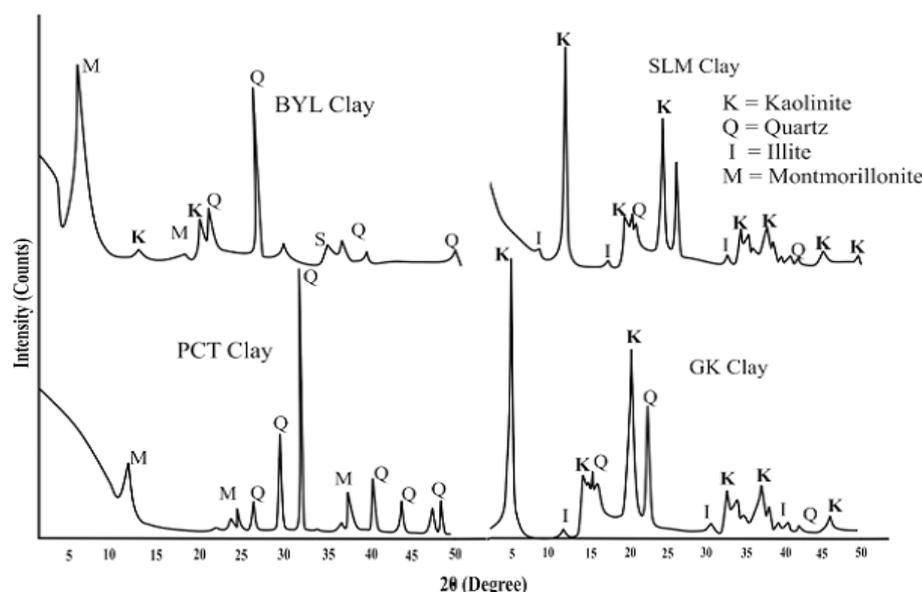
Figure 2. XRD diffractograms of samples showing the clay mineral identification

Figure 2 shows the result of the XRD analysis of the clay samples. The diffractogram of XRD indicates the presence of clay minerals such as montmorillonite, illite, kaolinite, but another impurity mineral such as quartz also present. These results have been confirmed by other researchers, which show that the existence of clay in the study area was heterogeneous of clay mineralogy contents [8, 9, 10, 11].

The semi-quantitative mineralogical composition is shown in Table 3. XRD analysis was found dominant for montmorillonite-type clay for BYL and PCT sample with percentages of montmorillonite 36.1% to 38.1%, respectively. Other samples are found dominant for kaolinite-type clay for SLM and GK sample with portions of kaolinite 35.1% to 36.1%, respectively. Other minerals such as quartz, plagioclase, feldspar, and other non-clay mineral were generally present in natural clay [29].

Table 3. Mineral Composition for the Clay Samples (% wt)

Mineral variety	BYL	SLM	GK	PCT
Montmorillonite	36,2	14,1	17,1	38,1
Illite	6,5	6,7	5,7	7,4
Kaolinite	2,3	35,9	36,4	11,6
Quartz	17	16	21	18
Plagioclase	12	11	6	7,8
K-Feldspar	11	7,2	6,8	7,4
Other non-clay minerals	14,4	8,7	6,7	9,4
Sum	99,4	99,6	99,7	99,7

Result of Batch Equilibrium Test

The result of batch equilibrium is shown in Figures 3 to 6 and Table 3. This test is conducted to obtain the Q_{max} value of the clay by using eight solutions. Figures 3 to 6 show the linear relationship between the values $1/Q$ and $1/C$ used to get the Langmuir constant value (K) and the Q_{max} value. The adsorption data in this experiment was obtained from $1/Q$ plot value in the $1/C$ function as the Langmuir model representation.
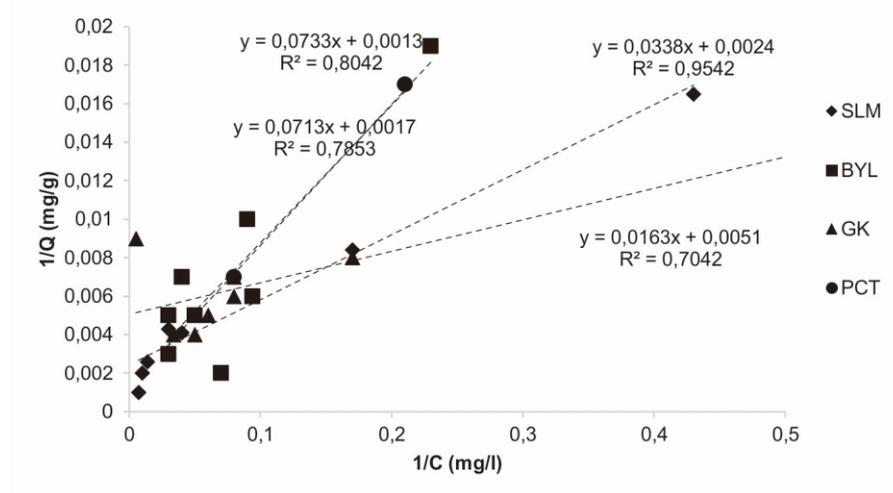
Figure 3. The linear relationship for $1/Q$ and $1/C$ of Cu
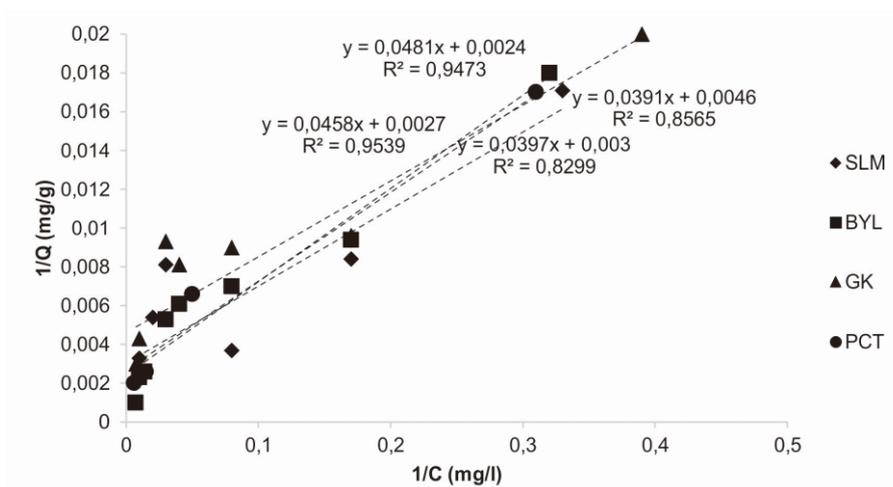
Figure 4. The linear relationship for $1/Q$ and $1/C$ of Pb
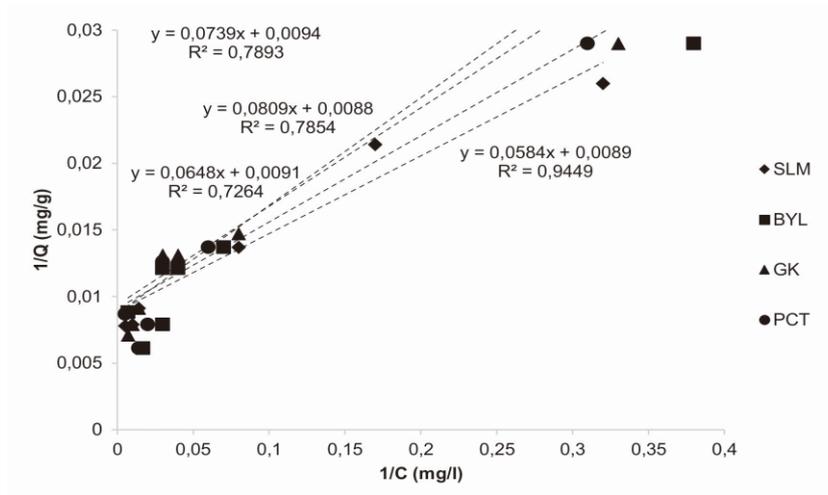
Figure 5. The linear relationship for 1/Q and 1/C of Zn
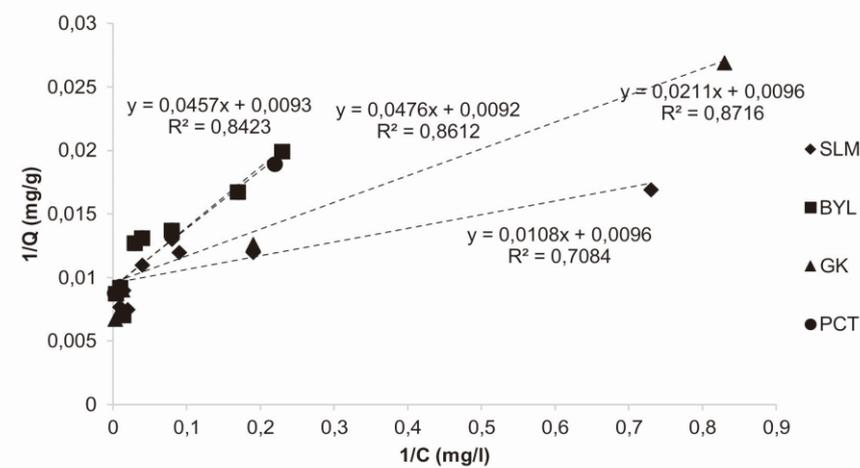
Figure 6. The linear relationship for 1/Q and 1/C of Cd

Table 4 shows the amount of the Q_{max} and K parameters, and the value of the linear regression, R^2. Adsorption isotherm models were recommended to determine adsorption capacity, as stated by several studies [30, 31, 32]. In this experiment, the Langmuir equation model defines the tendency of adsorption data with values of > 0.70 for R^2, as shown in Table 4. This adsorption experiment indicates that the Langmuir isotherm model represents the adsorption progress with a high coefficient of determination. The coverage of metal cations on the clay samples' surface was reflected by the high R^2 value obtained. In the Langmuir isotherm model, the equilibrium is limited to the molecular layer's determination and correlate to electrostatic chemistry in the outer sphere complex [33].

Table 4. K and Q_{max} Parameter from Experimental Data by the Langmuir Equations

Samples/ Parameters	Langmuir equations					
	Cu			Pb		
	K (l/mg)	Q_{max} (mg/g)	R^2	K (l/mg)	Q_{max} (mg/g)	R^2
BYL	0.017	769.23	0.804	0.049	416.67	0.947
SLM	0.710	416.67	0.954	0.075	333.33	0.829
GK	0.313	196.08	0.704	0.117	217.39	0.857
PCT	0.024	588.24	0.785	0.059	370.37	0.954

Samples/ Parameters	Langmuir equations					
	Zn			Cd		
	K (l/mg)	Q_{max} (mg/g)	R^2	K (l/mg)	Q_{max} (mg/g)	R^2
BYL	0.107	114.94	0.723	0.455	113.24	0.800
SLM	0.127	112.35	0.945	0.888	106.13	0.708
GK	0.152	106.38	0.789	0.107	104.17	0.872
PCT	0.109	113.64	0.785	0.204	107.53	0.842

The selectivity of four metals adsorption was exhibited by Q_{max} values (Table 4), and the value was not similar for metals investigated. Cu and Pb, the most greatly adsorbed metal in this experiment, were less influenced by competition than Zn and Cd for clay samples. This competition may be attributed to the fact that Cu and Pb were strongly adsorbed by the clay fraction and hence attempted effectively with the less adsorbed Cd and Zn and agree with another study [34]. Cu and Pb can enter clay lattices and form an insoluble group (e.g., Cu, Pb(OH)$_2$, as the alternative hydrolysis product of Cu, Pb). These are irreversible processes in a laboratory experiment range. They could cause an important constituent of Pb and Cu's addition to be unavailable for cation exchange reactions. Another parameter influence the selectivity was related to the hydrated radius of the cation, as described by other researchers [35, 36]. The hydration radius of the cations for Pb^{2+} (4.01Å), Cu^{2+} (4.19Å), Zn^{2+} (4.30Å) and Cd^{2+} (4.26 Å) respectively. Thus Pb and Cu seem to be less influenced by competition than other metals that are less adsorbed (Zn and Cd). The result revealed that Pb occupied a higher affinity for ion exchange on clay samples. This result of the selectivity is agreed with another researcher [37]. The adsorption of heavy metals ions on clay samples also depends on the ionic potential of the metals. The cations in the solution are connected with molecules of water in complex hydration. Generally, this hydration has a radius that was inversely corresponding to the cation radius. Hence, the smaller cations, the greater the hydration radius and cannot be easily eliminated from the clay surface. This finding also advises the low adsorption capacity of the Zn and Cd against the Cu and Pb component. In general, the adsorption order for the metals cations followed the selectivity order Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+}.

Generally, the montmorillonite type-mineral has a higher adsorption capacity than the kaolinite type-mineral. The adsorption capacity values may reach as three times or higher [27]. Adsorption of heavy metals on clay samples appearance to follow Langmuir isotherm with a maximum adsorption capacity, i.e., 769.23 mg/g for Cu of BYL clay sample. This maximum adsorption capacity was decreased to 196.08 for GK clay samples (see Table 4). Metals adsorption on clay sample is sensitive to the montmorillonite content. In this study, the BYL and PCT clay samples have higher montmorillonite content than SLM and GK samples. Other studies revealed that Pb's adsorption by montmorillonite clay from Pb solution up to 20 mg/g [38]. It was determined that adsorption capacity is higher on dominant montmorillonite on BYL and PCT samples (Cu: 769.23 mg/g, Cd: 588.24 mg/g) than on kaolinite on SLM and GK samples (Cu: 416.67 mg/g, Cu: 196.08 mg/g). In another study, the better removal efficiency was obtained for heavy metals removal using montmorillonite instead of another type of clay [39].

The higher maximum adsorption values obtained in the BYL and PCT samples, and the lower values obtained in the SLM and GK samples, are shown in Figure 7. This adsorption capacity was consistent with the results of another researcher who stated that clay mineral type such as, for example, higher montmorillonite content, influenced the maximum adsorption capacity value [26].
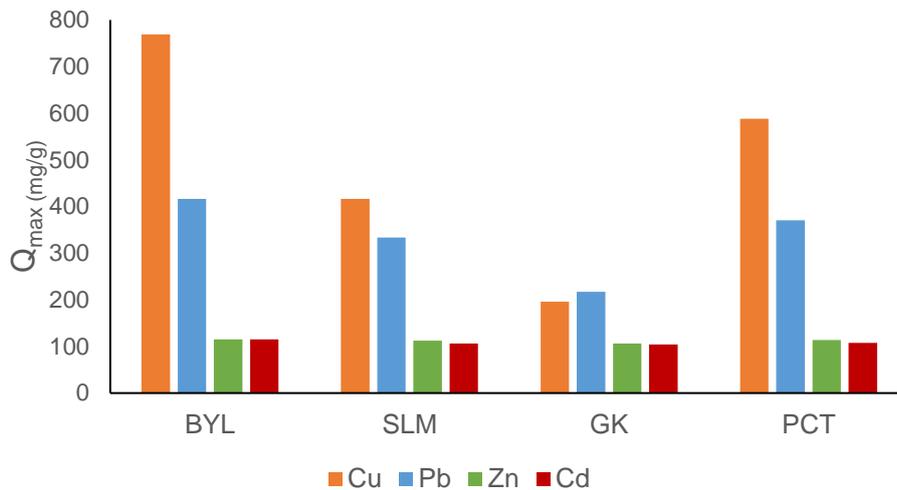
Figure 7. Comparison of adsorption capacity in four natural clay samples

Other research suggests that the high content of montmorillonite will provide high binding energy for metal absorption. The results obtained showed that clay samples had different behavior in adsorbing Cu, Pb, Zn, and Cd. This behavior might be related to the adsorption mechanism caused by the mineralogical content of the four types of clay samples studied, confirmed by other research [40]. These results indicated that the difference in the proportion of mineralogical contents in clay samples would affect the adsorption capacity of metal ions. This result shows that the order of maximum adsorption capacity of clay samples was BYL > PCT > SLM > GK sample is obtained by analyzing the values of maximum sorption capacities calculated from the Langmuir equations,

The graphical correlation between maximum adsorption capacity (Q_{max}), CEC, SSA, and % montmorillonite values are shown in Figure 8-10. The graph in Figure 8 to 10 indicates a good correlation between maximum adsorption and CEC, SSA, and % montmorillonite values with R^2 values of more than 0.6. This result is agreed with other research results, which mentioned that clays with higher CEC, SSA value, and % montmorillonite have higher adsorption values to adsorb metal cations [7, 41].
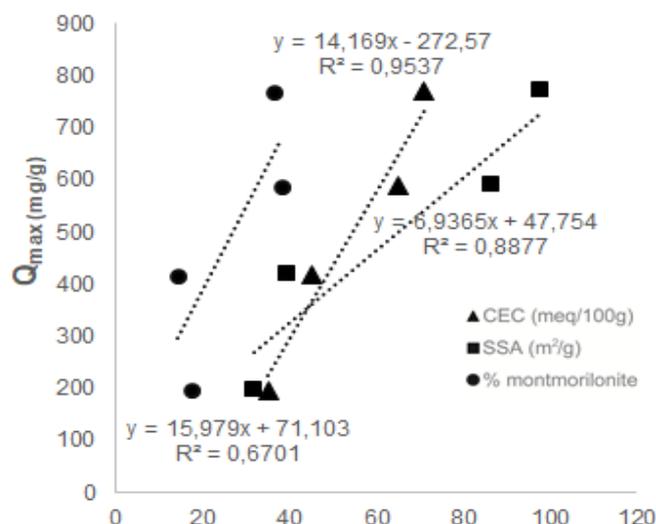
Figure 8. Graphical correlations (R^2>0.6) between maximum adsorption capacity, CEC and SSA value, and % montmorillonite for Cu
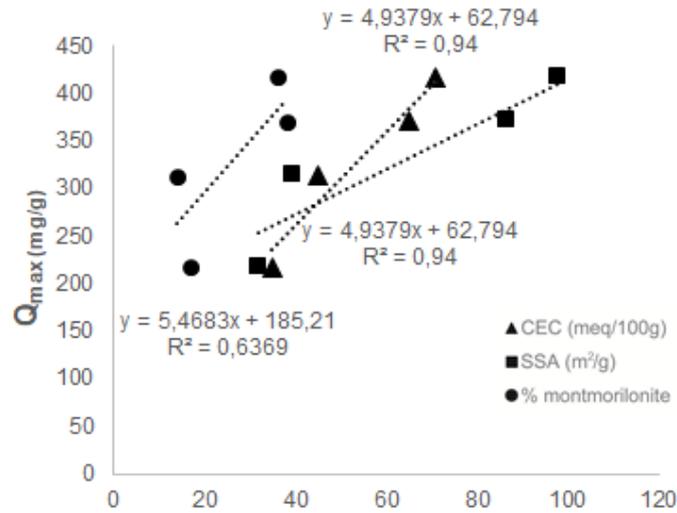
Figure 9. Graphical correlations ($R^2>0.6$) between maximum adsorption capacity, CEC and SSA value, and % montmorillonite for Pb
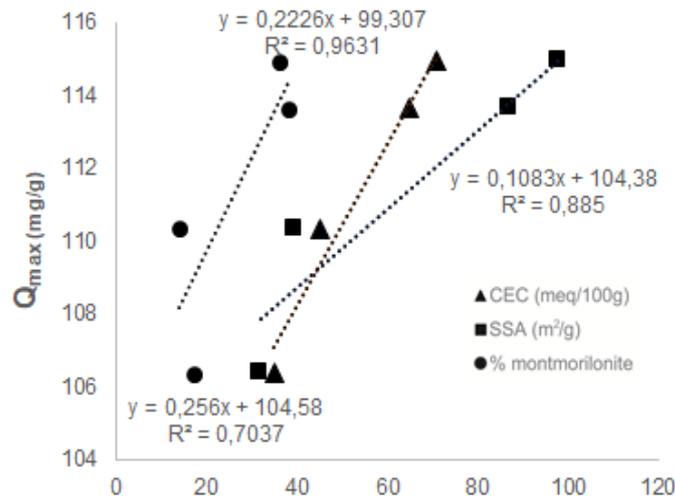
Figure 10. Graphical correlations ($R^2>0.6$) between maximum adsorption capacity, CEC and SSA value, and % montmorillonite for Zn
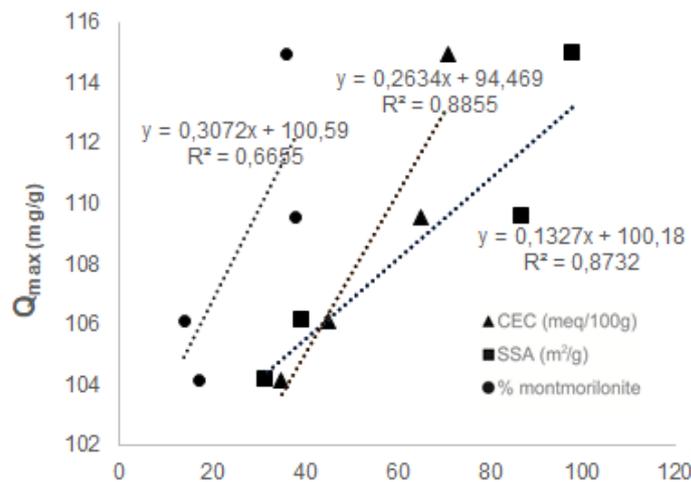
Figure 11. Correlations ($R^2>0.6$) between maximum adsorption capacity, CEC and SSA value, and % montmorillonite for Cd

Parametric Pearson correlation analyses were applied to the four parameters tested in pairs to assess the degree of association between the parameters examined. The Q_{max} of Cu, Pb, Zn, and Cd was strongly correlated with CEC, SSA, and % montmorillonite with Pearson's correlation coefficient of 0.01 and 0.05 level, as shown in Table 5. The results showed that CEC, SSA, and % montmorillonite had a strong correlation with Q_{max} of the four heavy metals. The trend shown by the Q_{max} values in the Langmuir model also suggested that adsorption capacity increased with CEC, SSA, and % montmorillonite.

Table 5. Pearson's Correlation between Qmax and the CEC, SSA, and % Montmorillonite (n = 4).

Parameters	CEC	SSA	% montmorilonite
Q_{max} Cu	.977**	.942**	.819**
Q_{max} Pb	.935**	.872**	.728*
Q_{max} Zn	.898**	.820**	.675*
Q_{max} Cd	.880**	.864**	.713*

Correlation coefficients marked by * and ** are significant at the 0.05 and 0.01 level, respectively (2-tailed).

The results indicated that the correlations between Q_{max} and % montmorillonite value more than 0.75 were the most significant, for Q_{max} of Cu. This highest correlation value may be attributed to the highest adsorption capacity (Figure 7). On the other hand, the correlations between Q_{max} and % montmorillonite value was less than 0.75. This correlation value showed a lower degree of significance for Q_{max} Pb, Zn, and Cd. This lower correlation value probably due to lower adsorption capacity (Figure 7). The statistical correlation of 0.01 and 0.05 level identified for % montmorillonite strongly influenced on Cu, Pb, Zn and Cd adsorption.

Conclusions

This work investigated the adsorption characteristics of four clay samples obtained from Java, Indonesia, and measured the adsorption of heavy metals by batch equilibrium test to evaluate the adsorption parameters. The four clay samples were composed of dominant kaolinite contents for SLM and GK samples, while the BYL and PCT clay samples were mainly montmorillonite mineral. The adsorption capacity from batch equilibrium tests indicates that BYL and PCT have higher adsorption capacity on heavy metals than samples SLM and GK. The study also found a positive relationship between the adsorption capacity and the clay mineralogy content of the clay samples. The adsorption capacity of natural clay containing dominant montmorillonite-clay mineral is much higher than of kaolinite-clay mineral for all the four metal ions used in the experiment. The study also suggests that physicochemical characterization and batch equilibrium tests can be beneficial in assessing clay for an adsorbent material. Both clay samples containing dominant kaolinite-clay mineral and montmorillonite-clay mineral are capable of removing Cu, Pb, Zn, and Cd from aqueous solution. This finding also shows that the proportion of different mineralogical content in clay samples is affected by heavy metal cations removal from wastewater. Future work for investigation of the study, such as the influence of pH, should be considered in the batch test. Also, comparison by using another isotherm model such Freundlich isotherm need to be done to get a more comprehensive understanding of the adsorption study. Finally, tentative finding obtained in this study shows that clay samples in this study is suitable and has potential value for the adsorption of heavy metal contamination from wastewater, considering it is a low-cost, abundant, and locally available material.

Acknowledgment

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