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Particle Size Distribution and Purification of Red Clay for Industrial Use

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Abstract: The objective of this study is to purify red soil from Indah Permai (IP) for industrial applications. Particle size distribution of IP soil was studied and impurities of clay was removed. A series of methods for the extraction of iron oxides from soil and clay was tested with using dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) as reducing agent at varied pH. Theoretically, the oxidation potential of dithionite increases with increase in pH. A buffer was used in method 1 to maintain the pH at the optimum level (alkalinity). NaHCO_3 is served as the buffer. HCl was used in method 2 to provide its acidic environment. However, method 3 reacts in neither acidic nor base environment. Results showed that different methods have different removal efficiency.

Key words: Clay purification, particle size distribution, metal elements

INTRODUCTION

Iron (Fe), oxygen (O), silicon (Si) and aluminum (Al) are the most abundant elements on the earth. These are present in clays and soils ubiquitous. For iron removal, many different reducing agents have been tried including hydrazine, hydrogen gas and hydrogen sulphide, but the most commonly used agents are dithionite and bacteria to dissolve these elements.

The removal of amorphous coating and crystals of free iron oxides is important in many types of analysis of soils and clay minerals. The removal of free iron oxides aids in dispersion of the silicate portion and it is essential to segregate effectively into different particle size fractions. Differential and integral thermal analysis, electron micrographs and cation exchange capacity are greatly improved after removal of free iron oxides. Citrate chelating agent can be used with $\text{Na}_2\text{S}_2\text{O}_4$ to help with iron extraction and also removes some coatings of alumina and thereby help in the dissolution of free silica cements that are stabilized by alumina coatings (Boussu *et al.*, 2006).

For iron removal, choosing the proper reducing agent and pH system is very important because it influences oxidation potential of the system. Due to limited stability of $\text{Fe}(\text{OH})_3$ (aq), the dissolution of iron oxides requires the consumption of either H^+ or OH^- to generate ionic species such as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ or $\text{Fe}(\text{OH})_4^-$. Hence, the acid dissolution is more important and solutions reactive

to iron oxides usually contain large acid capacities, either in the form of high H^+ concentrations, or in the form of weak acids that are iron (III) complexes. Many studies are on the mechanism of dissolution of iron oxides dealt with acidic solvents. Paradoxically, neutral or even alkaline are practically more important in many cases: mobilization of iron in the ground and in biological media are two examples (Bockheim *et al.*, 2005; Elsa *et al.*, 1992). Discovery of alkaline and neutral solvents is important in the history of chemical cleaning of metal surfaces.

Dithionite can dissolve iron (III) reductively and constitute into two large classes of reductants: complexing anions and low oxidation metal complexes (Elsa *et al.*, 1992) and it is known to form inner sphere complexes with surface iron (III) ions and then evolve through charge transfer from the reducing anion complex or from the bridged reduced metal ion. Therefore, dithionite/citrate became a model solvent to probe the changes in reactivity of iron oxides brought about by adsorption, ionic substitution or other factors.

A typical method involves preparing the clay suspension in an 8:1 (v/v). The temperature, time and dithionite/clay ratio all contribute to determine the extent of reduction. If the amount of dithionite to be added becomes too many, it may overcome the buffering capacity of the buffer. The buffering capacity must be at least 4 portions per dithionite molecule. Earlier studies indicate that the concentration of bicarbonate buffer typically used (1 M) may provide too much buffering

capacity for the amount of dithionite used, thus the pH can be increased to higher than 9. A proper balance between dithionite and buffer must be considered (Stephen and Martin, 1995).

Particle Size Distribution (PSD) is a soil property that provides basic information about the size and the distribution of the soil mass fraction. It is commonly used for soil classification as well as for the estimation of other soil properties, such as the water retention curve and the soil thermal conductivity. Standard methods to determine PSD are using dry sieving, wet sieving, pipette method and hydrometer method (Martín and Montero, 2002).

The objective of this study is to analysis red soils from Indah Permai (IP) place in Sabah. To study the particle size distribution of the sample and then purify the sample to produce a clean and high value added clay. The most appropriate method for free metal oxides is determined.

MATERIALS AND METHODS

Pretreatment of sample: Soil sample was collected at Indah Permai, Sabah during January to December 2007. Oven, mechanical sieving, hot-plate and centrifuge were used during the pretreatment and purification of the sample. Laser Scattering Particle Size Distribution Analyzer LA-300 and Atomic Absorption Spectrophotometer were used for analytical in this research. An empty tray was weighed. Then 400 g of sample soil was weighed on the tray. Then the tray was put into the oven in 85°C. After 3 h the tray was taken out and weighed. These steps were repeated with various temperatures, 95, 105, 115, 125 and 135°C. All values were recorded and compared after drying. To determine time that required for drying the soil completely, these steps were repeated but it was put into oven 105°C. The tray was taken out from the oven to weight every 30 min until a constant weight is obtained. Six metal trays with different sieve sizes were selected; they are 710, 425, 300, 212, 75 μm and a receiver. Any particles may be hand placed to see if they were fall through but they must not be pushed through. The material from the test sieves were rubbed with the pestle in the mortar and received to make sure that only individual particles were retained. The amount retained on the test sieve was weighed. These steps were repeated through all the test sieve sizes used. Care was taken to ensure that sieving is complete. After 60 min, soil on each sieve tray and the receiver was weighed. The percentage by mass of the soil retained on each test sieve was calculated.

Removal of carbonates and organic matter: A suitable aliquot of the suspension (Na saturated sample) containing about 100 to 200 mg of clay was placed in a 20 mL centrifuge tube. The clay was washed 3 times with

NaOAc solution of pH 5, the tube being places for 5 min in a boiling water bath for each washing, to insure complete dissolution of the carbonates. Then following this, 5 drops of NaOAc solution of pH 5 and 5 mL of 30% H_2O_2 were added. The tube containing the sample was heated on a steam plate bath (70-80°C) for about 3 h to complete the destruction of any residual organic matter such as organism growth or mineral-organic complexes.

Removal of metal elements

Method 1: Sodium dithionite-sodium citrate with NaHCO_3 buffer: One gram of the clay was placed in a 100 mL centrifuge tube. Forty milliliter of 0.3 M Na-citrate solution and 5 mL of 1 M NaHCO_3 solution were added into the tube. The temperature was brought to 80°C in a water bath (Mehra and Jackson, 1960). Then 1.0 g of solid $\text{Na}_2\text{S}_2\text{O}_4$ was added by means of a spoon. The mixture was stirred constantly for 1 min and then occasionally for a total of 15 min. At the end of the 15 min digestion period, 10 mL of saturated NaCl solution and 10 mL of acetone was added to the tube to promote flocculation (Rinker *et al.*, 1964). The suspension was then mixed, warmed in a water bath and centrifuged for 20 min at 2000 rev. min^{-1} . The clear supernatant was poured and the settled mass was used for Fe, Al, Si, Ca, Mg and K determination by AAS.

Method 2: Sodium dithionite in acid system: Four gram of clay sample was dispersed thoroughly in 50 mL of distilled water. Two gram of $\text{Na}_2\text{S}_2\text{O}_4$ was added and the mixture was digested for 30-50 min in a water bath at 40°C. The sample was centrifuged and treated twice again with 0.02 N HCl for 10-15 min. The clear supernatant was poured and the settled mass was used for Fe, Al, Si, Ca, Mg and K determination by atomic absorption spectrophotometer.

Method 3: Dithionite-citrate method: One gram of clay was weighed into a 150 mL conical flask. Fifty milliliter of 0.68 M sodium citrate solution was added into the flask. Then 0.8 g of solid dithionite was added. The flask was stopped tightly and was shake end-over-end and left for overnight. The sample in the flask was moved into a centrifuge tube. Then it was centrifuged for 15 min at 2000 rev min^{-1} . The clear supernatant was poured and the settled mass was used for Fe, Al, Si, Ca, Mg and K determination by AAS.

Particle size distribution of fine particle: To determine the particle size distribution for the soil that passed through the test sieve with size 75 μm , Laser Scattering Particle Size Distribution Analyzer LA-300 was used. This instrument can measure the particle sizes ranging from 0.1 to 600 μm and the results were analyzed with LA 300 software.

Concentration of metal elements in the clay: The extract initial metal elements concentration determination in clay was prepared by weight 0.1000 g of clay in a 150 mL conical flask. Then 25 mL of concentrated HNO₃ was added into the conical flask. Some slices of boiling particles were added into the flask. After that the sample was boiled on a hot plate until 5 mL of the liquid remain and left it to cool and the extract was filtered. Then the distilled water was added into the volumetric flask to dilute the extract to give a desired concentration. This liquid was used for AAS analysis. Standard solutions for Fe, Al, K, Ca, Si and Mg were prepared. Air acetylene flame was used for the determination of Fe, K, Ca and Mg and a nitrous oxide-acetylene flame was used for Al and Si.

Treated clay cleaning and drying: The clay was coagulated with an appropriate 1 M chlorite salt to introduce the required exchangeable cation, followed by at least two further washings (additions) to complete the exchange. Then the excess electrolyte was removed by washing with distilled water and centrifuging (2-3 times), then the clay was dried in an oven at 60°C overnight.

RESULTS AND DISCUSSION

Pretreatment of sample: When the temperature is higher than 125°C, colour of the dried soil becomes dark and exhibited burning smell. The most suitable temperature to dry the sample was 105°C. The optimum time for drying is 6 h and this is varied from the literature reviewed. This is due to moisture content in Malaysia is higher than in Europe countries. The moisture content of IP soil is 3.2%. After the soil was dried in the oven, it becomes hard and cohesive in larger palette. These solids should be ruptured by using mortar to become single particle form before sieving with mechanical sieve. The time duration of mechanical sieving must be long enough to get better result. The particle size which is approximately 2 µm, the standard particle size for clay, is about 10.07 % only. The contaminant of clay in this sample is very low, this is may be due to the sample collected was from road side.

Removal of metal elements: These three methods were analyzed in different pH. In method buffer was used to maintain the alkaline environment, method 2, acid was used. The color of clay was removed in every method to become white in colour. Method 2 is the fastest way to remove clay colour and method 3 takes overnight to turn red clay into white. Free Ca oxides were not found in the sample. The major impurity element in the clay is Al, followed by K, Fe and Mg whereas concentration of free

Table 1: Concentration of elements in the IP clay before and after chemical treatment

Element	Concentration (ppm)			
	Initial	Method 1	Method 2	Method 3
Ca	0.11	0.10	0.030	0.070
K	11.32	11.14	11.010	11.080
Fe	8.90	3.50	1.418	2.200
Mg	2.88	2.81	2.780	2.820
Al	30.33	27.98	29.980	28.040
Si	0.72	0.72	0.648	0.218

Table 2: Particle size distribution of IP soil

Sieve size (µm)	Percentage
710	2.75
425	5.65
300	11.36
212	13.95
75	38.39
Receiver	27.90
Total	100.00

Si oxide is very low. The analysis also shows that K and Mg elements couldn't be removed by using these methods. These three methods are effective to remove free Fe oxide from clay and slightly on free Al and free Si removal. For Al removal, method 3 is the best followed by method 1 and only very little of Al can be removed by method 2. Meanwhile, method 1 is the most sufficient to remove Si, Si content in the clay after treated with method 1 was not found. This is followed by method 3 and lastly method 2. For Fe removal, method 2 is the most effective chemical treatment as shown in Table 1.

The order in which reagents were mixed and the resulting pH will greatly influence the rate of dissolution of Fe₂O₃. It was suggested that pH 7.3 is the optimum pH for the most effective and rapid removal of free ion oxides (Mehra and Jackson, 1960).

Purified clay cleaning, drying, size: After drying, the clay which treated with method 1 has the white colour. Meanwhile, clay which treated with method 2 has some yellowish on its surface before segregation. Clay which treated with method 3 is slightly greyish when compared to the method 1 clay. This difference in color can be avoided if the clay is washed with NaCl solution with more time to ensure all excess salts are dissolved. From the Table 2, 75% of the particle size distribution is larger than 710 µm, 5.65% is larger than 425 µm, 11.38% is larger than 300 µm, 13.95% is larger than 212 µm, 38.39% is larger than 75 µm and 27.91% of the soil is smaller than 75 µm. The analysis of particle size revealed that average particle size in the sieve receiver is 6.9211 µm. Besides that, there is 10% of the soil in receiver is 2 µm. Overall, only 2.81% of the IP soil is considered as clay in respect of particle size.

CONCLUSION

The moisture content of IP soil was 3.2% after two days it was collected. The most suitable temperature to dry the sample was 105°C. The best time duration for drying is 6 h. Al and Mg are the major components in the soil. Method 1 is the best to remove Si element from clay, Si was removed completely by this method. Meanwhile, method 2 is the best method to remove Fe from clay; Fe content was decreased from 8.9 to 1.418 ppm by this method. Method 3 is the most suitable to remove Al, Al concentration in the sample was decreased from 30.336 to 25.045 ppm. The clay was changed from brownish colour to white colour after these treatments.

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