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COPPER MOBILITY ASSESSMENT USING SPECIATION SCHEMES: CASE STUDY–MANTRIJERON DISTRICT, YOGYAKARTA, INDONESIA

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Abstract

Heavy metals mobility in soils is controlled by many factors such physical and chemical properties, especially mineralogical composition of such environment. This study focused on the mineralogical of two soils types (fine sandy loam and loamy fine sand) to retain/mobile Cu. Two non contaminated soils from Yogyakarta urban area, Indonesia, were artificially contaminated with Cu solution. Subsequently, soils artificially contaminated were extracted from various geochemical phases of soil by sequential extraction procedure. The results show that both of soils types can retain Cu well with maximum is 5.8 mg/g of loamy fine sand and 3.9mg/g of fine sandy loam. Additionally, the iron amorphous phase content in clay fraction is influence Cu retains in these soils. This is advantage in environment of Yogyakarta urban area, Indonesia, where this area underlain by loamy sand soil.

Keywords: *Copper, mobility, iron, sequential extraction.*

1 Introduction

Last few decades, environmental effects due to urbanization and industrialization extend very fast. Both surface water and groundwater is mainly vulnerable to contaminate from discharge of waste-water by various industries, especially in developing countries. Heavy metals is major contaminant from industry area, which represents a serious problem to environment due to their great toxicity (Bhagure and Mirgrane, 2001). Since copper is not only widespread toxic metal to environments but also “soft or intermediately soft” toxic metals. Therefore, Cu release and retain to soil much concern. Understanding of copper mobility can provide important information for remediating contamination sites as well as land use planning.

Geochemical process is an important factor control in heavy metal mobile or retain in the soil. The knowledge of how contaminants partition among the various geochemical phases allows for better insight into the mechanisms of heavy metals retention and mobile (Cabral and Lefebvre, 1998). In the past, several chemical extraction processes have been investigated for various propose (Gibson and Farmert, 1986; ANZECC and ARMCANZ, 2000; Plassard *et al*, 2000; Mullerova *et al*, 2003; Snape *et al*, 2004; Al-Zahrani and Kennichi *et al*, 2008; Abdul-Majid, 2009) such as heavy metals retention in soil/heavy production in soil, retention phase.

This study is dealing with Copper migration

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through the soils which lead to groundwater contamination. The technique of sequential extraction (Tessier *et al*, 1979 and Kennichi *et al*, 2008) was employed to assist in the determination of the partitioning of Copper, among of the geochemical phases in fine sandy loam and loamy fine sand, commonly found in urban area of Yogyakarta, Indonesia.

2 Background

Yogyakarta City is situated in Yogyakarta Special Province, Central Java Island, Indonesia, an educational, a cultural and a tourism city in Indonesia. To its north is Merapi Volcano (peak of the volcano reaches the elevation of 2911 m above sea level, Karnawati *et al*, 2006) and to its south is the Indian Sea. Based on the population census conducted in the year 2004, the population of the city has reached the numbers of 3,257,000 with the growth rate of 0.39%. Population density was 12,206.5/km^2 at the city (Karnawati *et al*, 2006). The high population growth in Yogyakarta is attributed to the high number of people that migrates into this city every year. Many establishments such as home stays, shopping center, hotels, industry and schools had been built. Since the result of population increase, the requests of humans for natural resources also increase which may cause quite serious problems of environmental degradations. One of the most important resources in Yogyakarta is shallow groundwater.

Mantrijeron District or the study areas is specifically located in the south part of Yogyakarta Special Province with elevation is 90–100 m above the sea level (Figure 2). The study area mostly covers by batik home industry areas and hotel approximately covering 30 ha.

3 Materials and methods

3.1 Materials

Two soil samples (loamy fine sand and fine sandy loam) were collected from surface depth to water table, at Mantrijeron District, Yogyakarta, Indonesia where batik home industry is dominant within this area. Two soil samples are group of sand and loamy with low clay fraction content. Loamy fine sand were collected from a depth of 1.6 m, while fine sandy loam were collected at the same location from a depth of 3.2 m. Soil properties were summary in Table 1. The soil samples were freeze-dried and sieved under 2mm before being stored for the subsequent experiment. After that, soil samples were measured mineralogy and chemical composition/extractable metals. Mineral phase and mineral chemical composition were identified by X-ray diffraction (XRD) analysis using RINT-2100V/PC diffractometer (Rigaku, Japan), although soil properties of both soils are different but mineralogy is similar (Figure **??**). The main mineral of these soil are anorthite, albite, and small amount of kaolinite and amorphous iron, while energy dispersive X-ray fluorescence spectrometer, Xepos (Rigaku, Japan) was identified for chemical composition; the major chemical composition of these soil are Si, Al , Ca and Fe which average chemical compositions were shown in Table 2. Detection of high quantity of iron in these soils (Table 2) indicated that iron oxide is an important component of these soils.

Table 1: Soil properties of soils at Mantrijeron District, Yogyakart Indonesia.

Soil Properties		
Properties	Fine sandy loam	Loamy fine sand
Bulk density (rb)	2.02	1.83
Dry density (rd)	1.62	1.56
Porosity, n (%)	40.37	43.46
Volumetic water content, V (%)	40.5	27.92
Specific gravity	2.72	2.75
Gran size		
Gravel (%)	0.61	7.81
Sand (%)	70.87	73.99
Silt/Clay(%)	28.52	18.21
Permeability (m/sec)	6.40E-06	4.80E-06

3.2 Batch experiments

Soil samples were sieve under 2mm for artificial soils procedure. Artificial soil contaminant

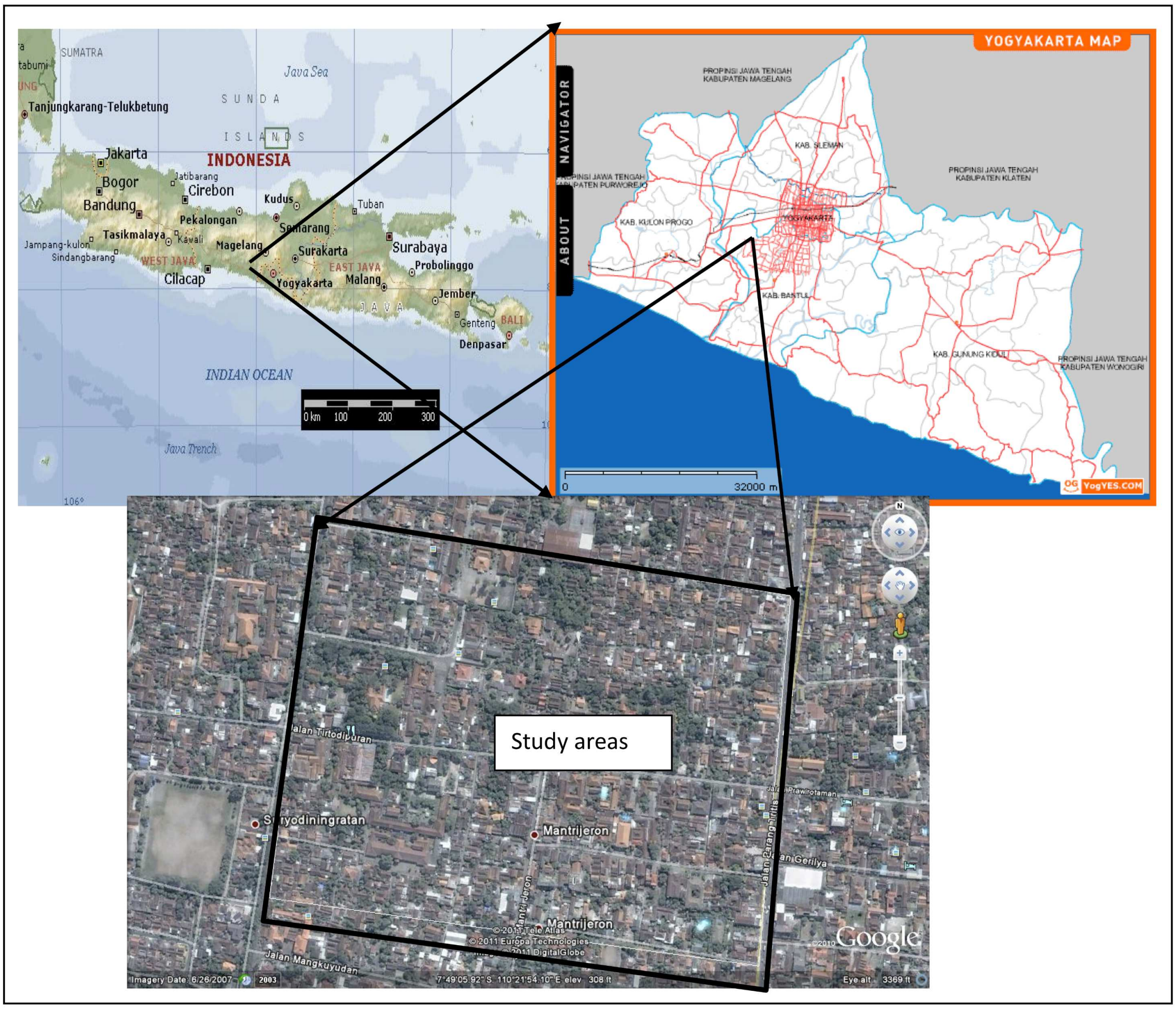


Figure 1: Study area.

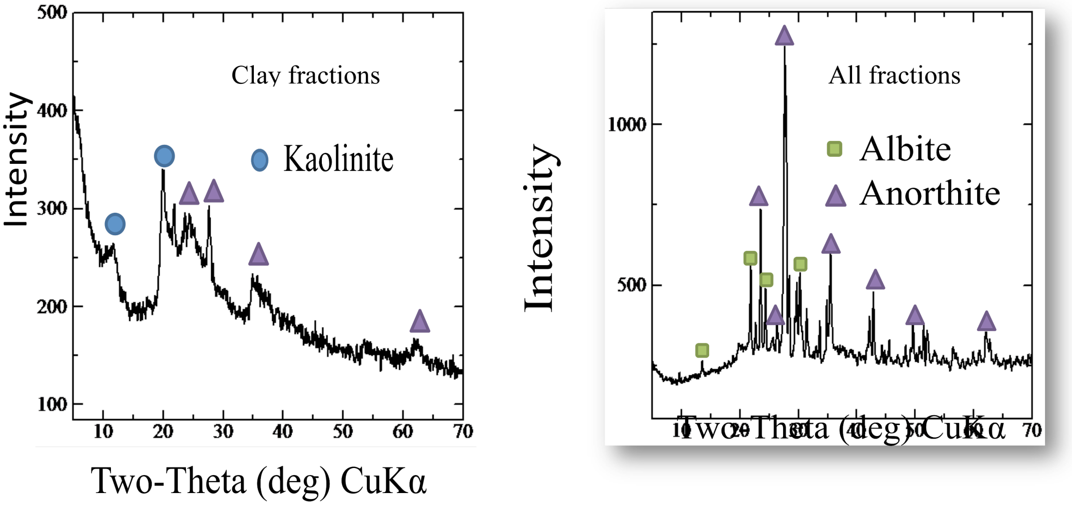
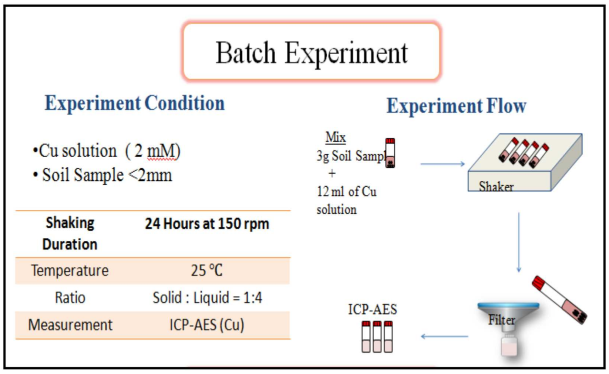


Figure 2: XRD pattern of soil at study area.

Table 2: Average Chemical Composition of Soil at Mantrijeron Dicstrict.

Chemical composition	Weight (%)
SiO_2	56.3
$Al2O_3$	21.67
CaO	8.03
Fe_2O_3	6.99
Na_2O	2.59
MgO	1.37
TiO_2	0.64
P_2O_5	0.32
MnO	0.18
SO_3	0.04
Cl	0.02
V_2O_5	0.03
Co_2O_3	0.02
CuO	0.01
ZnO	0.02
SrO	0.05
BaO	0.01
PbO	0

by Cu solution were perform by batch sorption experiments, 3g freeze-dried soils were added to 12 mL of $CuSO_4$ (2mM) solution in centrifuge tube and shake for 24 hours, the separation did by centrifuge 3000rpm for 20 minutes and filtered by 0.2μm membrane filter (Figure 3). The amount of Cu in solution was measured by ICP-AES. freeze-dry. Finally, all soil samples will and stored for sequential extraction.



Batch Experiment

Experiment Condition

- Cu solution (2 mM)
- Soil Sample <2mm

Shaking Duration	**24 Hours at 150 rpm**
Temperature	25 °C
Ratio	Solid : Liquid = 1:4
Measurement	ICP-AES (Cu)

Figure 3: Batch experiment flow.

3.3 Chemical extraction

All fraction and clay fraction of soil samples were extracted metal in geochemical phases except the one that bound to silicate by mixing 6M HCl solution (ANZECC and ARMCANZ, 2000 and Snape *et al*, 2004) with grained dry-freez soil into ratio 1:1000 of solid:solution at 80°C for 2 hr. All metals were separated by centrifuge 3000rpm for 20 minutes and filtered by 0.2μm membrane filter. Finally, Cu concentrations of each step were measured by ICP-AES.

Clay fraction of soil samples were extracted metal that bound to to amorphous, poor crystalline Iron Aluminum minerals by mixing 0.2M Ammonium oxalete solution (pH 3.0) into ratio 1:600 (solid:solution) at room temperature for 2hr with darkness condition. This extraction call TAO extraction (Kennichi *et al*, 2008).

3.4 Sequential extraction

In past decades, sequential extraction was performed to strengthen heavy metals bonding onto mineral surfaces in many fields of researches (Tessier *et al*, 1979; Plassard *et al*, 2000; ANZECC and ARMCANZ, 2000; Mullerova *et al*, 2003; Kennichi *et al*, 2008). In this study, artificial soil contaminant was prepared by ground to become powder, soil samples (2g) from batch experiments were processed five steps of extraction from Kennichi, *et al* (2008) (Table 3) to determine the dominant form of Cu in the soil.

(F1) Water extraction: metal phases soluble with water. By mixing dieonized water (pH 5.8–6.3) into ratio 1:10, 2g of soil with 20ml of deionized water at room temperature for 6hr.

(F2) MgCl extraction: the residue from (F1) were added to 1M $MgCl_2$ solution (pH 7.0) into ratio 1:25 (solid:solution) at room temperature for 4hr, apportion of exchangeable matals was obtained.

(F3) TAO extraction: the residue from (F2) was added to 0.2M Ammonium oxalete solution (pH 3.0) into ratio 1:600 (solid:solution) at room temperature for 2hr with darkness condition, metals bound to amorphous, poor crystalline iron and aluminum minerals were acquired.

(F4) CDB extraction: metals bound to iron minerals were obtained by mixing the residue from (F3) with 0.3M Sodium acid citrate, 0.2M Sodium hydrogen carbonate and 0.1g/L Sodium dithionite (pH 8.5) into ratio 1:100 of solid:solution at 80°C for 30 min.

(F5) HCl extraction: the residue from (F4) was mixed with 6M HCl into ratio 1:1000 of solid:solution at 80°C for 2hr, metals bound to clay mineral was gained.

In each step, the separation did by centrifuge 3000rpm for 20 minutes and filtered by 0.2μm membrane filter. Finally, Cu concentrations of each step were measured by ICP-AES. Summary of Sequential extraction steps are shown in Table 3 and Figure 4.

4 Result and Discussion

4.1 Batch experiment

The results of batch experiment show that loamy fine sand and fine sandy loam take up almost 100% of Cu from solution within one hour (99.95% of loamy fine sand; and 99.93% of fine sandy loam). Based on Xaixongdeth *et al*, (2012), the Cu uptake capacity of soil in the study area is correlated to the clay fraction, high clay fraction content is observed in loamy fine sand (6.61%) and fine sandy loam (4.69%), while lower clay content characterizes sandy loam (2.78%) and sand (1.89%). maximum Cu sorption capacity in loamy fine sand and fine sandy loam is 5.8mg/g and 3.9mg/g, respectively.

4.2 Chemical extraction

The amount of metals from metals extraction was agreed to XRF result which Al and Fe is main chemical composition in these soil, the summary of the result of metals extraction are shown in Table 4.

In clay fractions, the amounts of Cu that can be extracted from in amorphous iron phase were similar to amount of Cu that obtained from metals extraction. Loamy fine sand, Cu that detected from metals extraction is 164 mg/kg whereas in amorphous iron phase Cu detection is 175mg/kg. Fine sandy loam, Cu detection in metals extraction is 61.2mg/kg while Cu that detected from in amorphous iron phase is 91.8 mg/kg. Although that Cu from TAO extraction were higher than HCl extraction, the reason could be because of soil samples that was take for both TAO and HCl extraction was dry and grinded in different time which could be give a little different between TAO and HCl extraction. This can be prove that in natural soil of loamy fine sand and fine sandy loam from Mantrajeron, Yogyakarta, Indonesia, Cu sorption to these soil are influence by iron amorphous. Metals bound to clay fraction in loamy fine sand and fine sandy loam are shown in Table 5.

4.3 Sequential extraction

The result of sequential extraction showed that copper sorption to many phases in different amount. This experiment copper sorption mainly influenced by iron amorphous phase which copper detected in this phase is 86.4% (648 mg/kg) in loamy fine sand and around 65% (492.6 mg/kg) in fine sandy loam. In exchangeable phase and iron mineral phase, Cu detect in fine sandy loam better than fine sandy loam. Loamy fine sand could detect Cu 3.3% (24.77 mg/kg) in exchangeable phase and 2.84% (21.3mg/kg) in iron mineral phase, while fine sandy loam could retain Cu 15.37% (116.75 mg/kg) in exchangeable phase and 16.07% (122 mg/kg) in iron mineral phase. In contrast with exchangeable and iron mineral phase, clay mineral phase, Cu that detect in loamy fine sand higher than fine sandy loam, 7.41% (55.6 mg/kg) and 3.68% (28 mg/kg), respectively. Overall of the result of sequential extraction, Cu sorption in loamy fine and fine sandy loam are mainly in amorphous iron phase which agreed to chemical extraction, although that in another phases the result were different. The details of Cu distribution in these soils are shown on Figure 5.

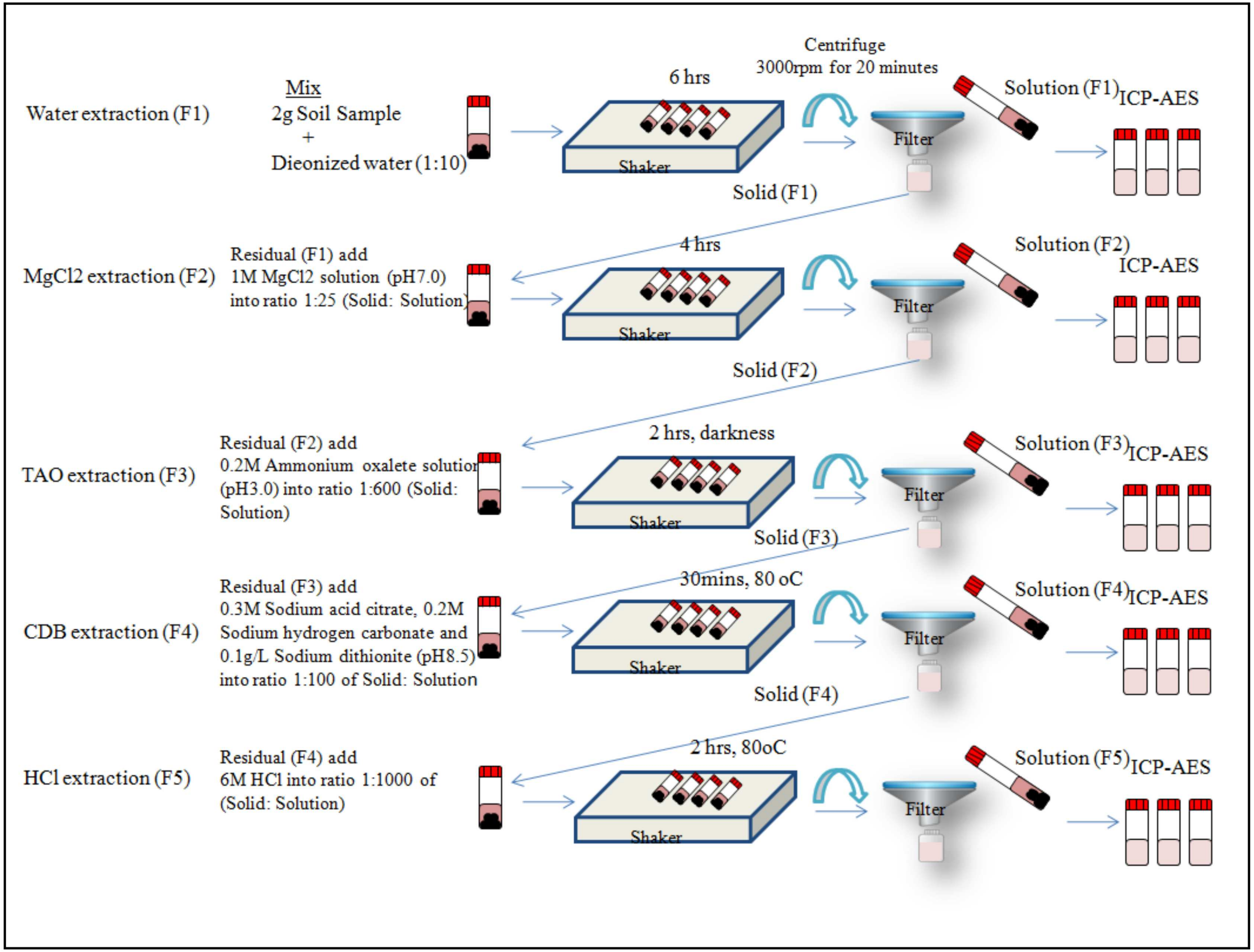


Figure 4: Experiment flow of sequential extraction.

Table 3: Selective extraction scheme: (Tessier and Campbell 1988, Plassard *et al*, 2000 and Kennichi *et al*, 2008).

Step	Method	Target	Solvent	Condition		
F1	Water extraction	Soluble ion	Deionized water(pH5.8-6.3)	10ml/g	Room Temp.	6h
F2	MgCl2 extraction	Exchangeable ion	1M MgCl2 solution(pH7.0)	25ml/g	Room Temp.	4h
F3	TAO extraction	Amorphous, poor crystalline Iron and Aluminum minerals	0.2M Ammonium oxalete solution(pH3.0)	600ml/g	Room Temp.	2h (Dark ness)
F4	CDB extraction	Iron minerals	Mixed solution by 0.3M Sodium acid citrate, 0.2M Sodium hydrogen carbonate, 0.1g/L Sodium dithionite(pH8.5)	100ml/g	80°C	30 min
F5	HCl extraction	Clay minerals	6M HCl	1000ml/g	80°C	2h

Table 4: Summary of metals extraction in mg per kg of soil.

Soil	Al*	Al**	Cu*	Cu**	Fe*	Fe**	Mn*	Mn**	Pb*	Pb**	Zn*	Zn**
Loamy fine sand	33800	85200	0	164	37000	65100	426	809	0	60	56.2	273
Fine sandy loam	33000	102000	0	61.2	31800	44800	588	2120	0	0	25	125

Note * all fractions ** Clay fractions

Table 5: Total Cu obtained from amorphous iron in clay fractions.

Sample list	Al	Cu	Fe	Mn	Pb	Zn
Loamy fine sand	9120.00	175.80	17880.00	678.00	UDL	196.20
Fine sandy loam	22140.00	91.80	23160.00	2382.00	2.70	78.00

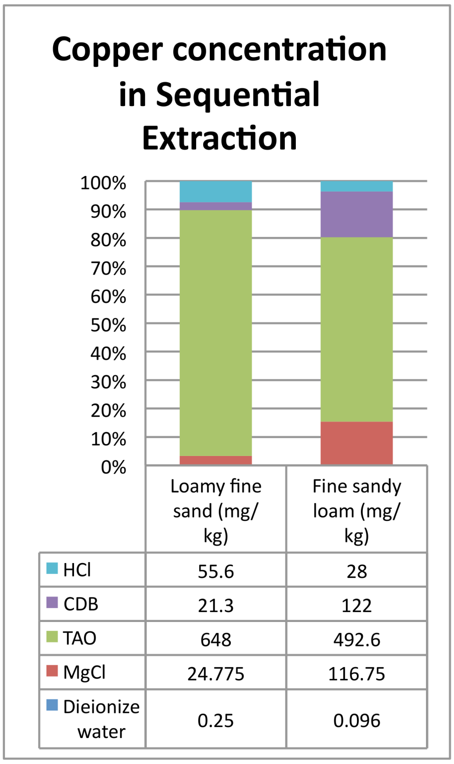


Figure 5: Distribution of Cu in soil after batch experiment with extraction phases.

5 Conclusion

Loamy fine sand and fine sandy loam from urban area at Mantrijeron, Yogyakarta, Indonesia, are good for Cu sorption (low mobility) with maximum Cu sorption capacity in loamy fine sand and fine sandy loam is 5.8mg/g and 3.9mg/g, respectively. Cu distribution in both soil were many phases in different amount. Sequential extractions strong agree to the result from chemical extraction, which Cu distribution influenced by amorphous iron in clay fraction.

According to result of chemical extraction and sequential extraction, can be concluding that iron amorphous in clay fraction was influenced for Cu sorption (mobility) in these soil. This is advantage in environment of Yogyakarta urban area, Indonesia, where this area underlain by loamy sand soil amorphous were influenced for Cu sorption in this study area.

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