Techno-Science Research Journal 4 (2016) 49-61

Content list available at ITC

Techno-Science Research Journal

Journal Homepage : www.itc.edu.kh

Techno-Science Research Journal

MODIFIED ZEOLITE AND BENTONITE AS ADSORBENTS OF HEAVY METAL IONS FROM POLLUTED GROUNDWATER IN YOGYAKARTA URBAN AREA, INDONESIA

Bunchoeun PICH[1], I Wayan WARMADA[2], Heru HENDRAYANA[2], and Tetsuro YONEDA[3]

[1,2]Department of Geological Engineering, Faculty of Engineering, Gadjah Mada University, Yogyakarta, Indonesia
[3]Division of Solid Waste, Resources and Geo-environmental Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, Japan

ABSTRACT
Groundwater quality in Yogyakarta city has become the major concern due to the presence of heavy metals originated from batik home industries, slaughterhouses, and leather factories, especially in shallow groundwater. In response to the above problems, the naturally abundant zeolite and bentonite in Sidomulyo and Bandung areas were respectively sampled along with the metal-containing groundwater in Yogyakarta urban area for batch adsorption experiment. Before put into experiment, the zeolite and bentonite were characteristically investigated by means of XRD, SEM, chemical composition, and physical property analyses. Also, they were thermally activated to improve their qualities in terms of increase in CEC, whereas the groundwater was analyzed for heavy metal concentrations (Cd, Cr, Cu, Fe, Zn) and its physical property. Five logarithmic amounts of this modified zeolite or bentonite were separately and incrementally introduced into the same three solutions of heavy metals. After the experiment, all the solutions were re-analyzed for the rest of heavy metals to figure out the optimum adsorption capacity of zeolite and bentonite. The outcomes of this experiment will be beneficial in enhancing the groundwater quality for consumptions in Yogyakarta city as well as other places in Indonesia, and will also imply the zeolite and bentonite in commercialization.

Keywords: *zeolite, bentonite, groundwater, heavy metal, adsorption*

INTRODUCTION

Background
Yogyakarta urban area is considered as a place facing groundwater problems. As a result of landuse development, the groundwater quality has been significantly deteriorating due to the human activities which lead to the groundwater pollution sources such as the oil stocks, batik home industries, slaughter houses, and leather factories. According to the previous researches of the graduate students (e.g. Keophousone, 2007; Huyen, 2007; Raksmey, 2007), the contaminants or pollutants namely heavy metals, nitrates, organic substances, coli-form bacteria, and viruses are mostly found in shallow groundwater; amongst these contaminants, the heavy metal ions such as lead (0.32 mg/l), chrome (0.47 mg/l), iron (0.06 mg/l), copper, cadmium, and zinc are the major concern of the locals. The researches have been conducted just to assess the groundwater contaminant loading potential (Keophousone, 2007), to model the groundwater flow (Huyen, 2007), and to map the groundwater vulnerability (Raksmey, 2007) in Yogyakarta urban area, not yet has any research on real groundwater remediation been done there.

In response to these groundwater problems, the natural zeolite (zeolitic tuff) which is abundant in the Sidomulyo area, Gunung Kidul Regency, Yogyakarta Special Province and natural bentonite (bentonitic tuff) which is mostly present in the Bandung area, Boyolali Regency, Central Java, Indonesia are utilized in this research as adsorbents, based on their appropriate characteristics resulted in the previous researches by using zeolite as an adsorbent (Prasetya *et al.*, 2006) and a fertilizer (Idrus *et al.*, 2006; Titisari *et al.*, 2006), and using bentonite as an adsorbent (Vega *et al.*, 2005) and a diarrhea healer (Titisari *et al.*, 2007), to remove or adsorb the heavy metal ions from the groundwater in Yogyakarta urban area. The outcomes of groundwater treatment under the aid of rock-forming zeolite or bentonite will be beneficial in enhancing the quality of groundwater for the consumption in Yogyakarta city as well as in other places in Indonesia. Moreover, the experiment results will imply the quality of zeolite and bentonite in stimulating the development of their industrial applications.

Objectives
This research is implemented:

1. to characterize the zeolite and bentonite involving the quality studies about mineralogy, chemical composition, physical properties in an initial or un-activated condition (natural zeolite and bentonite);

2. to improve the quality of the zeolite and bentonite in terms of cation exchange capacity (CEC) at the optimum condition of heating temperature and duration (modified zeolite and bentonite);

3. to experiment on the heavy-metal adsorption capacity of the modified zeolite and bentonite in the real polluted groundwater by method of batch adsorption; and
4. to interpret the adsorption data in forms of capacity curve or adsorption isotherm by focusing on the heavy-metal adsorption effectiveness of the modified zeolite and bentonite in terms of speed and their concentrations.

Study Areas

Since this research is the integrated work between groundwater and minerals, the research work are conducted in two different sample-collected areas as shown in Figure 1: (1) groundwater: from most polluted dug-well in Yogyakarta urban area with the coordinate of X = 0430901 and Y = 9136764 (Fig. 2 & Fig. 6), and (2) minerals: zeolite and bentonite respectively in Sidomulyo Village, Gedangsari District, Gunungkidul Regency, Yogyakarta Special Province and in Bandung Village, Wonosegoro District, Boyolali Regency, Central Java, Indonesia (Fig. 3, Fig. 4, & Fig. 5). The groundwater sample's location is chosen due to the result of groundwater analysis of Keophousone (2007) and the mineral samples' locations are selected based on their dominances and occurrences resulted in the preliminary studies of Idrus *et al.*, 2006; Idrus *et al.*, 2007; and Titisari *et al.*, 2006 for zeolitic tuff and of Titisari *et al.*, 2006; Titisari *et al.*, 2007; and Suwasti, 2005 for bentonitic tuff.

Hydrogeology of Yogyakarta Urban Area

Due to the hydrogeological stratigraphy, the aquifer type of Yogyakarta urban area is the unconfined aquifer system with shallow groundwater composed of top soil and unconsolidated rocks such as thick coarse sand layers followed by thin layer of gravel, thick layer of middle coarse sand. The previous researches of Keophousone (2007), Raksmey (2007), and Huyen (2007) indicate that most groundwater flows from north-east to south-west (Fig. 2) with approximately 72-104 m contour line of water table and the rivers are mostly gaining streams (effluents) namely the Winongo River and the Code River.

Regional Geology of the Sidomulyo Area

Located in the northwestern part of the Southern Mountain, Sidomulyo (Fig. 3) is an area belonging to the Kebobutak Formation which is composed of interbedding sandstone, vitreous tuff and zeolitic green stone layers which are the Late Oligocene – Lower Miocene in age (Soeria-Atmadja *et al.*, 1991). This area is comprised of Oligocene-Miocene volcano-clastic sediments whose layers relatively dip towards the south (van Bemmelen, 1970). The zeolitic tuff unit is a member of the Kebobutak Formation which is covered conformably by the Semilir Formation characterized by dacitic breccia, dacitic pumice tuffaceous and white tuff (Marks, 1957).

Regional Geology of the Bandung Area

Located in the western part of the Kendeng Anticlinorium, Bandung (Fig. 4) is an area belonging to the Kerek Formation whose lower part consists of interbedding of argillaceous marl, marl, claystone, and intercalation of calcareous tuff sandstone, tuffaceous sandstone, and calcarenite; whose middle part is found interbedding of claystone and pyroclastic rocks; and whose upper part is the clastic limestone. This area is among the faults which are the boundary of the unit lithology on different formations: the Pelang Formation is covered conformably by the Kalibeng Formation and is overlaid conformably by the Kerek Formation (Genevraye and Samuel, 1972).

METHODOLOGY

A total of 6 natural zeolite samples from the Sidomulyo area, Gedangsari district, Gunungkidul regency, Yogyakarta special province along with the totally 6 natural bentonite ones from the Bandung area, Wonosegoro district, Boyolali regency, central Java, Indonesia were analyzed in terms of mineralogical characteristics (XRD investigation and SEM observation), chemical composition analyses (major oxides), and physical property analyses (CEC and pH). These Sidomulyo zeolitic tuffs and the Bandung bentonitic tuffs were investigated by the XRD equipment at the Geochemistry Laboratory, Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Indonesia. Also, they were observed by SEM equipment at the Quarter Geology Laboratory, Geology Survey Center, Bandung, Indonesia. The chemical composition analyses (ICP-MS) were done in Canada, but the physical property (initial/un-activated CEC and pH) were analyzed in the Chemical Engineering Department, Faculty of Engineering, Gadjah Mada University, Indonesia. Moreover, these tuffs were thermally activated at the Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Indonesia in order to improve their qualities in terms of increase in CEC before put into the batch adsorption experiment with solution of heavy metal concentrations. Meanwhile, the metal-polluted groundwater sample was analyzed for initial concentrations of five heavy metals of case study, namely Cd, Cr, Cu, Fe, Zn at the Hydrology Laboratory, Geography Faculty, Gadjah Mada University, Indonesia and it was re-analyzed for their final/remaining concentrations after the experiment. The treatment of polluted groundwater itself by method of batch adsorption was done at the Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Indonesia. The entire research methodology can be seen in Figure 7. The results of the analyses and the experiment are beneficial in interpreting the characteristics and the adsorption capacity of the zeolite and bentonite and in enhancing the quality of groundwater in Yogyakarta urban area.

Characterization

Physical Properties

The Sidomulyo zeolitic tuff (Fig. 5) is predominantly composed of zeolite mineral and tuff. It is physically green in color, clastic-textural, coarse-fine, and grain-sized (Idrus *et al.*, 2006), whereas the Bandung bentonitic tuff (Fig. 5) abundantly contains montmorillonite mineral and tuff. It is grayish-white in color, conchoidal-fractural, earthy-plastic when moistened, argillaceous-odorous when breathed upon (Titisari *et al.*, 2006). In terms of physical property, the cation exchange capacities (CEC) of the Sidomulyo zeolitic tuff and the Bandung bentonitic tuff in the initial/un-activated condition are 44.4 mgr.eq.Na_2O/100 gram zeolite and 20.0 mgr.eq.Na_2O/100 gram bentonite, respectively.

Chemical Compositions

Due to the late result from Canada, the chemical compositions in terms of major oxides/elements of the Sidomulyo zeolitic tuff and the Bandung bentonitic tuff, however, can be expected based on the previous studies (Table 1) in the Gedangsari and Wonosegoro areas. Idrus *et al.* (2006) and Idrus *et al.* (2007) indicated, from geochemistry analysis, that the Sidomulyo zeolite (Gedangsari) is composed of 72 wt. % of SiO_2, 9-11 wt. % of Al_2O_3, 1.6 wt. % FeO, 0.8-1.2 wt. % of MgO, 3.3-4.5 wt. % of CaO, 1.1-1.5 wt. % of Na_2O, 0.7-1 wt. % of K_2O, and 8 wt. % of H_2O. Another study of Titisari *et al.* (2006) in the Gedangsari area revealed that the zeolitic tuff contains 53.27 wt. % of SiO_2, 11.12 wt. % of Al_2O_3, 2.20 wt. % of K_2O, 3.17 wt. % of Na_2O, 5.08 wt. % of Fe_2O_3, 0.02 wt. % of MnO, 0.14 wt. %, and 3.17 wt. % of CaO. As for the Wonosegoro, Titisari *et al.* (2007) showed that the bentonitic tuff is comprised of 53.92-62.98 wt. % of SiO_2, 0.50-0.93 wt. % of TiO_2, 15.17-21.58 wt. % of Al_2O_3, 0.40-3.17 wt.% of FeO, 2.81-4.28 wt. % of Fe_2O_3, 0.03-0.13 wt. % of MnO, 1.47-2.32 wt. % of MgO, 1.44-3.84 wt. % of CaO, 0.31-1.33 wt. % of Na_2O, 0.64-1.89 wt. % of K_2O, and 3.59-7.66 wt. % of H_2O.

XRD Analyses

The XRD analysis result shows that the Sidomulyo zeolitic tuff bears several types of minerals namely clinoptilolite-heulandite, mordenite, montmorillonite, quartz, plagioclase (albite), and orthoclase (Fig. 8). This agrees with the result of Idrus *et al.* (2006) but it is just that, in this study, the clinoptilolite can be seen more than the mordenite which is opposite from that of Idrus *et al.* and this is maybe because of different locations of samplings. The Bandung bentonitic tuff from the XRD result displays the content of montmorillonite, clinoptilolite-heulandite, quartz, illite, kaolinite, chlorite, plagioclase (albite & anorthite), and orthoclase (Fig. 8). This also agrees with the findings of Titisari *et al.* (2006).

SEM Analyses

The SEM analysis results are late during this time. However, several results from the previous studies in the same areas could be used as references. The SEM results of Idrus *et al.* (2006) and of Titisari *et al.* (2006) exhibit the structural characteristics of the Gedangsari zeolite (Sidomulyo) and the Wonosegoro bentonite (Kedungbedah). From the photomicrograph of the Gedangsari zeolite (Fig. 9), the tabular structure of clinoptilolite, the fibrous structure of mordenite, the webby structure of montmorillonite can be clearly recognized and identified. Regarding the Wonosegoro bentonite, the photomicrograph exposes the webby structure of montmorillonite (Fig. 9), the blade structure of clinoptilolite, the hairy structure of illite, and the sheet structure of dickite. Also, volcanic glass altered to zeolite and clay minerals can be detected in the photomicrographs of the rocks. This can prove to the results of XRD analyses that the Sidomulyo rock and the Bandung rock are certainly the zeolitic tuff and the bentonitic tuff.

Activation Process

Referring to the previous researches of Idrus *et al.* (2006) and Titisari *et al.* (2007), the optimum condition for activation process is suggested at the heating temperature of 250 ºC during 1 hour for the Sidomulyo zeolitic tuff and that of 300 ºC during 1 hour for the Bandung bentonitic tuff. Following this, the CEC of the Sidomulyo zeolitic tuff and the Bandung bentonitic tuff are then increased to 65.3 mgr.eq.Na_2O/100 gram zeolite and 28.6 mgr.eq.Na_2O/100 gram bentonite, respectively.

Groundwater Analyses

With the equipment of AAS (atomic absorption spectrophotometer), the initial concentrations of heavy metals containing in the Yogyakarta urban area groundwater can be identified: Cd^{2+} = 0.01 ppm, Cr^{6+} = 0.04 ppm, Cu^{2+} = 0.14 ppm, $Fe^{2,3+}$ = 0.02 ppm, and Zn^{2+} = 0.11 ppm. Determined by pH meter, the groundwater sample has pH of 6.7. Comparing to the guideline of drinking water standard (WHO), this kind of groundwater could give adverse impacts to health. For this reason, the groundwater is considered polluted and need to be treated.

Adsorption Experiment

Materials

1. 2 minerals: modified zeolite and modified bentonite (Fig. 5)
2. 5 heavy metals: Cd, Cr, Cu, Fe, Zn in a solution of 1 groundwater sample (Fig. 6)
3. 15 reaction glasses

Limitations

1. 250 ml of solution of heavy metals
2. initial metal concentrations in solution are known

3. solution solubility (pH) is known and is re-measured after the experiment
4. particle size (-100+200 mesh)
5. ambience temperature (tº = 25 ºC)
6. duration needed (t = 24 h)

Procedure

The experiment on groundwater treatment using modified zeolite and bentonite with the method of batch adsorption is done by mixing the considerate amounts of zeolite and bentonite with the solution of heavy-metal concentrations in reaction glasses. Five logarithmic amounts of the modified zeolite and bentonite are chosen: 1 g, 2 g, 4 g, 8 g, and 15 g. These 5 amounts are called five data points to plot a capacity curve or adsorption isotherm of the zeolite and bentonite. Each amount of the modified zeolite and bentonite requires 3-time experiments (for correlations of each data point), done at the same time, leaving 24 hours of mixing time (considered enough to achieve equilibrium conditions) at constant temperature (25 ºC), to keep adsorbent (zeolite or bentonite) in suspension (polluted solution – zeolite or bentonite) and to allow the ion exchange reaction between the cations Na^+, K^+, Ca^{2+}, Mg^{2+} of the modified zeolite and bentonite with the ions (Cd^{2+}, Cr^{6+}, Cu^{2+}, Fe, and Zn^{2+}) of heavy metals in solution. After the experiment, all the solutions are re-analyzed by AAS (atomic absorption spectrophotometer) for the rest of heavy metals to figure out the optimum adsorption capacity of zeolite and bentonite. The formula to calculate the cation adsorption capacity (CAC) or the concentrations of heavy metals adsorbed by the modified zeolite or bentonite is expressed below:

$$CAC = \frac{C_i - C_f}{C_f} \times 100 \quad \text{or} \quad C_{ads} = C_i - C_f$$

where: CAC: cation exchange capacity (percentage adsorption/extraction)
C_{ads}: concentration of heavy metal adsorbed by zeolite or bentonite
C_i : initial concentration of heavy metal (before the experiment)
C_f : final concentration of heavy metal (after the experiment)

Then the data obtained are collected and organized by statistic software SPSS (statistic package for the social science) to make adsorption isotherm in order to easily interpret the adsorption capacity of the modified zeolite and bentonite as well as the heavy metal ions adsorbed by them as shown in an example in Fig. 10.

EXPECTED OUTCOMES

The results of the research are expected as follows:

1. The mineralogical characteristics, chemical compositions and the physical properties of the Sidomulyo zeolitic tuff and the Bandung bentonitic tuff obtained will be regarded as one more achievement in addition to the previous studies on zeolite in Gedangsari district (Idrus *et al.*, 2006; Idrus *et al.*, 2007; Titisari *et al.*, 2006) and on bentonite in Wonosegoro district (Titisari *et al.*, 2006; Titisari *et al.*, 2007) and will also be one more reference for the next studies in these areas.
2. The heavy-metal concentrations containing in the polluted groundwater from the quality analysis may also be one more result adding to the work of Raksmey (2007), Keophousone (2007), and Huyen (2007) and this result may be useful for the next researches in Yogyakarta urban area.
3. The output of polluted groundwater treatment will play an important role in solving groundwater quality problems, particularly in Yogyakarta urban area. This can results in obtaining more useable groundwater for humans with social benefit and no health impacts.
4. The effectiveness of the zeolite and bentonite as adsorbents for removing heavy-metal ions from polluted groundwater will imply their qualities and their usefulness as industrial mineral products. This result will be beneficial in improving the groundwater quality for environment and providing general understandings or education about the useful minerals.
5. The research result may also take part in stimulating other useful nature minerals' application in prospective experiment research as materials for industries and in possible commercialization as well as in developing the local economy growth, for instance other types of clay minerals.

DISCUSSION

Though this research hasn't completely finished with all results of analyses as well as the results of the experiment of groundwater treatment, based on the previous researches, the characteristics of the Sidomulyo zeolitic tuff and the Bandung bentonitic tuff can be expected to be composed of clinoptilolite-heulandite, mordenite, montmorillonite, plagioclase, quartz, orthoclase and montmorillonite, clinoptilolite-heulandite, illite, kaolinite, chlorite, quartz, plagioclase, orthoclase, respectively with the evidence of XRD results agreeing with the SEM results of previous studies of Idrus *et al.*, 2006; Idrus *et al.*, 2007; Titisari *et al.*, 2006; and Titisari *et al.*, 2007 showing the zeolite's and bentonite's structural characteristics with the presence of volcanic glasses which are their precursors. Briefly, the zeolitic tuff predominantly contains volcanic glass and clinoptilolite ($(Na,K)_6[Al_6Si_{30}O_{72}].24H_2O$) and the bentonitic tuff abundantly contains volcanic glass and montmorillonite ($Na_{0.33}[Al, Mg]_2Si_4O_{10}(OH)_2 . (H_2O)n$). Moreover, the same studies also indicated the major oxides of the zeolite and bentonite which play important roles in exchanging with the heavy-metal ions of groundwater. This is supported by the works about the utilization of zeolite as adsorbent (Prasetya *et al.*, 2006) and as fertilizer (Idrus *et al.*, 2006;

Titisari *et al*., 2006) and the utilization of bentonite as adsorbent (Vega *et al.*, 2005) and as diarrhea healer (Titisari *et al*., 2007). The ion exchange capacity of the Sidomulyo zeolitic tuff is 44.4 mgr.eq.Na_2O/100 gram zeolite and that of the Bandung bentonitic tuff is 20.0 mgr.eq.Na_2O/100 gram bentonite which are then increased to 65.3 mgr.eq.Na_2O/100 gram zeolite and 28.6 mgr.eq.Na_2O/100 gram bentonite after thermally activated at considerate duration and heat. The results of the adsorption experiment are expected that the zeolite adsorbs the heavy-metal ions faster and more effectively than the bentonite. The more amount of zeolite or bentonite is put into solution of heavy metals, the more concentrations of heavy metals will be expected to be adsorbed. Amongst the five heavy metals in the case study, the selectivity series/sequence of heavy metals for clinoptilolite (zeolite) and montmorillonite (bentonite) in the sodium form will be expected to obtain as follows: $Cd^{2+} > Cu^{2+} > Cr^{6+} > Zn^{2+}$ (Zamzow *et al.*, 1969). The authors hope that all the results of the research will be used as references for next studies, that the groundwater will be effectively treated by the modified zeolite and bentonite so that the quality of groundwater will be improved for the locals' consumption in the city with no adverse impacts on health, and the natural zeolite and bentonite will be more commercialized for industries.

CONCLUSIONS

Due to the favorable behaviour of the natural zeolite and bentonite from characterization studies and through thermal activation process to become the modified zeolite and bentonite with the increase in CEC, the Sidomulyo zeolite and the Bandung bentonite are known as good adsorbents for the removal of heavy-metal ions from groundwater. Their natural ion exchange capacities are 44.4 mgr.eq.Na_2O/100 gram zeolite and 20.0 mgr.eq.Na_2O/100 gram bentonite which are then increased to 65.3 mgr.eq.Na_2O/100 gram zeolite and 28.6 mgr.eq.Na_2O/100 gram bentonite, respectively after activation. Because of its multi-porous structure, zeolite is considered more effective and faster than bentonite in adsorption process. This is referenced by several previous studies like Prasetya *et al.*, 2006; Idrus *et al.*, 2006; Titisari *et al*., 2006; Vega *et al.*, 2005; Titisari *et al*., 2007. As expectation for the results of the adsorption experiment, the more amount of zeolite or bentonite is put into solution of heavy metals, the more concentrations of heavy metals will be adsorbed and the selectivity sequence of heavy metals for clinoptilolite and montmorillonite will be as follows: $Cd^{2+} > Cu^{2+} > Cr^{6+} > Zn^{2+}$ (Zamzow *et al.*, 1969), and at last, the groundwater is hoped to be treated and the zeolite and bentonite will be known even more useful for groundwater treatment.

ACKNOWLEDGEMENTS

The authors are thankful to the Japanese International Cooperation Agency (JICA) who funded the ASEAN University Network/Southeast Asia Engineering Education Development Network (AUN/SEED-Net) Program. Our thanks also go to Anita Yuliyanti for her cooperative assistance on the fieldwork and the laboratory work.

REFERENCES

Genevraye, P., de and Samuel, L., 1972, *Geology of the Kendeng Zone (Central and East Java)*, Proceedings of the First Indonesian Petroleum Association Annual Convention, Jakarta

Keophousone, P., 2007, *Assessment of Groundwater Contaminant Loading Potential for Yogyakarta Urban Area*, Thesis, Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Yogyakarta.

Huyen, D.T., 2007, *Groundwater Modeling in Yogyakarta Urban Area*, Thesis, Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Yogyakarta.

Idrus, A., Titisari, A.D., Sudiyo, R., and Soekrisno, R., 2006, *Development of A Zeolites-Based Industry Through and Integrated Study on Characterization Quality Improvement and Utilization as Additive Fertilizer Materials of Natural Zeolite Deposits from Yogyakarta, Indonesia*, Proceedings of Final Report of Hi-Link Project Research, Gadjah Mada University, Yogyakarta, Indonesia.

Idrus, A., Titisari, A.D., and Kurniawan, A.P., 2007, *Characteristics, Quality Improvement and Exploitation of Zeolitic Tuff of the Sidomulyo Area, Gunung Kidul Regency, Yogyakarta Special Province*, Proceedings Joint Convention Bali 2007, The 32nd HAGI and The 36th IAGI Annual Convention and Exhibition, Bali, Indonesia.

Marks, P., 1957, *Stratigraphic Lexicon of Indonesia*, Publikasi Keilmuan no 31, Seri Geologi, Pusat Djawatan Geologi, Kementrian Perekonomian R.I. Bandung, 233 p.

Prasetya, A., Purnomo, C.W., and Rifai, A., 2006, *In-Situ Heavy Metal Contained Wastewater Remediation of Small and Medium Scale Industries (SMIs) Using Natural Zeolite and Modified Fly Ash Compound*, Proceedings of Final Report of Hi-Link Project Research, Gadjah Mada University, Yogyakarta, Indonesia.

Raksmey, R., 2007, *Groundwater Vulnerability Assessment in Yogyakarta Urban Area*, Thesis, Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Yogyakarta

Soeria-Atmadja, R., Maury, R.C., Bellon, H., Pringgoprawiro, H. Polve, M., and Priadi, B., 1991, *The Tertiary Magmatic Belt in Java*, Proceedings of Symposium in the Dynamic of Subduction and Its Products, Research and Development Center of Geo-technology, Indonesia Institute of Science (LIPI), Bandung, pp. 98-121.

Suwasti, 2005, *Geology of Wonosegoro, Boyolali Regency, Central Java, Indonesia*, Geological Mapping Report, Geological Engineering Department, Gadjah Mada University, unpublished.

Titisari, A.D., Idrus, A., and Widiasmoro, 2006, *Mineralogical Characteristics of the Sampang Zeolitic Tuff, Gunungkidul-Indonesia, and its Utilization as Fertilizer*, 4th International Workshop on Earth Science and Technology, 4-5 December 2006, Kyushu University, Japan.

Titisari, A.D., and Widiasmoro, 2006, *Mineralogical Characteristics of the Kedungbedah Bentonite, Boyolali, Indonesia*, Proceedings of The 8th Field Wise Seminar on Geological Engineering Field and The 3rd International Symposium & Exhibition on Earth Resources and Geological Engineering Education, Gadjah Mada University, Yogyakarta, Indonesia, p. 309-315.

Titisari, A.D., Widiasmoro, and Idrus, A., 2007, *The Characteristics and Quality of Kedungbedah Bentonite at Wonosegoro Area, Boyolali Regency, Central Java and its Utilization for Healing (Anti-Diarrhea)*, Proceedings of Joint Convention Bali 2007, The 32nd HAGI and The 36th IAGI Annual Convention and Exhibition, Bali, Indonesia.

van Bemmelen, R.W., 1970, *The Geology of Indonesia: General Geology of Indonesia and Adjacent Archipelagoes*, 2nd ed., Vol. 1A, Martinus Nijhoff, The Haque, 732 p.

Vega, J.L., Ayala, J., Loredo, J., and Garcia Iglesias, J., 2005, *Bentonite as Adsorbent of Heavy Metals Ions from Mine Waste Leachates: Experimental Data*, 9th International Mine Water Association Congress (IMWAC), Oviedo, Spain, pp. 603-609.

Zamzow, M.J. and Murphy, J.E., 1992, *Removal of metal cations from water using zeolites*, Separation Science and Technology 27 14, pp. 1969–1984.

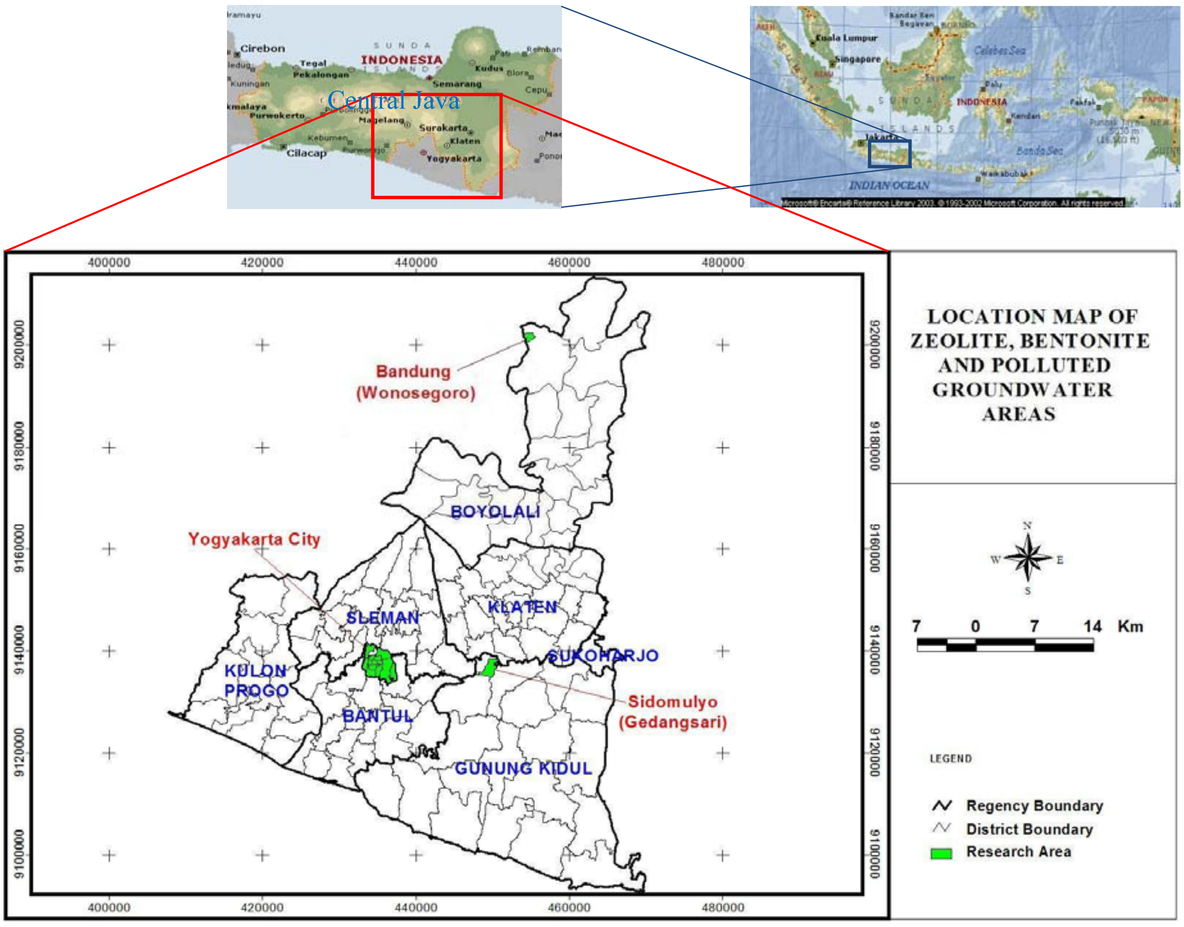

Figure 1. Location map of study areas

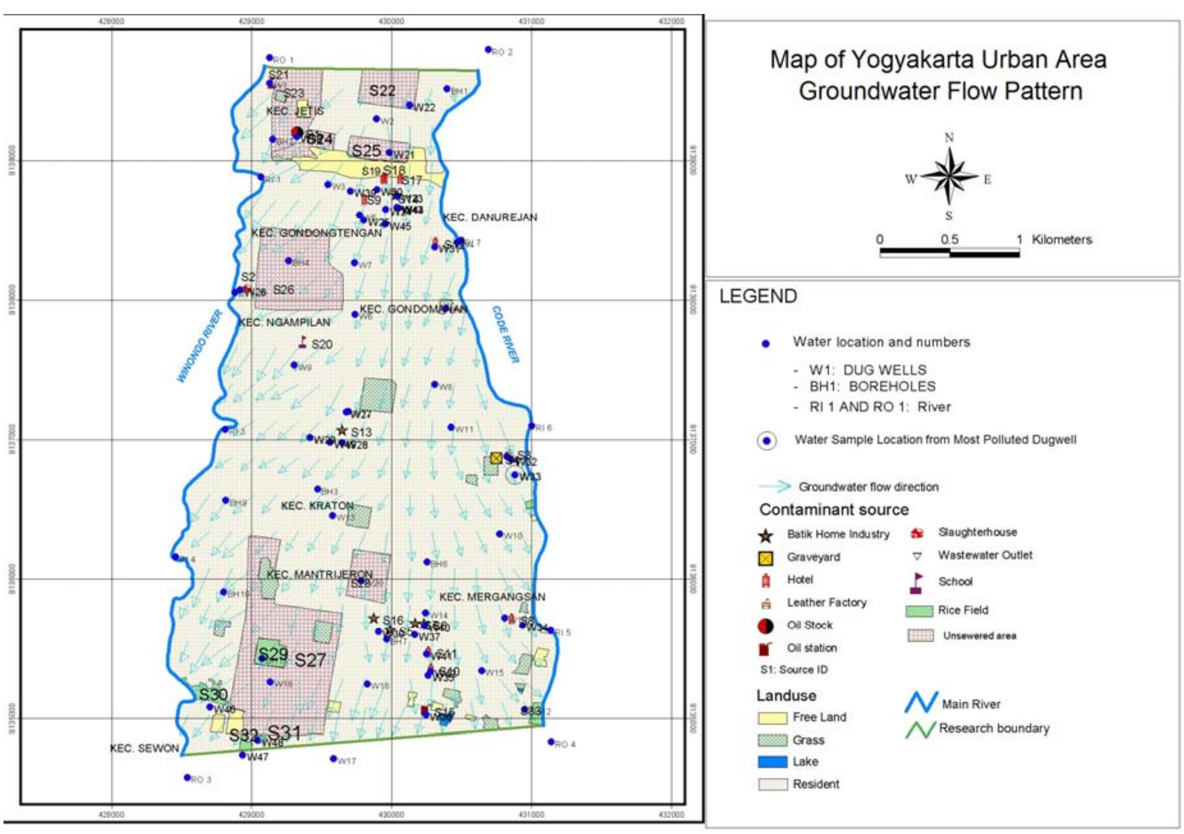

Figure 2. Map of Yogyakarta urban area groundwater flow pattern (modified from Keophousone, 2007)

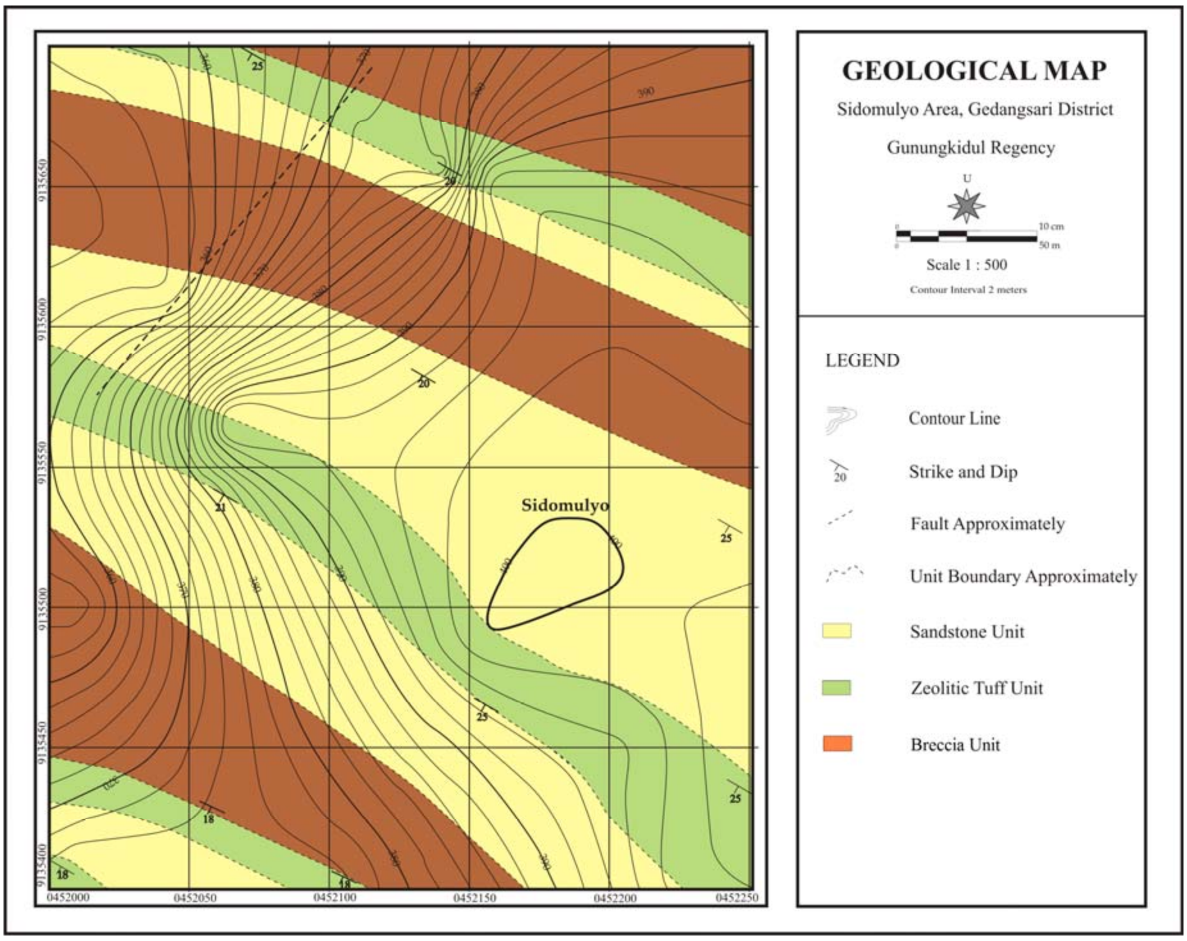

Figure 3. Detailed geological map of Sidomulyo area, Gunungkidul regency, Yogyakarta special province, Indonesia (modified from Idrus *et al.*, 2006; Idrus *et al*., 2007)

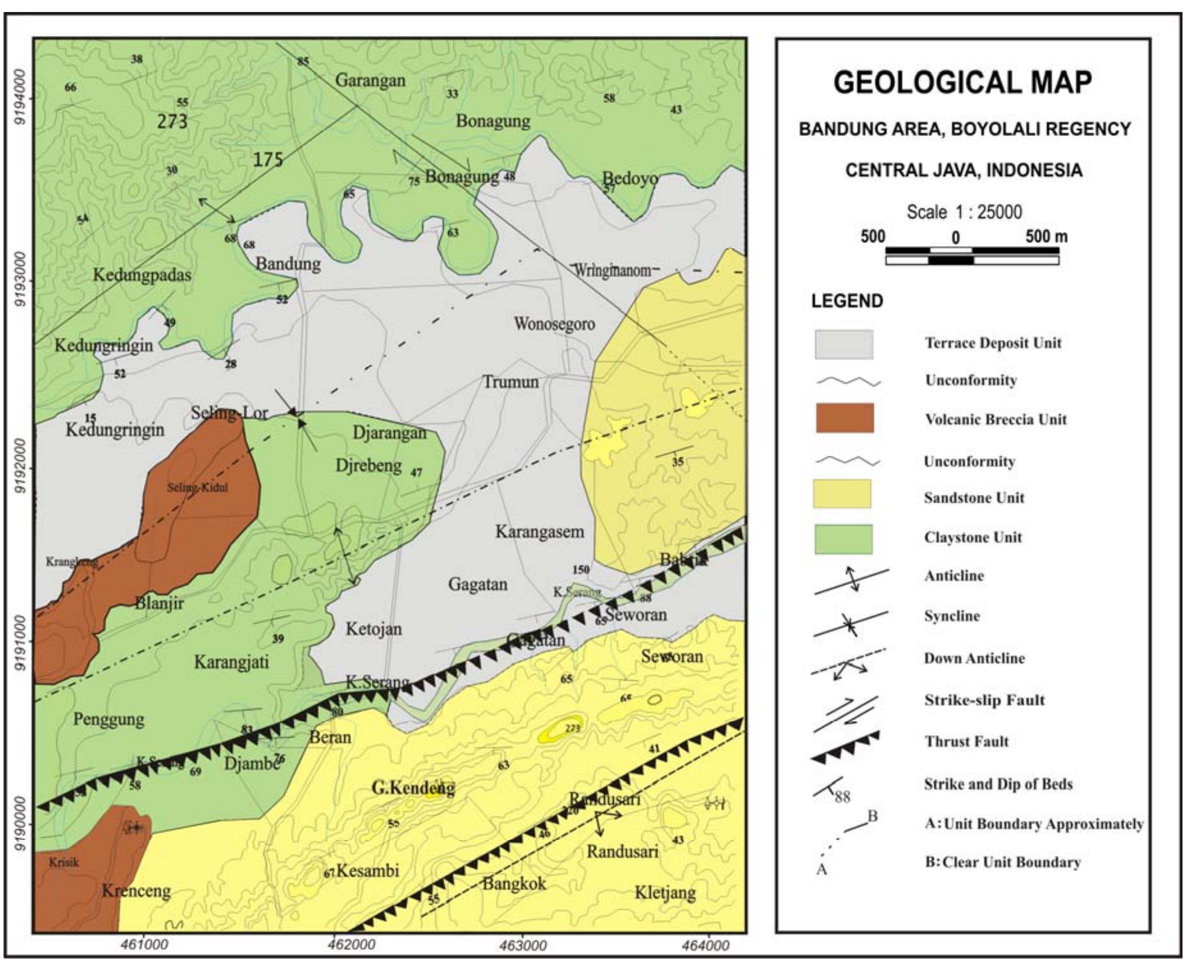

Figure 4. Geological map of Bandung area, Boyolali regency, central Java, Indonesia (modified from Suwasti, 2005)

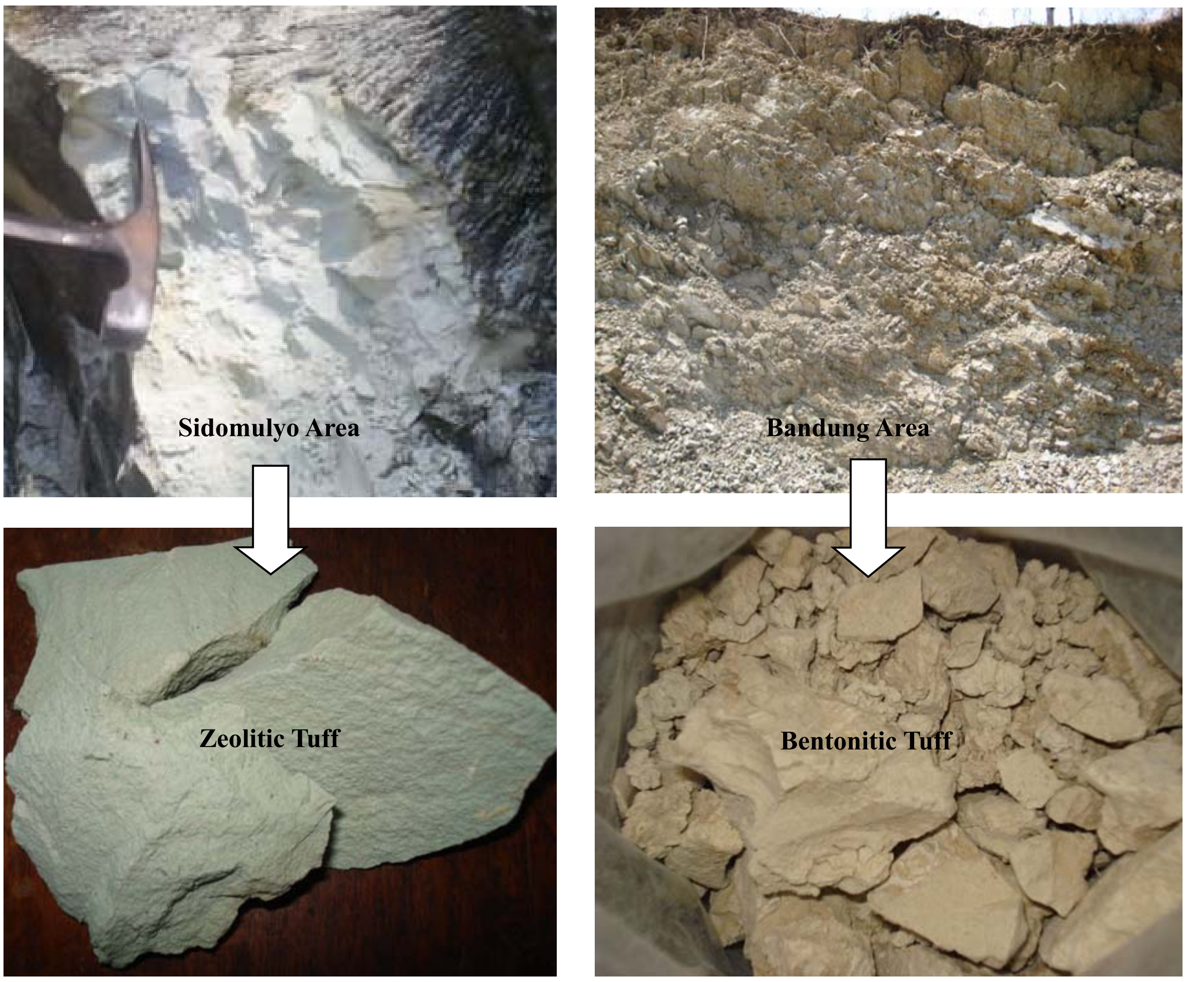

Figure 5. The surficial zeolitic and bentonitic tuff at the Sidomulyo area (Gunungkidul regency) and the Bandung area (Boyolali regency), respectively, Java island

Figure 6. Metal-polluted water from dug-well in Yogyakarta urban area

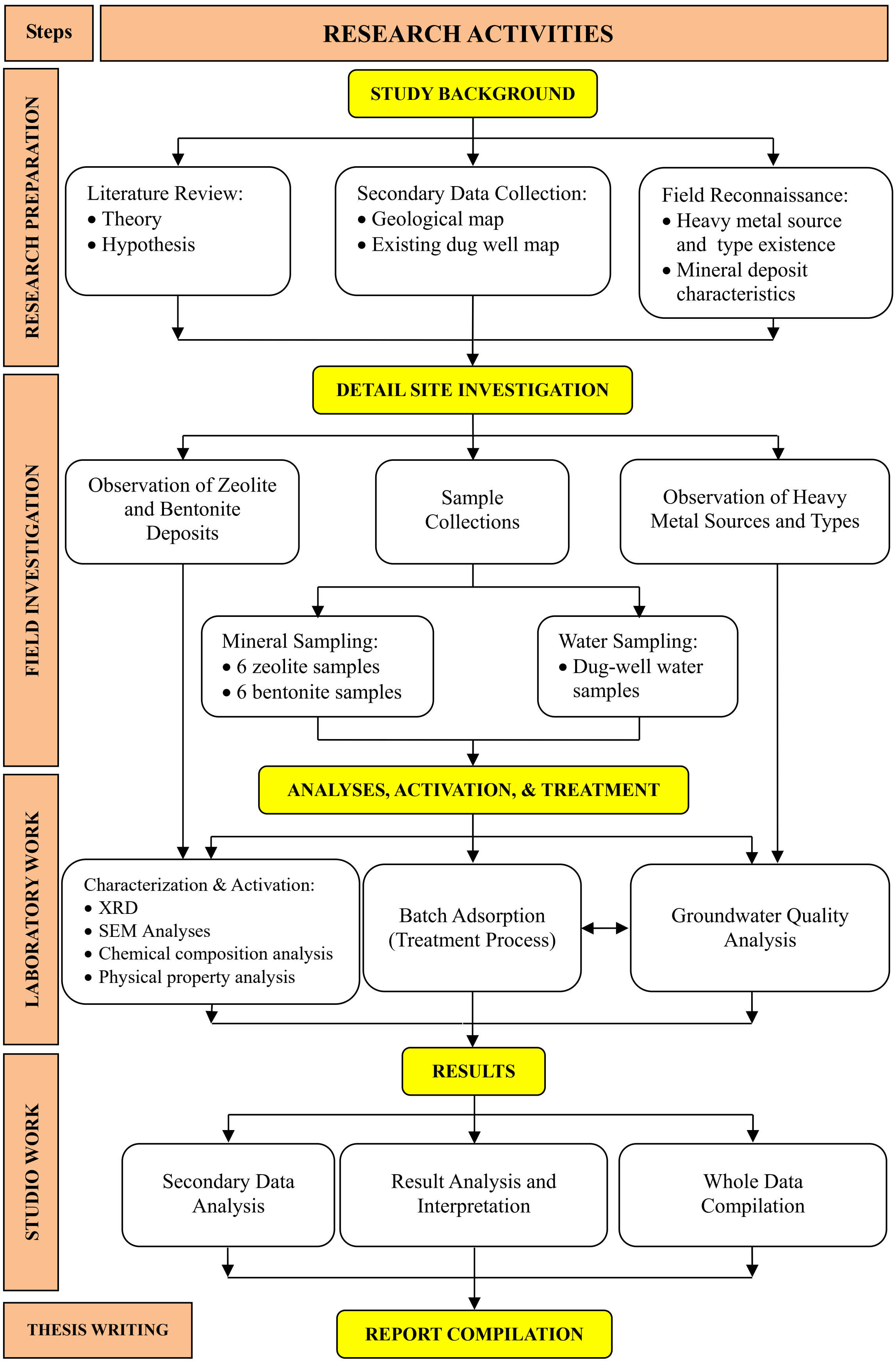

Figure 7. Flow chart of research methodology

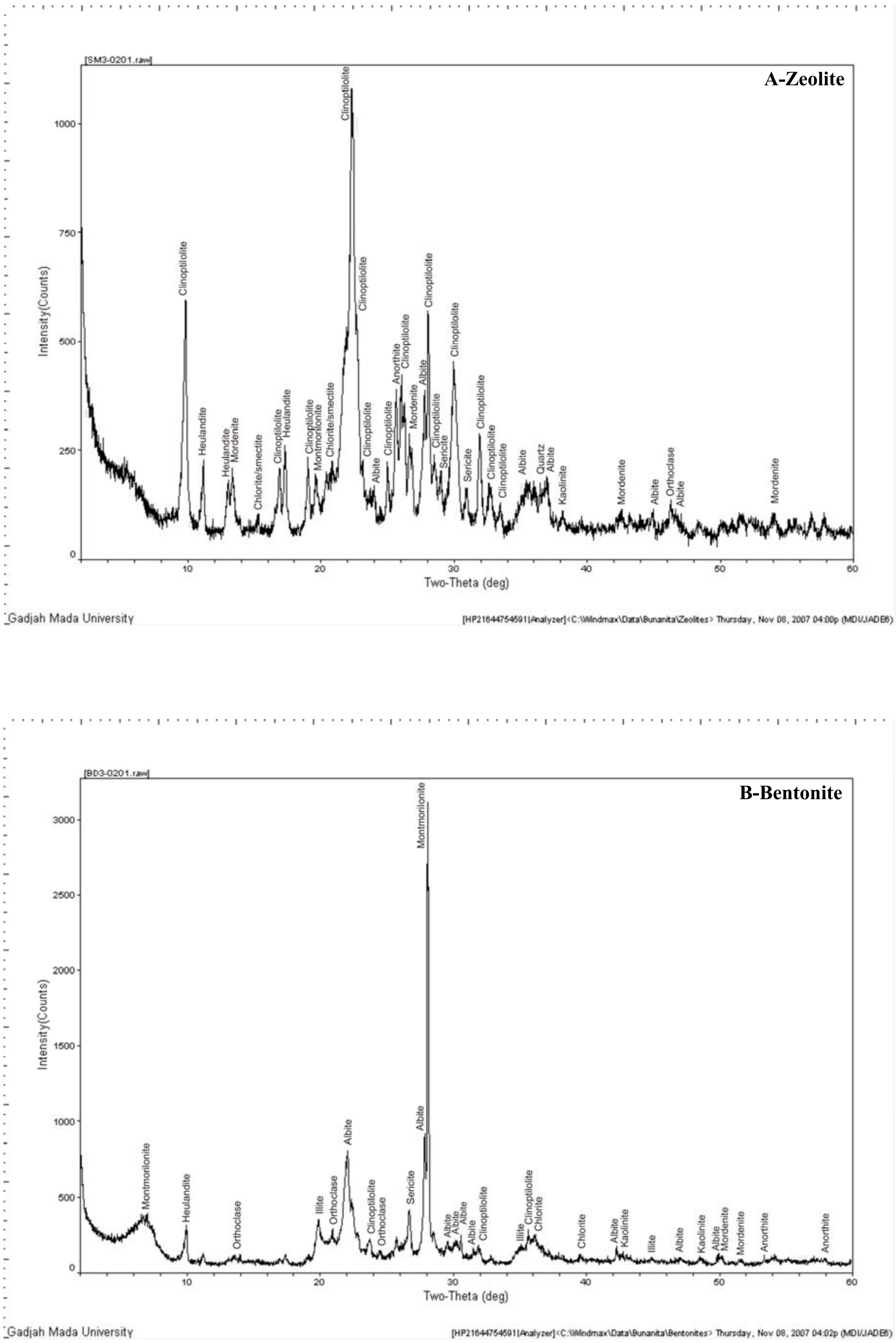

Figure 8. The XRD investigation results of the representative Sidomulyo zeolitic tuff and the representative Bandung bentonitic tuff from Gunungkidul regency (Yogyakarta special province) and Boyolali regency (central Java), respectively, Indonesia

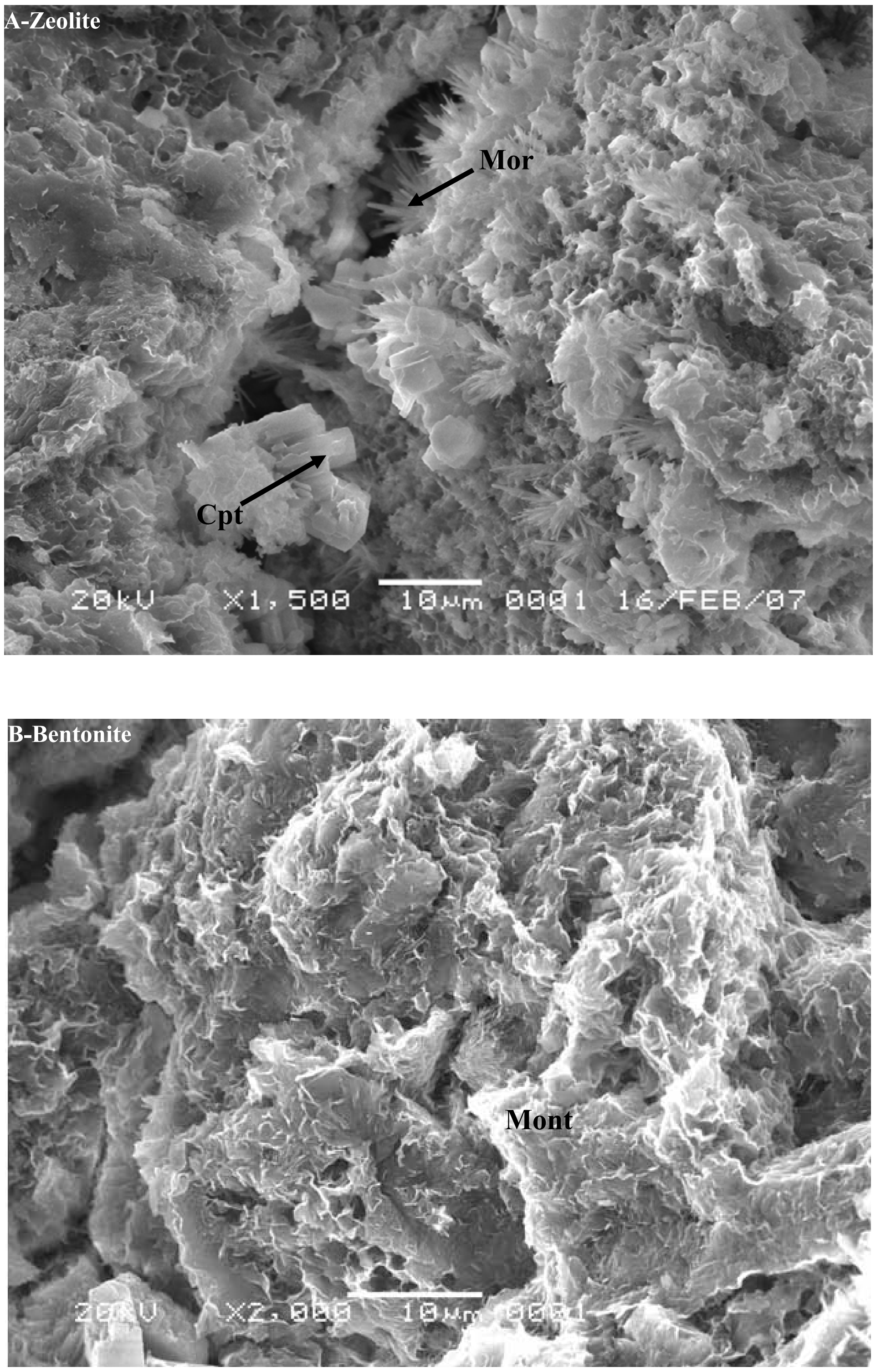

Figure 9. The SEM photomicrograph result of (A) the representative Gedangsari zeolitic tuff, showing the presence of zeolite minerals including clinoptilolite (Cpt) in tabular structure and mordenite (Mor) in fibrous structure (Idrus *et* al., 2006; Idrus *et al*., 2007), and (B) the representative Wonosegoro bentonitic tuff exhibiting the dominance of montmorillonite (Mnt) with its webby structure and other volcanic glasses (Titisari *et al*., 2006; Titisari *et al*., 2007)

Table 1. List of chemical compositions of the Gedangsari zeolite and the Wonosegoro bentonite (Idrus *et al.*, 2006; Idrus *et al.*, 2007; Titisari *et al.*, 2006; Titisari *et al.*, 2007)

Major Oxides/Elements	Gedangsari zeolite		Wonosegoro bentonite
	Idrus *et al.* (2006/2007)	Titisari *et al.* (2006)	Titisari *et al.* (2007)
SiO_2	72	53.27	53.92-62.98
TiO_2	-	-	0.50-0.93
Al_2O_3	9-11	11.12	15.17-21.58
FeO	1.6	-	0.40-3.17
Fe_2O_3	-	5.08	2.81-4.28
MnO	-	0.14	0.03-0.13
MgO	0.8-1.2	-	1.47-2.32
CaO	3.3-4.5	3.17	1.44-3.84
Na_2O	1.1-1.5	3.17	0.31-1.33
K_2O	0.7-1.0	2.20	0.64-1.89
H_2O	8.0	-	3.59-7.66

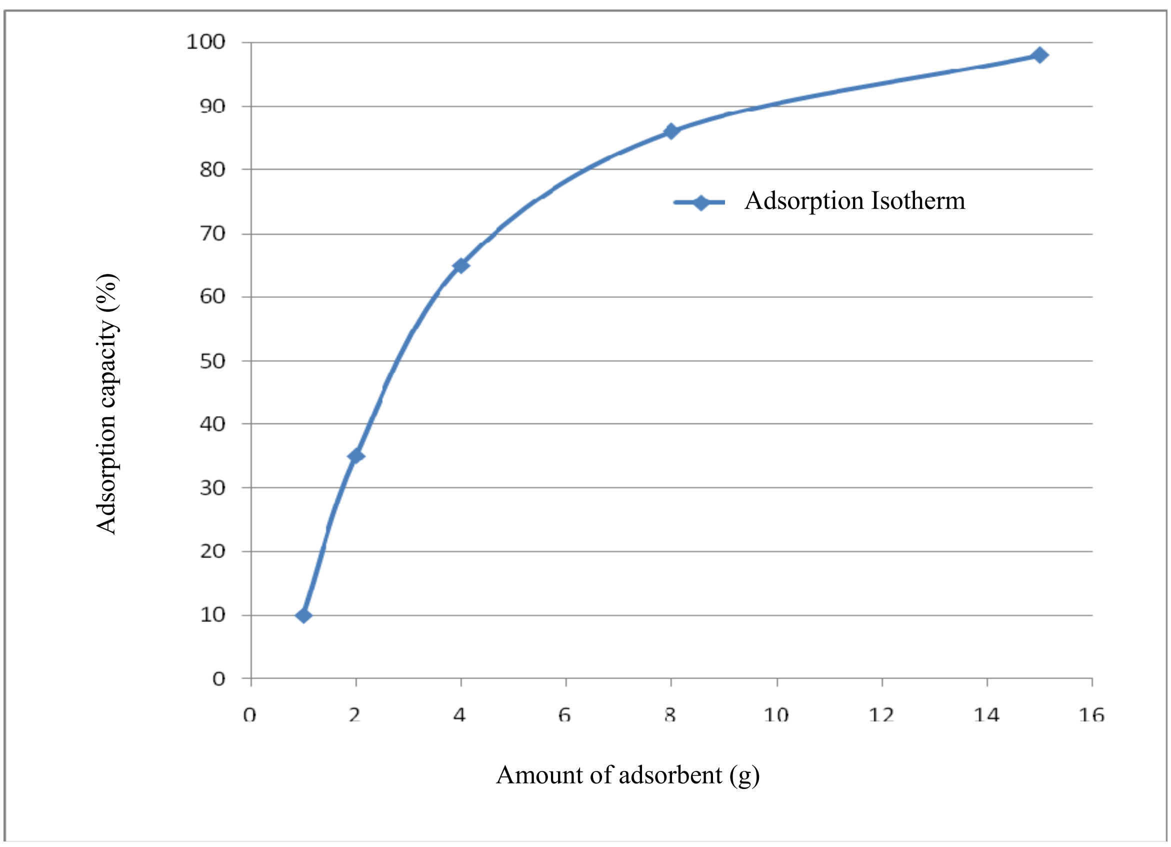

Figure 10. Typical adsorption isotherm of adsorbent (zeolite or bentonite) in terms of heavy-metal ions adsorption capacity (CAC, %) of adsorbent (zeolite or bentonite) as a function of adsorbent amounts (g)