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REMOVAL OF HEAVY METALS FROM POLLUTED DUG-WELL WATER (CASE STUDY: IN YOGYAKARTA URBAN AREA) BY UTILIZING ACTIVATED ZEOLITE AND BENTONITE IN ADSORPTION EXPERIMENT

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ABSTRACT

Due to human activities such as batik home industries, abattoirs, and tanneries, the existence of heavy metals in dug-well water has been known as the cause of groundwater pollution in Yogyakarta City. To treat this dug-well water, a batch adsorption experiment by utilizing the activated zeolite and bentonite was carried out. Prior to the treatment, the zeolite and bentonite were characterized by means of XRD, SEM, XRF, and various ICP and modified to improve their CECs by thermal activation process, whereas the dug-well water was initially analyzed for certain heavy metals like Cd, Cu, Fe, Zn, Pb by AAS. In the course of treatment, the activated zeolite and bentonite powders at the same amount of 1g, 2g, 4g, 8g, and 15 g were separately put into the natural dug-well water sample of 250 ml; all the solutions were afterwards mixed by magnetic stirrer and kept for 24 hours to reach the equilibrium condition.The results showed that the activated zeolite which contains Ca-clinoptilolite and bentonite which mostly consists of Ca-montmorillonite are potential adsorbents with the selectivity series as Pb>Cu>Zn>Fe>Cd if the metals in their contents are not taken into account. In contrast, if considered, they polluted the dug-well water.

Keywords: zeolite, bentonite, dug-well water, heavy metal, adsorption

INTRODUCTION

Due to the human activities which lead to the groundwater pollution sources such as the oil stocks, batik home industries, abattoirs, and tanneries. Yogyakarta Urban Area is considered as a place facing groundwater problems. As a result of landuse development, the groundwater quality has been significantly deteriorating. According to the research of Phonhalath (2007), the contaminants namely heavy metals, nitrates, organic substances, coli-form bacteria, and viruses are mostly found in shallow groundwater; amongst these, 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.

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 natural zeolite (zeolitic tuff) and natural bentonite (bentonitic tuff) were utilized in this research as adsorbents.

The main objectives of this study are to characterize the natural zeolite and bentonite, to improve their quality by thermal activation, and to utilize them in treating the most polluted dug-well water by method of batch adsorption experiment.

MATERIALS AND METHODS

Materials

The natural zeolite (zeolitic tuff) and natural bentonite (bentonitic tuff) from the Sidomulyo area (Gunung Kidul Regency–Yogyakarta Special Province) and the Bandung area (Boyolali Regency–Central Java), Indonesia, respectively were collected for laboratory analyses to study the characteristics and to apply for dug-well water treatment in case study of Yogyakarta Urban Area dug-well water.

Modification and Characterization

At the optimum conditions of the previous studies of Idrus *et al.* (2006) and Titisari *et al.* (2006), the natural zeolite and bentonite were modified by thermal activation during the same 1 hour at the heating temperatures of 200 °C and 300 °C, respectively. In this case, the natural zeolite and bentonite were called "*activated zeolite and activated bentonite*".

Table 1. pH and CEC Values of zeolite and bentonite

Values (CEC, $mg.eq.Na_2O.100g^{-1}$)	Zeolite	Bentonite
pH	7-9	7-9
Natural CEC	42.0	20.0
Modified CEC	44.6	28.0

Prior to the experiment, some analyses for behavior studies of zeolite and bentonite were performed such as XRD (X-ray diffractometry) at Geological Engineering Department (Gadjah Mada University, Yogyakarta–Indonesia), SEM (scanning electron microscopy) and XRF (X-ray fluorescence spectroscopy) at the Quarter Geology Laboratory (Geology Survey Center, Bandung–Indonesia), and various ICPs methods such as FUS-ICP, TD-ICP, INAA in Canada. As for the groundwater, some heavy metals such as Cd (cadmium), Cu (copper), Fe (iron), Pb (lead) and Zn (zinc) were measured as initial concentrations by AAS (atomic absorption spectrophotometer) at the Civil Engineering Department (Gadjah Mada University, Yogyakarta–Indonesia).

Batch Adsorption Experiment

The experiment on groundwater treatment using activated zeolite and bentonite with the method of batch adsorption was done by mixing the considerate amounts of zeolite and bentonite with the solution of heavy-metal concentrations in reaction glasses. Five amounts of the activated zeolite and bentonite were chosen: 1 g, 2 g, 4 g, 8 g, and 15 g.

Table 2. Chemical composition in activated zeolite and bentonite

Chemical composition	Unit	Activated zeolite	Activated bentonite
		Various ICPs	XRF
SiO_2	%	66.46	63.46
Al_2O_3	%	10.20	13.84
Na_2O	%	0.40	1.86
CaO	%	3.07	2.64
K_2O	%	1.31	0.55
MgO	%	0.92	1.53
Fe_2O_3	%	1.20	2.91
TiO_2	%	0.227	0.35
Cd	ppm	0.5	0.2
Cu	ppm	10	3
Fe	ppm	N/A	3
Pb	ppm	5	N/A
Zn	ppm	20	3

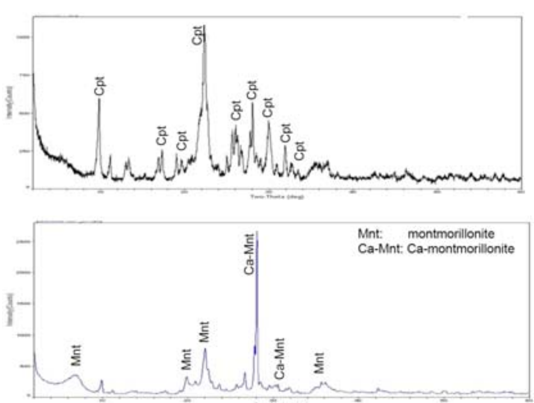


Figure 1. X-ray diffractogram of activated zeolite and bentonite

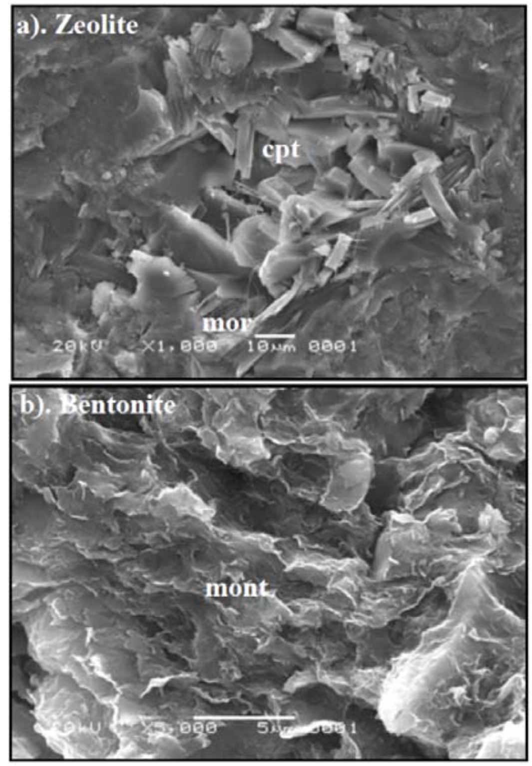


Figure 2. Scanning electron micrographs of activated zeolite and bentonite

Each amount of the activated zeolite and bentonite requires 3-time experiments for correlations of each data point, done at the same time, leaving 24 hours of mixing time which was considered enough to achieve equilibrium conditions at constant temperature of 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 activated zeolite and bentonite with the ions (Cd^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Zn^{2+}) of heavy metals in solution. After the experiment, all the solutions were re-analyzed by AAS (atomic absorption spectrophotometer) for final concentrations to interpret the adsorption capacity of zeolite and bentonite. The formula to calculate the cation adsorption capacity (CAC) or the concentrations of heavy metals adsorbed by the activated zeolite or bentonite is expressed below:

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

$$C_{ads} = C_i - C \quad \text{(Vega et al., 2005)}$$

where: CAC: cation adsorption capacity (%)

C_{ads}: concentration of heavy metal adsorbed by zeolite or bentonite (ppm)

C_i: initial concentration of heavy metal before the experiment (ppm)

C_f: final concentration of heavy metal after the experiment (ppm)

Some limitations were set for the experiment as follows: (1). 250 mL of solution of heavy metals; (2). initial metal concentrations in polluted dug-well water; (3). solution solubility (pH); (4). zeolite and bentonite powders in particle size (-100+200 mesh); (5). ambience temperature (tº = 25 ºC); and (6). duration needed (t = 24 h).

RESULTS AND DISCUSSION

Characteristics of Activated Zeolite and Bentonite

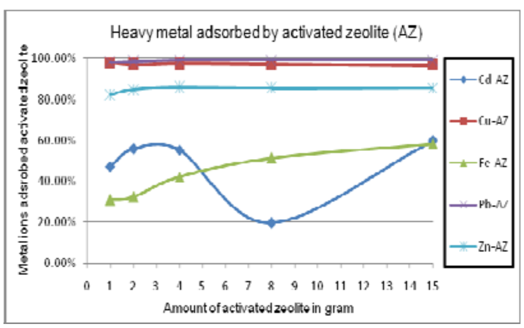
The mineralogical, composition, and physical properties of activated zeolite and bentonite have been studied. Physically, the activated zeolite and bentonite have the similar solubility of 7-9 which are base and have been improved by 2.6 mg.eq.Na_2O.100g^{-1} and 8.0 mg.eq.Na_2O.100g^{-1}, respectively (see Table 1). It can be said that the activated bentonite has more ion exchange capacity than the activated zeolite. The X-ray diffractograms in Figure 1 mostly show the presence of clinoptilolite and mordenite which are the mineral types of zeolite and the presence of Ca-montmorillonite which is the mineral type of bentonite clay. In addition, the scanning electron microscope microphotographs in Figure 2 also display these contents which assure the interpretation of results. Last but not least, Table 2 reveals the composition results of activated zeolite and bentonite which comprise of abundant silicate and alumina and also kinds of metals which these materials were utilized to treat the polluted dug-well water.

Adsorption of Metals on Activated Zeolite and Bentonite

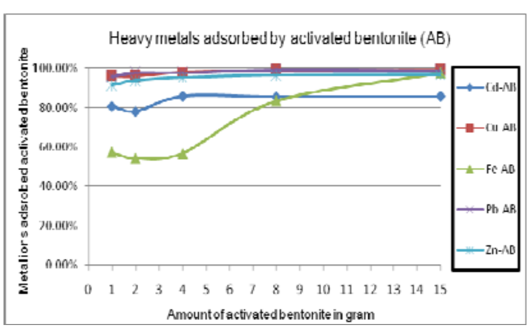
The adsorption capacities of activated zeolite and bentonite are described in Figure 3. The discussion here has not been taken the metal ions in the contents of materials. Thus, the metals adsorbed are also included both in the materials and the dug-well water.

From Figure 3.A, it can be seen that the higher amount of powdered, activated zeolite are put into the solution, the high concentration of metal ions are adsorbed by it, except that of cadmium ion which tends to be lower first and then to be higher. Amongst all the metals, lead and copper ions are much more adsorbed (up to 100%) by activated zeolite than the other ions while iron ion is least adsorbed. From this description, a selectivity sequence of clinoptilolite in the calcium form can be defined as follows: Pb>Cu>Zn>Fe>Cd. This nearly agrees well with the selectivity series of that in the sodium form by Zamzow *et al.* (1992) which determined Pb>Cd>Cu>Zn>Fe.

As for the activated bentonite, Figure 3.B shows that lead and copper ions are, as activated zeolite, higher than any other ion and the iron is the lowest ion adsorbed at initial points but is more adsorbed than the cadmium ion after 8 g of activated bentonite. It seems that all the metal ions adsorbed increase and increase nearly more than 50% at the starting points and up to 100% when more and more bentonite power is put into the solution. To make overall description to the metals adsorbed by activated bentonite, a selectivity sequence of bentonite in form of the calcium can be determined as follows: Pb>Cu>Zn>Fe>Cd.



(A)



(B)

Figure 3. Heavy metal ions adsorbed by (A)-activated zeolite (AZ) and (B)-activated bentonite (AB)

Comparison between Adsorption of Metals on Activated Zeolite and Bentonite

Experimental data from Cd, Cu, Fe, Pb, Zn solutions in Table 3 show that Cu, Fe, and Zn ions are removed by activated bentonite more than activated zeolite and Cd and Pb ions adsorbed are lower at 1g, 2g, and 4g but higher after 4g. The different concentration of Zn adsorbed by activated zeolite and bentonite is not significant but the ones of Cu and Fe are slightly significant. All in all, the activated bentonite is more effective in adsorbing/removing the metal ions from the polluted solution in terms of adsorption capacity due to the lower concentrations of metals in its content compared to the concentrations in the zeolite's content.

Table 3. Sorption rate of activated zeolite and bentonite in contact with Cu, Cd, Fe, Pb, and Zn in the polluted dug-well water by not considering the existing initial concentrations of metal ions in the mineralogical contents (initial condition: 250 mL of each solution, pH = 7-9)

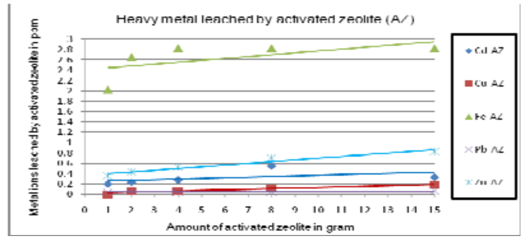
Powder amount		1 g	2 g	4 g	8 g	15 g
Adsorbed Cd (%)	Zeolite	47.22	55.72	55.26	19.68	59.72
	Bentonite	80.78	78.20	85.89	85.59	85.75
Adsorbed Cu (%)	Zeolite	97.88	97.10	97.56	97.21	96.59
	Bentonite	96.26	96.03	98.04	98.89	99.28
Adsorbed Fe (%)	Zeolite	30.97	32.32	42.09	51.40	58.18
	Bentonite	57.29	54.31	56.80	83.48	97.76
Adsorbed Pb (%)	Zeolite	98.18	98.41	98.96	99.08	99.03
	Bentonite	96.00	97.77	97.84	99.26	98.98
Adsorbed Zn (%)	Zeolite	82.13	84.76	85.79	85.42	85.55
	Bentonite	91.60	93.83	95.39	96.57	96.93

Leach of Metals from Activated Zeolite and Bentonite

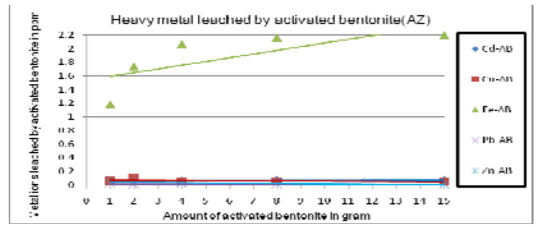
Related to the dug-well water quality after the treatment, Figure 4 indicates the leach rate of heavy metals from the activated zeolite and bentonite during the treatment. Different from Figure 3, this description is done by taking account of metals in the materials' contents. In this case, it turns out that the zeolite and bentonite is likely to pollute the dug-well water, instead, due to their significant metal concentrations.

Figure 4.A illustrates the pollution of solution by activated zeolite. It clearly shows that Fe is most significantly present (up to more than 3 ppm) in the zeolite content and Pb is least leached by activated zeolite. All metals have tendency to increase in the solutions as the amount of zeolite is higher, in which apart from Fe, the other metals are less than 1 ppm leaching into the solution. This can be assumed that the sequence of metal present in the activated zeolite is Fe>Zn>Cd>Cu>Pb which is opposite from the description without taking metals in the zeolite into consideration.

Illustrated by Figure 4.B, the activated bentonite in this study leached most significant concentration of Fe into the solution and least concentration of Pb. Except Fe and Cd, the activated bentonite also take part of treating the dug-well water for the metal types such as Cu, Zn, and Pb as their concentrations seem decreased with the increase in amount of activated bentonite.



(A)



(B)

Figure 4. Leach concentration of existing metal ions from (A)-activated zeolite and (B)-activated bentonite to the polluted dug-well water in contact with Cu, Cd, Fe, Pb, and Zn (initial condition: 250 mL of each solution, pH = 7-9)

CONCLUSIONS

The experimental data obtained from removing the metal ions from the dug-well water in case study of Yogyakarta Urban Area by utilizing the Sidomulyo activated zeolite and the Bandung activated bentonite lead to consider these materials into aspects as follows: 1). Without taking metals in the materials' contents into account, the activated zeolite and bentonite are characteristically considered as potential adsorbents to remove metals in both the polluted dug-well water and their contents themselves. The higher adsorption the powered zeolite or bentonite obtains as its higher amount is put into the solution. The selectivity series for zeolite (Ca-clinoptilolite) and bentonite (Ca-montmorillonite) seem the same: Pb>Cu>Zn>Fe>Cd. 2). In contrast, by considering the metals in the materials' content, the activated zeolite and bentonite are not suggested to be good adsorbent as they pollute the dug-well water, especially the zeolite due to its higher metal ions. The significant metal in the materials is Fe which is up to more 3 ppm whereas the other metals are lower than 1 ppm. Fortunately, the activated bentonite more or less treats the solution due to the low metal ions in its content.

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