

Activated Bentonite: Low Cost Adsorbent to Reduce Mercury Content in A Solution

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Abstract: The purpose of this study is to find the best activator for bentonite to reduce the mercury content in a solution. Bentonite was activated by HCl, H₃PO₄, NaCl, ZnCl₂, NaOH and KOH use different concentration such as 0.5, 1.0 and 1.5M. Activated bentonite has been characterized by x-ray diffraction, scanning electron microscope with energy dispersive spectroscopy and atomic absorption spectrometry. Bentonite characterization showed that bentonite contains kaolinite, montmorillonite, quartz and cristobalite. Activated bentonite has bigger pores than natural bentonite. Atomic absorption spectrometry showed that H₃PO₄, HCl, NaCl, ZnCl₂, NaOH and KOH can reduce the mercury around 99.99, 99.87, 97.48, 9.24, 99.81 and 99.86%. Thus, best activator for activated bentonite as a low-cost adsorbent is H₃PO₄.

Key words: Bentonite, activated bentonite, activator, mercury, natural bentonite, low-cost adsorbent

INTRODUCTION

Heavy metals is dangerous material (Gai *et al.*, 2019). Mercury is a volatile metal in liquid phase at 25°C and easily to react with another compound (Aerts *et al.*, 2014). Mercury can give some impact for environment and human health such as visual impairment, poisoning and death (Bernhoft, 2012). Thus, removal mercury from water has become an urgent problem.

Mercury is an impact of industrial activities such as gold mining, acid mine drainage on coal mining and another else (Kahhat *et al.*, 2019; Li *et al.*, 2012; Mason *et al.*, 2019). In gold mining, mercury was used to draw gold granules. This activity will give some negative impacts in environment. Contaminated water by mercury can reduce use adsorption method (Liu *et al.*, 2018). For the complete removal of mercury from solution, numerous techniques such as chemical precipitation, ion exchange, coagulation, reduction, membrane filtration and adsorption have been explored, among these techniques, adsorption is deemed to be most practical and economical approach (Fu and Wang, 2011). The identification of efficient sorbents is the key to designing a good adsorption process. In this context, bentonite have received considerable attention as sorbent caused by their widespread, exceptional water filtration capabilities, availability and high heavy metal adsorption capabilities (Jimtaisong and Sarakonsri, 2019).

Activated bentonite which are cheap and environmentally benign sorbents (Naswir *et al.*, 2019) have been extensively used for mercury adsorption. Indonesian bentonite deposit is 380 million of tons are spreading in Sumatera and Java Island. Jambi province have 650 ha of bentonite as potential low-cost sorbent (Naswir *et al.*, 2019). Bentonite have 2 layers that give impact for good ion exchange.

Bentonite can activation use chemical and physical methods. Chemical activation use acid or base solution such as CaCl₂, Ca(OH)₂, NaCl, MgCl₂, HNO₃, HCl, Ca₃(PO₄)₂, H₃PO₄, ZnCl₂. Every activator give different impact for pores and surface area, activation made ion exchange (cation with H⁺). Activated bentonite use acid activators make biggest pores and surface area than base activation, it will give an impact for better sorption (Toor *et al.*, 2014, 2015).

MATERIAL AND METHODS

Characterization and activators: Bentonite was collected from Sungai Rengas, Jambi Province, Indonesia. Activated bentonite characterized use x-ray diffraction, scanning electron microscope with energy dispersive spectroscopy and atomic absorption spectrometry. Acid activator used for bentonite activation are Hg(NO₃)₂, H₃PO₄, ZnCl₂, NaCl, NaOH, dan KOH.

Bentonite preparation and activation: The bentonite used in this study were produced by pyrolyzing natural bentonite. Firstly, bentonite prepared to reduce water content in furnace at 105°C for 24 h. Bentonite was pyrolyzed at temperature of 200°C for a hour. The 50 g bentonite with particle size is 100 mesh was mix with activators in Erlenmeyer. The 200 mL of activators with different concentration (0.5, 1.0 and 1.5M) mixed in 50 g of bentonite in Erlenmeyer. These treatment is done for enlarge the pores and surface area of bentonite. After that bentonite has filtered and washed out to reduce activators fom the bentonite. Distilled water has chosen because have neutral pH, so, it will prevent the reaction between bentonite and activators. The resulting residue is dried by heating. In the heating process after activation, the activating material enters between layers and then opens

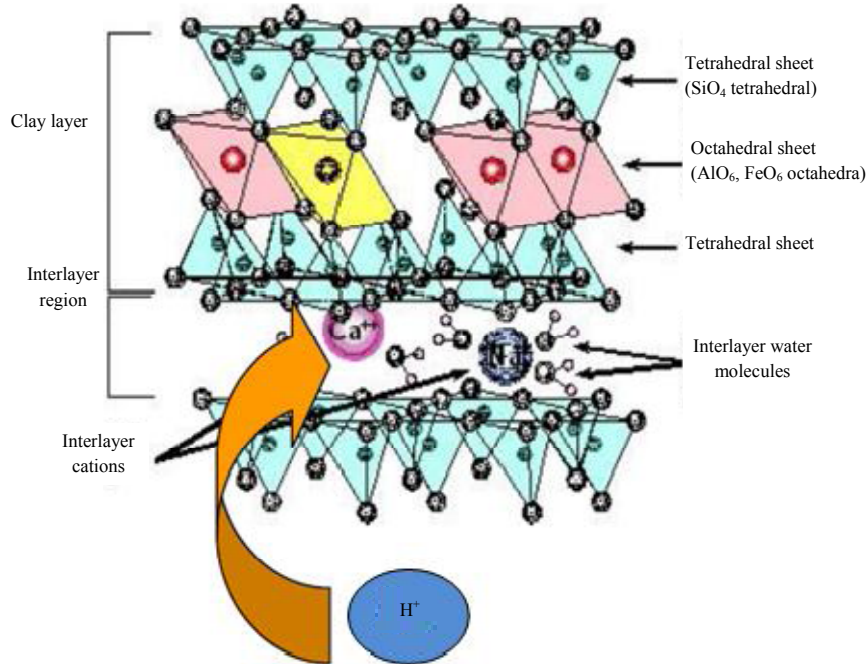
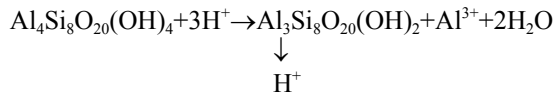


Fig. 1: Bentonite reaction use HCl and H₃PO₄

the closed surface. Bentonite activation used HCl and H₃PO₄ to change ion of H⁺ by releasing Al³⁺, Fe³⁺ dan Mg²⁺ (Fig. 1). Ion exchange of activated bentonite with HCl and H₃PO₄. Activated bentonite was mixed in 20 mL of 5 ppm Hg(NO₃)₂ and mix by magnetite stirrer with 200 rpm for 30 min.

RESULTS AND DISCUSSION

Bentonite activation: Activation of bentonite purpose to maximization of bentonite sorption. Chemical activation use H₃PO₄, HCl, ZnCl₂, NaCl, NaOH, dan KOH with different concentrations. HCl and H₃PO₄ can change the minerals (Ca²⁺ dan Mg²⁺) in interlayers with H⁺. Chemical activation use HCl and H₃PO₄ on bentonite bellow:



This reaction inform Al has changed to hydroxyl structure that give an impact of change of octahedral to tetrahedral. Changed of octahedral to tetrahedral made the crystal lattice is negatively charged, negative charged will neutralizing by alkali in bentonite (Krupskaya *et al.*, 2019). Activated bentonite used ZnCl₂ and NaCl make an exchange of Zn and Na. ZnCl₂ is hydrating agent. Hydrating agent can make biggest pores and surface of bentonite. Bentonite was soaked in deionization solution

for reduce bentonite pores from another residues. NaCl is an effective activator because easy to find and non-toxic. NaCl in solution phase will be dissociated and made positive and negative ions are Na⁺ and Cl⁻. Na will be surrounded by negative partial from water and Cl⁻ will be surrounded by positive partial by water molecules.

Base activators (NaOH and KOH) will give an impact for silica and alumina in bentonite reacted with base solution and made salt product. These activators can reduce impurity and make biggest pores and surface area. Therefore this treatment can improve sorption ability (Pawar *et al.*, 2016).

Characterization

X-ray diffraction: X-ray diffraction used to find peak of natural bentonite and activated bentonite and find the different of these peaks. X-ray diffraction of natural and activated bentonite informs that bentonite has created by kaolinite, montmorillonite, quartz and cristobalite. Samples were examined by using BRUKER D8 Advance Model x-ray diffractometer with Cu Kα radiation operated at 40 mA and 40 kV with a 0.01 step size, Ni β-filter and Lynx-eye® position sensitive detector. Characterizations were made using randomly oriented grains. For this purpose, samples were finely grounded and put into an oven at 200°C for 1 h before analysis. Then, these samples were put into sample holders and a flat glass plate pressed by hand to obtain powder having a flat compact surface. The natural bentonite have high 2θ angles (27°) with counts almost 9000 (Fig. 2). Bulk

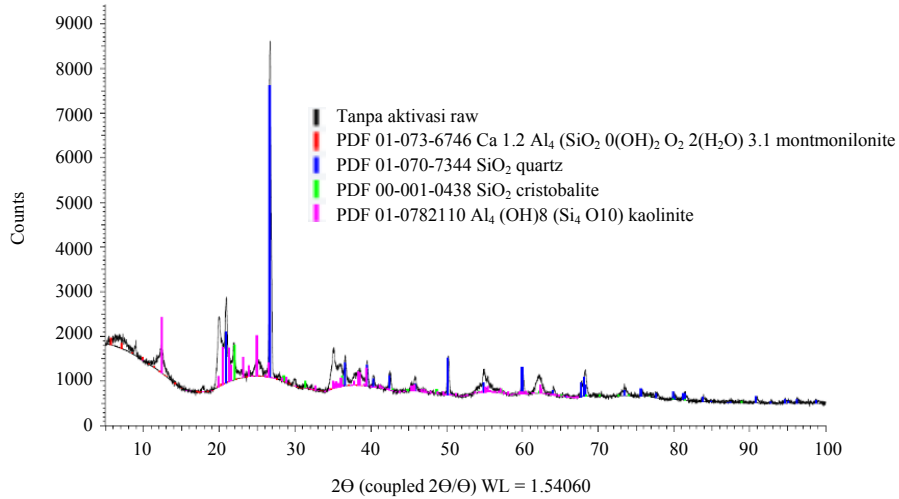


Fig. 2: XRD pattern of natural bentonite

samples were scanned between 5° and 65° 2θ range using a 1 mm divergent slit. Natural bentonite composed by montmorillonite (PDF 01-073-6746), quartz (PDF 01-070-7344), cristobalite (PDF 00-001-0438) and kaolinite (01-078-2110).

Activated bentonite use HCl, H₃PO₄ and ZnCl₂ has characterized by x-ray diffraction. XRD pattern informs that activated bentonite use ZnCl₂ have strong intensity than ZnCl₂ and H₃PO₄. Intensity of activated bentonite by HCl, ZnCl₂ and H₃PO₄ activation is between 8000-9000 and 9000-1000. The 2θ of x-ray diffraction is in 27° in all of bentonites.

Activated bentonite used H₃PO₄, HCl, ZnCl₂ have minerals composition such as montmorillonite (Ca1.2Al4(Si₈O_{20(OH)2})O₂. The 2(H₂O), quartz (SiO₂), cristobalite (SiO₂) and kaolinite (OH)8(Si₄O₁₀). Generally, all of bentonites does not have significant changed with the different treatment. These peaks inform that no strain caused no movement of peaks in diffraction line.

Scanning electron microscope with energy dispersive spectroscopy: Scanning electron microscope used to find pore sizes of bentonites. Scanning electron microscope showed that the texture of had a coarser surface, a more abundant pore structure and rich white spherical particles with diameters between 0.5 and 2 μm. Natural bentonite have smooth surface than activated bentonite, activated bentonite used H₃PO₄ and ZnCl₂ have coarser surface than activated bentonite used HCl (Fig. 3). The different of pores in surface area caused by different activators. Activator can make surface area coarser and biggest pores, it will give an impact of ability sorption. The correspondence energy dispersive spectroscopy informs elements of bentonite such as C, O, Na, Mg, Al, Si, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, P and bentonites compounds such as C, MgO, Al₂O₃, SiO₂, Cl, K₂O, CaO, TiO₂, MnO, FeO, CuO, P₂O₅ZnO and Na₂O. Note A is natural bentonite; B is activated bentonite use H₃PO₄; C is activated bentonite

Table 1: Element of bentonites

Element	Sample of bentonites (%)			
	A	B	C	D
C	-	4.77	14.24	14.83
O	64.61	48.13	41	40.13
Na	-	-	-	0.47
Mg	-	-	0.11	-
Al	12.25	13.30	17.79	13.09
Si	20.29	23.92	20.62	23.66
Cl	-	-	0.75	2.71
K	0.68	1.08	0.04	-
Ca	-	-	-	-
Ti	0.25	-	0.4	-
Mn	-	-	0.25	-
Fe	1.91	2.53	1.73	2.76
Cu	-	-	3.08	-
Zn	-	-	-	2.35
P	-	6.27	-	-
Component				
C	-	4.77	14.24	14.83
MgO	-	-	0.19	-
Al ₂ O ₃	31.72	25.13	33.61	24.72
SiO ₂	62.93	51.17	44.11	50.62
Cl	-	-	0.75	2.71
K ₂ O	1.21	1.3	0.04	-
CaO	-	-	0.01	-
TiO ₂	0.61	-	0.66	-
MnO	-	-	0.32	3.55
FeO	3.54	3.26	2.22	-
CuO	-	-	3.85	-
P ₂ O ₅	-	14.38	-	-
ZnO	-	-	-	2.92
Na ₂ O	-	-	-	0.64

use HCl and; D is activated bentonite use ZnCl₂ (Table 1). Elements changed of bentonite caused by pyrolysis and activation process by different activators. Undetected element caused by element too small and undetected by scanning electron microscope with energy dispersive spectroscopy such as carbon, natrium, magnesium, chlorine, calcium, manganese, copper, zinc and phosphor and MgO, Cl, K₂O, CaO, TiO₂, MnO, CuO, P₂O₅, ZnO and Na₂O.

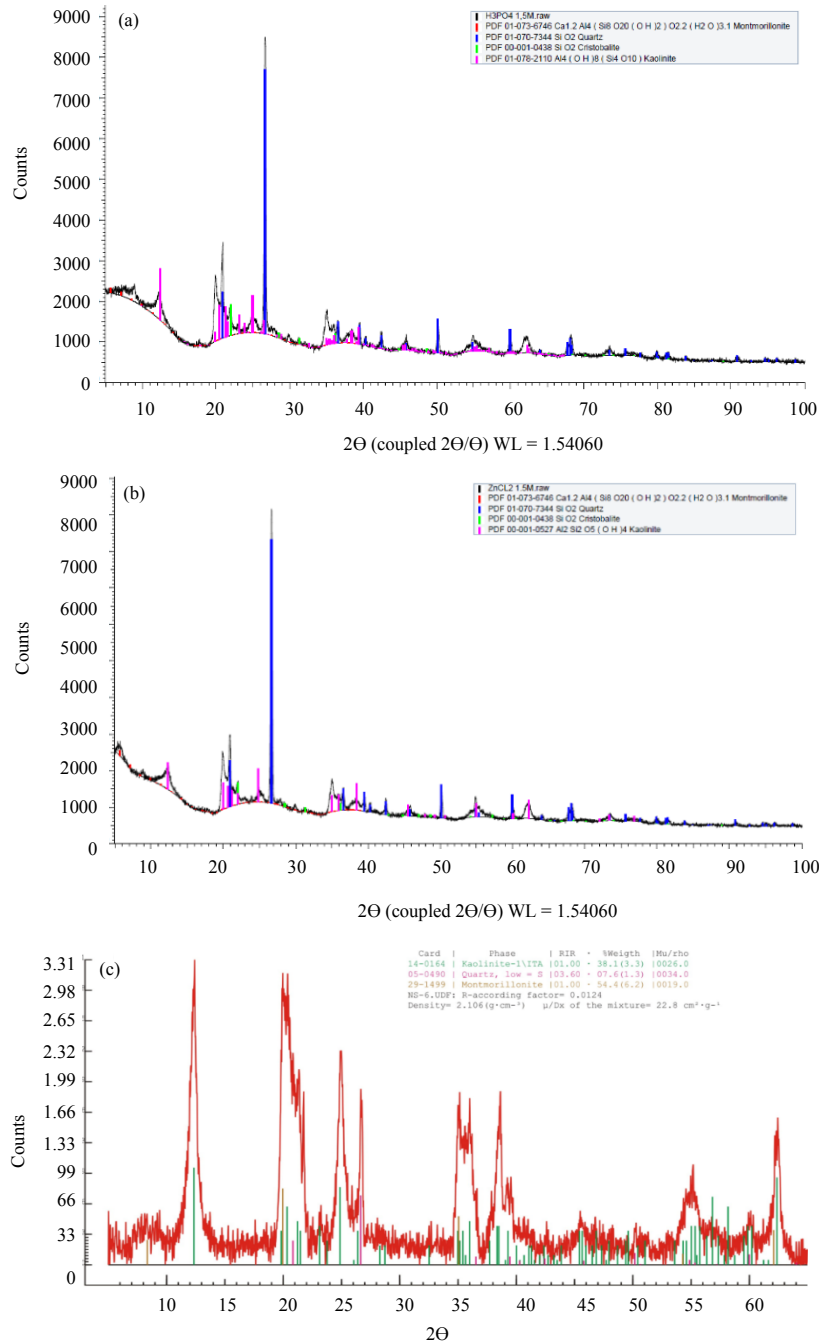


Fig. 3(a-c): XRD pattern of activated bentonite use (a) H₃PO, (b) ZnCl₂ and (c) HCl

Hg sorption by activated bentonite: Calibration curve was created to find calibration standard of Hg. Hg was created by 1000 ppm of Hg(NO₃)₂ was diluted to 100 ppm (Fig. 4). Standard of Hg solution are 0, 10, 20, 30 and 40 ppm.

First calibration curve has created by five different ppm and have calibration curve $y = 0.2163x + 0.00832$

with correlation coefficient (r) is 0.9991. Result of calibration curve showed linear line with standard concentration solution. It's inform more big concentration will need big adsorbent. This calibration curve will use to find sample concentration use equation:

$$Y = bx + a$$

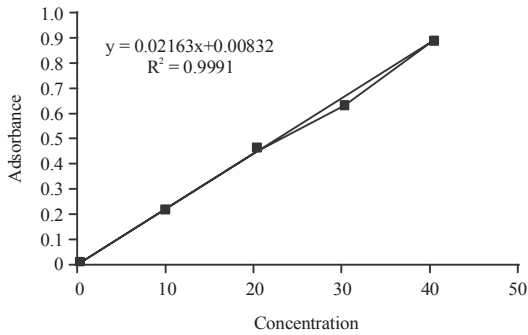


Fig. 4: Standard Calibration curve of Hg

Table 2: Efficiency of 0.5 M Hg

Activators	Concentration (ppm)		Efficiency (%)
	First	Last	
H ₃ PO ₄	5	0.002016	99.96
HCl	5	0.03376	99.33
NaCl	5	0.125948	97.48
ZnCl ₂	5	0.137608	97.24783
NaOH	5	0.009290	99.81
KOH	5	0.138328	97.22

Table 3: Efficiency of 1 M Hg

Activator	Concentration (ppm)		Efficiency (%)
	First	Last	
H ₃ PO ₄	5	0.000853	99.98
HCl	5	0.006735	99.87
NaCl	5	0.484348	90.31
ZnCl ₂	5	0.241523	95.16955
NaOH	5	0.116664	97.66
KOH	5	0.138809	97.22

Table 4: Efficiency of 1.5 M Hg

Activator	Concentration (ppm)		Efficiency (%)
	First	Last	
H ₃ PO ₄	5	0.000332	99.99
HCl	5	0.056607	98.87
NaCl	5	0.644833	87.1
ZnCl ₂	5	0.15513	96.8974
NaOH	5	0.117806	97.64
KOH	5	0.006567	99.86

Where:

b : Slope

a : Intercept

Y : Absorbance

X : Concentration

r : Regression linear

Result of atomic absorption spectrometry of Hg in solution is more than 97% in 0.5 M (Table 2), 90% in 1M (Table 3) and 87% in 1.5 M (Table 4), these phenomena inform that every single activator did not

have significant different, especially, HCl and H₃PO₄. It caused by acid activators will give an impact for ability sorption.

Equilibrium sorption of adsorbate is use to find sorption sioterm. The isotherm results of activated bentonite at a constatnt temperature of 105° were analyzed using four important isotherms including the Langmuir, Freundlich, Temkin and Dubinin-Redushkevich (D-R) isotherm models.

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface with no lateral inter-action between the adsorbed molecules. The Langmuir adsorption isotherm has been successfully used in many monolayer adsorption processes. The expression of the Langmuir Model is given by equation:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}$$

where, q_e (mg/g) and C_e (mg/L) are the amount of adsorbed adsorbate per unit mass of adsorbent and un-adsorbed adsorbate concentration in solution at equilibrium, respectively. The value of Q₀ (mg/g) is the maximum amount of adsorbate per unit mass of adsorbent to form a complete monolayer on the surface bound at high C_e and b is a constant related to the affinity of the binding sites (L/mg). The Langmuir equation can be described by the linearized form

$$\frac{C_e}{Q_e} = \frac{1}{Q_0} C_e + \frac{1}{Q_0 b}$$

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor RL that is given by the following equation:

$$RL = \frac{1}{1 + b C_0}$$

Where:

C₀ (mg/L) : Initial concentration of adsorbate

b (L/mg) : Langmuir constant

There are four probabilities for the RL value: for favorable sorption, 0 < RL < 1, for unfavorable sorption, RL > 1, for linear sorption, RL = 1, for irreversible sorption, RL = 0.

The Freundlich isotherm can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The Freundlich equation is expressed as:

$$q_e = K_f C_e^{1/n}$$

where K_f and n are Freundlich constants with K_f (mg/g) (L/mg)^{1/n} being the sorption capacity of the adsorbent and n giving an indication the favorability of the sorption process. Values of $n > 1$ represent favorable adsorption condition. To determine the constants K_f and n , the Freundlich equation can be described by the linearized form:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Temkin and Pyzhev considered the effects of some indirect adsorbate/adsorbate interaction on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin isotherm has been generally applied in the following form:

$$q_e = \left(\frac{RT}{b}\right) \ln (ACe)$$

and can be linearized as:

$$q_e = B \ln A + B \ln C_e$$

Where:

- B = RT/b, b : The Temkin constant related to heat of sorption (J/mol)
- A : The Temkin isotherm constant (L/g)
- R : The gas constant (8.314 J/mol K)
- T : The absolute temperature (K)

The equilibrium data were also applied to the D-R model to determine the type of sorption (physical or chemical). The linear form of D-R isotherm is presented as the following equation:

$$\ln q_e = \ln q_m \beta^2$$

where, q_e is the amount of aniline adsorbed onto per unit dosage of Cr-bentonite (mol/g), q_m is the theoretical monolayer sorption capacity (mol/g), β^2 is the constant of the sorption energy (mol²/J²) which is related to the average energy of sorption per mole of the adsorbate as it is transferred to the surface of the solid from infinite distance in the solution and β is Polanyi potential which is described as:

$$\beta = RT \ln \left(1 + \frac{1}{C_e}\right)$$

Where:

- T : The solution temperature (K)
- R : The gas constant and is equal to 8.314 J/mol K.

The value of mean sorption energy, E (kJ/mol) can be calculated from D-R parameter β as follows:

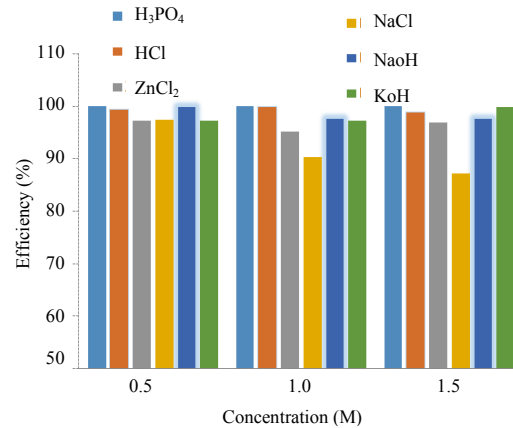


Fig. 5: Efficiency of activated bentonite

$$E = \frac{1}{\sqrt{-2\beta}}$$

The value of mean sorption energy gives information about chemical and physical sorption. The E value ranges from 1-8 kJ/mol for physical sorption and from 8-16 kJ/mol for chemical sorption (Zheng *et al.*, 2009).

Chemical activator in these research have three reaction such as mineral acid can reduce Fe₂O₃, Al₂O₃, CaO and MgO in adsorbent pores. These phenomena make the pores bigger that make better surface area. Second reaction is Ca²⁺ and Mg²⁺ in surface area of crystal has changed with H⁺ from acid mineral. Then, The Ca²⁺ and Mg²⁺ ion that changed with H⁺ will change with Al³⁺ in acid mineral. As the result of this research best activator of bentonite is H₃PO₄ that can sorption 99.99% mercury in solution (Fig. 5)

CONCLUSION

Mercury is dangerous material that give negative impact for environment and human health. Bentonite as a local material can utilize as an adsorbent to reduce mercury in a solution. Bentonite has characterized use x-ray diffraction and scanning electron microscope with energy dispersive spectroscopy. Bentonite has activated used KOH, NaOH, HCl, ZnCl₂ and H₃PO₄. These activators used to find the best activator for activated bentonite to reduce mercury 0.5 M, 1.0 M and 1.5 M in a solution. Result of this study showed that H₃PO₄, HCl, NaCl, ZnCl₂, NaOH and KOH can reduce the mercury around 99.99, 99.87, 97.48, 9.24, 99.81 and 99.86%. Thus, best activator for activated bentonite as a low-cost adsorbent is H₃PO₄.

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