Adsorption Of Fe^{2+} In Groundwater By Fly Ash Coal Adsorbent East Kalimantan

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Abstract

This research has investigated adsorption of Fe with using fly ash adsorbent. Phases of adsorption of Fe is activated with H_2SO_4 after that the fly ash were characterized by using XRF, FTIR and SEM. Determination of optimum conditions on the adsorption of Fe with adsorbent mass variations, variations in contact time, pH variation and variation concentration and adsorption isotherm study. Resulth show that the adsorption of Fe in optimum condition occurs in adsorbent mass of 2.5 g, for 60 minutes contact time with pH 4 at a concentration of 20 ppm. The results also able to adsorp up to 94% Fe. The adsorption of Fe with using fly ash adsorbent was more fitted to the Langmuir model than to Freundlich model.

Key words: adsorption, fly ash, isotherm adsorption

Abstrak

Telah dilakukan penelitian adsorpsi logam Fe dengan menggunakan adsorben abu layang Batubara. Tahapan adsorpsi logam Fe yakni mengaktivasi abu layang batubara dengan H_2SO_4 setelah itu abu layang dikarakterisasi dengan menggunakan XRF, FTIR dan SEM. Penentuan kondisi umum pada adsorpsi logam Fe dilakukan dengan variasi massa adsorben, variasi lama kontak, variasi pH dan variasi konsentrasi serta mempelajari isotherm adsorpsinya. Hasil penelitian menunjukkan bahwa adsorpsi logam Fe pada kondisi optimum terjadi pada massa adsorben 2,5 g, lama kontak selama 60 menit dengan pH 4 pada konsentrasi 20 ppm. Hasil penelitian ini juga mampu mengadsorpsi logam Fe hingga 94%. Adsorpsi logam Fe pada adsorben abu layang lebih sesuai dengan model Freundlich daripada model Langmuir.

Kata kunci: *abu layang, adsorpsi, isoterm adsorpsi*

1. Introduction

Fly ash of coal are produced in the burning of the coal in the PLTU in the form of ash particles that are carried by exhaust gas while the remain ashes and removed at the bottom of the furnace called as bottom ashes. In Indonesia, the fly ashes and bottom ashes productions increases from year to year. In 2009, the fly ashes production has reached 2.78 million tons.[1]

The fly ashes of coal in general are thrown away at the landfill or stacked at the industrial area. The fly ashes handling of the coal still limited at the pilling up a the vacant land. It has danger potentials for the environment and societies around if it is carried in the waters. If it is left continuously, then the fly ash do not have economic value even danger for the environment around, such as societies will experience the respiratory tract infection, the equipments and dried clothes will be dirty because of the ashes.

Beside the negative impacts, the fly ashes also have positive sites, that is the chemical composition mostly consist of metal oxide especially SiO_2 and Al_2O_3 that has active site so it is possible to be used as adsorbent for the heavy metals.[2]

To get adsorbent with high adsorption ability can be done through activation by using acid solution (H_2SO_4).[3] The activation is aimed at improving the pore specifics area and the active site. The activation treatment by using acid solution able to dissolve the impurities at the materials so the pores widen so the pore specific area widen and the adsorption capacity of adsorbent also increase. The fly ash usage as adsorbent able to separate the COD from the domestic liquid waste. The research results showed the adsorption capacity value reached 13.60 mg/g with efficiency of 91%.[4]

Fly ashes also can be used as adsorbent to separate the metal from the water disposal. Beside that the separation of Cr in the water disposal by using fly ashes of coal where the efficiency of the fly ashes from the thermal power plant as adsorbent in separating the COD reached 87.89% for the domestic sources.[5]

The research also aimed at knowing how far the fly ashes adsorption to the Fe at the ground water at the Balikpapan because the ground water quality or the drilled water at the Balikpapan still under standard and not proper for consumption, because contain high Fe, beside that the water in yellow and with odor. It can be observed with naked eye where the formation of yellow mosses at the bath up, and the deposition at the bottom of the bath up is the indication of water that contains high turbidity. The occurred condition because the ground water of the community is not processed firstly. Although the ground water is not proper for consumption, the communities still use the ground water for bath, washing plates, washing clothes, and daily needs.[6]

At the Kelurahan Lamaru of RT 20 at the Balikpapan is consist of 152 KK that able to get clean water only 28 KK so the remains rely on the rain water and ground water that do not fulfill the standard so the population in general use low quality water. It has bad consequences for the community health such as irritation. The metal high concentration that causes the yellow color and odor that shows the presence of Fe content more than maximum content in water of 1.0 mg/l (Per Menkes RI No 416/Per/IX 1990). Some researches to decrease the metal content of the waste, one of them by using adsorption. The adsorption processes is one of alternatives to manage water that able to separate the impurities, the adsorption process is simple and economic.[7] The used materials as the adsorbent by the Lamaru communities of Balikpapan only by using sands and pebbles then be placed at the drum but the obtained water still turbid and with little odor. The alternative materials for adsorbent in the process can be from various materials such as fly ashes. The advantages of the fly ashes are the low cost. Beside that the adsorbent can be used well for liquid waste and can be used to separate heavy metals and colored waste.[8]

The research focus is to study the influence of H_2SO_4 activation with characterization of XRF, FTIR, and SEM. Then also to study the influence of adsorbent mass, contact time, pH and adsorbate concentration to the Fe adsorption by using fly ashes adsorbent by using batch method. The interaction determination that occurred between adsorbent with adsorbate is determined by Langmuir an Freudlich modeling. To know the influence of adsorbent mass, contact time, pH and concentration of the adsorbate, then it will be used the mass variation of 1, 1.5, 2, 2.5, 3, 3.5, and 4, while for contact time of 15, 30, 45, 60, 75, 90 and 105 minutes, for pH of 2, 3, 4, 5, 6, 7 and 8 while the concentration of adsorbate 10, 20, 30, 40 and 50 ppm.

2. Experiment

Chemicals and instrumentation

The used chemicals in the research are fly ashes, ground water, H_2SO_4 pa (98%, bj 1.84), NaOH (p.a), $FeSO_4$, aquades and filter paper of whatman No 41.

The used instrumentation is oven of Fisher Scientific Isotemp Oven of 655F, sieve (150 and 180 mesh), analytic scale of Mettle AE 50, glass equipment set, shaker rotator of type H-SR-200, pH meter (Onilab, Schott Gerate pH Meter CG 820), the magnetic stirrer (Heidolp MR 1000), Infra Red Spectrophotometer (FTIR-8000 PC Shimadzu), Scanning Electron Microscope (SEM) JEOL JSM-6390A, spectrophotometer Shimadzu UV-160 A and Spectrophotometer of Atom Adsorption (AAS).

Procedure reaction

Preparation of the fly ashes

The 30 g fly ashes are washed by aquades, then be dried in the oven with temperature of 110^oC for 3 hours and be placed in the desiccators. The dried fly ashes then be weighted up to obtain the constant weight then be filtered by sieve of 150 mesh, the passed solid then be sieved again with 180 mesh. The detained solid at the second sieve be used for the next research.

Activation of coal fly ashes

The prepared fly ashes then be weighted for 10 g and be entered into chemical glass and added with 30 mL of H_2SO_4 with concentration of 4 M, 6M or 8 M. The mixture is soaked for 24 hours after that be filtered and washed with aquades up to pH 7. The fly ashes then be dried in oven with 110 ^oC for 3 hour.

Characterization of fly ashes

The composition of fly ashes are determined by using x ray fluresecence spectrometer, the presence of active site at the fly ashes adsorbent are determined by FTIR and the surface of the fly ashes before and after activation then be observed by using SEM.

The determination of optimum condition for Fe adsorption

The influence of adsorbent mass of the coal fly ashes

Preparing 5 solution of $FeSO_4$ each for 100 ml with optimum concentration then be added with fly ashes with weight variation of 0.5;1;1.5; 2; 2.5; grams then be stirred with 100 rpm for 30 minutes. Then the solution is filtered by using filter paper and the filtrate is taken for 5 ml and be diluted in the 100 ml aquades and analyzed by AAS with the wavelength of 248.3 nm. Then it is made the curve between the adsorbed %Fe with the adsorbent weight, from the curve it will be got the optimum weight.

The influence of contact time to the Fe adsorption

Preparing 5 solution of $FeSO_4$ each for 100 ml with optimum concentration then be added with fly ashes with optimum weight then be stirred with 100 rpm for 15, 30, 45, 60 and 75 minutes. Then the solution is filtered with the filter paper and the filtrate is taken for 5 ml, and be diluted at the 100 ml aquades then be analyzed by AAS with wavelength of 248.3 nm. Then it is made the curve between the adsorbed %Fe with the stirring time, from the curve it will be got the optimum stirring time.

The influence of pH to the Fe adsorption

Preparing 5 solution of $FeSO_4$ each for 100 ml with optimum concentration then be added with fly ashes with optimum weight after that be regulated with pH variation of 2, 3, 4, 5 and 6 then be stirred with 100 rpm for optimum time. Then the solution is filtered with the filter paper and the filtrate is taken for 5 ml, and be diluted at the 100 ml aquades then be analyzed by AAS with wavelength of 248.3 nm. Then it is made the curve between the adsorbed %Fe with the pH variation, from the curve it will be got the optimum pH.

The influence of adsorbate concentration to the Fe adsorption

Preparing 5 solution of FeSO4 each for 100 ml with concentration variation of 10, 20, 30, 40 and 50 ppm then be added with fly ashes with optimum weight after that be regulated with optimum pH be stirred with 100 rpm for optimum time. Then the solution is filtered with the filter paper and the filtrate is taken for 5 ml, and be diluted at the 100 ml aquades then be analyzed by AAS with wavelength of 248.3 nm. Then it is made the curve between the adsorbed %Fe with calculation by using isotherm of Langmuir and Freundliq.

Experiment with original samples

The obtained optimum condition then be conditioned to the original sample. 50 ml original sample be added with fly ashes with optimum weight then be regulated with optimum pH then be stirred with 100 rpm for optimum time. Then be filtered by filter paper and the filtrate is taken for 5 ml be analyzed by AAS with wavelength of 248.3 nm.

3. **Result and Discussion**

Preparation of fly ashes

The initial stage of fly ashes by using fly ashes homogenization aimed at homogenizing the fly ashes size. If the size is not homogenous then the surface area that is passed through by the Fe become varied. It causes the area of adsorption contact of Fe at the fly ashes surface become varied so the adsorption process become less optimum. The 150-180 mesh are selected because the size is the optimum size for adsorption process.[9]. If the size less than 150 then the fly ashes surface are become small so the adsorption process of Fe decreases. But if the size larger than 180 mesh then the space among the fly ashes molecule become smaller so the Fe metal will difficult to reach and interact with the fly ashes. Because of that, as the preliminary investigation at the research it is used 150-180 mesh. Then the fly ashes are washed by water and rinsed with aquades to remove the attached dust at the fly ashes. Then the fly ashes are dried in 110^oC for 3 hours to evaporate water in the pores of fly ashes crystal.

Activation of fly ashes by using H_2SO_4

The activation of H_2SO_4 aimed at dissolving the impurities minerals at the fly ashes so the fly ashes pores become widen so able to replace the exchanged cation (alkali or soil alkali) in the fly ashes structure with ion H^+ so the fly ashes have bronsted acid group. Bearing in mind the H^+ size is smaller than metal cation so physically able to widen the pore space. Beside that the H atom at the Bronsted acid group easily to be released again as H^+ through ion exchange.[10] The metal ion exchange at the fly ashes with the ion H^+ because of fly ashes activation by H_2SO_4 able to cause the Bronsted acid group (Figure 1).[11]

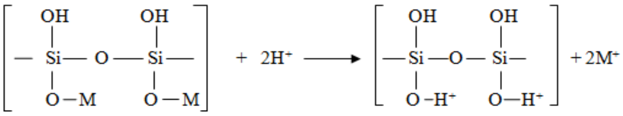


Figure 1. The acid activation process at the fly ash. (M is metal)

The next step is to filter and rinse the mixture between the fly ashes of coal by using aquades up to the pH reached 7 because to remove the acid excess during the H_2SO_4 solution addition. The water content in the fly ashes can be removed by oven in 110^oC to dry. The treatment is expected able to set aside the active sites that contain metal such as Si and Al that is not used up because of drying.[12]. The heating results then be stored in the desiccators for the next test.

Characterization results of the activated fly ashes

Characterization by XRF

Based on the characterization results by using XRF from the fly ashes before activation, activation with H_2SO_4 4 M, 6M, and 8 M, is presented in table 1.

Table 1. Composition of fly ashes from XRF results

Element	Persentase			
	before aktivation	H_2SO_4 4M	H_2SO_4 6M	H_2SO_4 8M
Fe	42,4	33,8	38,5	10,3
Ca	28,4	8,99	12,6	8,6
Si	16,5	47,8	34,4	45,75
Al	6,1	0,1	0,1	29,4
K	1,77	3,49	3,06	0
Ti	1,2	1,8	1,63	1,1
S	0,85	0,1	2,9	1,35
V	0,04	0,06	0,04	0,1
Cr	0,098	0,13	0,1	0,35
Mn	0,35	0,28	0,28	0,11

Based on the characterization results of XRF from the fly ashes before activation, the activation by using H_2SO_4 4 M, 6M, and 8 M, Fe composition at the fly ashes before activation still high that is 42.4% while the Si composition only 16.5%. At the activation of H_2SO_4 4 m and 6 m the Si element increase that is 47.8% an d 34.4% but the Fe element still high 33.8% and 38.5%. If the Fe element still high, the percentage will influence the adsorption process because able to impede the presence of active group at the fly ashes adsorbent.[13]. Based on the table 1, that the H_2SO_4 activation 8 M, element Si and Al increase 45.75% and 32.4% while the Fe element decrease 10.3%. If the more Si and Al in the fly ashes then it is expected the adsorption process will maximum. So at the next characterization by using fly ashes before activation and after activation 8M.

Characterization by FTIR

Identification of functional groups to the fly ashes is done by using infrared spectrophotometer at the 4000-4400 cm-1 by using pellet KBr. The analyzed samples were before activation (as control variable) and after activation 8M (as optimum variation). From characterization by FTIR from fly ashes before activation and after activation by H_2SO_4 8 M is presented in figure 2.

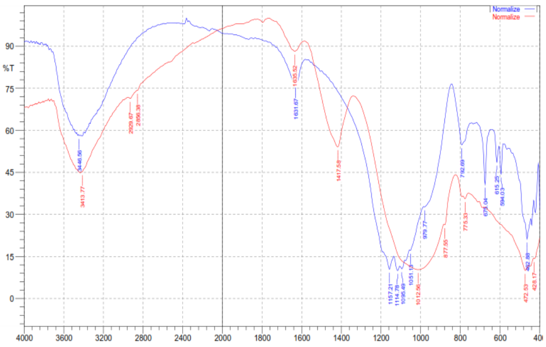


Figure 2. spectra in the fly ash before activated (red line) and after activated (blue line).

Figure 2. spectra in the fly ash before activating contained absorption bands at wavelengths of 3413.71 cm-1 is the OH vibration, wavelength 2929.67, 2856.38 cm-1 is the CH stretching, the wavelength of 1417.58 cm-1 is the CN stretching. Absorption band changes occurred after fly ash activated with the loss of 8M H_2SO_4 absorption band at a wavelength of 2929.67 cm-1, 2856.38 cm-1 and 1417.58 cm-1 which is the group that lost to activation of impurities.

Characterization by SEM

Surface morphology of fly ashes adsorbent before activation can be identified by SEM with object magnification of 6000 times that the results can be seen in the figure 3.

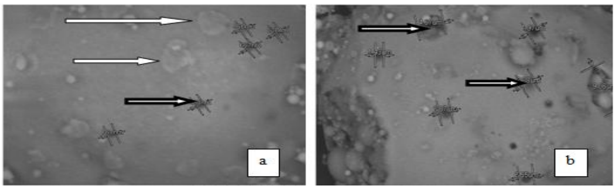


figure 3, micrograph of SEM of fly ashes before activation (a) Micrograph of SEM of fly ashes after activation (b) impurities on the surface of adsorbent, pore.

Figure 3. (a) The difference in surface morphology of fly ash from fly ash before activation and after activation of H_2SO_4. In (a) visible pores fly ash still covered by impurities and pore number less than the pore diameter and pore activated after 566 nm - 761 nm. In (b) visible surface of fly ash after activation of impurities is not covered and the amount of fly ash pore pore looks more and pore diameter is also larger than the pores of fly ash before activation (1,43 to 9,06 μm). According to research[9] that the fly ash activated with 8M H_2SO_4 has a specific surface area greater than the untreated fly ash activation is equal to 16.1306 m^2 / g whereas fly ash without activation only 4.3461 m^2 / g.

Cation Exchange Capacity

Cation Exchange Capacity of the fly ashes is the quantity measure of the fly ashes to bind the ions that can be exchanged and depend on the active groupos amount per fly ashes weight. At the cation exchange capacity of inactivated fly ashes with activated fly ashes with H_2SO_4 8M can be seen in table 2.

Table 2. The capacity data of cation exchange to the Fe^{2+} cation.

Cation	CEC (mek/100 g)	
	before activation	After activation
Fe^{2+}	0,6432	17,0448

At the table 2, it can be seen that the cation exchange capacity of the fly ashes that is activated by H_2SO_4 is stronger than the non activated fly ashes. It is because able to increase the ion H^+ amount into the fly ashes structure then the higher metal cation amount in the fly ashes that are replaced by ion H^+ so the fly ashes that have active groups that easily to release the proton. The metal ion exchange event at the fly ashes with the hydrogen ions is showed in the figure 1.

The influence of adsorbent mass to the Fe adsorption

The results of treatment for the adsorbent mass influence to the adsorption mass is presented in figure 4.

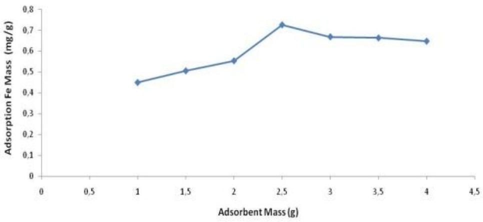


Figure 4. Curve of the adsorbent mass influence to the adsorption mass.

Based on figure 4, it can be observed that the adsorption mass of Fe increase up to the use of adsorbent 2.5 g. At the situation, the use of adsorbent mass is higher and do not increase the adsorption mass because the equilibrium of adsorption has been reached. After the adsorption equilibrium is reached, then the desorption rate become more dominant than adsorption rate, so the bound Fe to the fly ashes surface will be released again in the solution. The adsorption equilibrium is occurred when the adsorption rate equal with the desorption rate.[14] The phenomenon causes the adsorbed mass of Fe decrease as can be seen in figure 5 by using adsorbent mass 2.4-4.0 g. The optimum condition of adsorption is reached at the adsorbent mass usage of 2.5 g with adsorbed mass value of 0.72 so the research is using adsorbent mass of 2.5 g.

The influence of contact time to the Fe adsorption

The determination of contact time aimed at knowing how long the time is needed by adsorbent to adsorp the Fe maximally up to the equilibrium. The investigation of the contact time is done by batch method a the contact time of 15, 30, 45, 60, 75, 90, and 105 minutes. The research was done at the adsorbate concentration of 20 ppm with optimum adsorbent mass of 2.5 g, with the stirring speed of 100 rpm.

The influence of contact time is done because the contact time showed able to influence the adsorption equilibrium. The contact time able to influence the attractive power between adsorbent and adsorbate like the Van Der Waals force and electrostatic force.[15] The relation between the contact time with the Fe adsorption percentage by fly ashes of coal can be seen in figure 5.

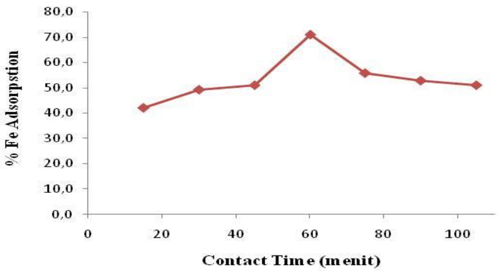


Figure 5. The influence of contact time to the % adsorption

Based on the curve, at the contact time 15 to 60 minutes there is adsorption percentage increase because of the longer contact time cause the interaction between fly ash with the Fe become greater, the more Fe be adsorbed by the fly ashes.

The decrease of adsorbed Fe percentage occurred at the minute 60 to 105 because of the concentration differences of Fe that is adsorbed at the fly ashes surface greater than the remain Fe in the solution cause the bound Fe will be re-desorbed into the solution. The optimum contact time is occurred at the minute 60 with the adsorption percentage of 70.34% so the next research will use 60 minutes.

The influence of solution pH to the Fe adsorption

The determination of pH influence to Fe synthesis is done by using fly ashes adsorbent with optimum mass of 2.5g, contact time of 60 minutes, pH = 4 and stirring speed of 100 rpm. The pH investigation done by batch system at pH variation of 2, 3, 4, 5, 6, 7 and 8. The relation between pH of Fe solution with the adsorbed Fe percentage by fly ashes is shown in figure 6.

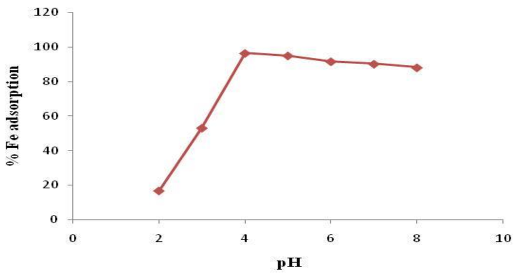


Figure 6. The curve of pH influence to the % adsorption

Based on figure 6 at pH 2 to pH 4, there is increase of adsorption percentage. It is caused by the Fe ion adsorption is dominated by electrostatic interaction or ion exchange with ion H^+ at the adsorbent active groups.

Ion H^+ at the hydroxide form will run down and easy to release and cause the Fe will be bound and adsorbed strongly to the adsorbent.[16]

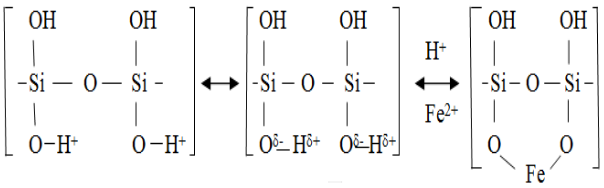


Figure 7. Ion exchange reactions between Fe^{2+} with H^+

At pH 5 to pH 8 showed the decrease of adsorption percentage. It is expected because of the metal ion able to experience hydrolysis reaction at the pH > 6 that is suitable with the hydrolysis adsorption because Fe will be hydrolyzed then will cause the decrease of electrostatic force. While the decrease of electrostatic force will decrease the adsorption force. At the alkali pH will occur the decrease of adsorption, it is expected because the deposit Fe as the Fe hydroxide with the pass over of smallest value of Ksp $Fe(OH)_2$ of 2.10^{-16}. The optimum condition of adsorption is reached at the pH 4 with adsorption percentage value of 95.73% so the next research will use pH 4.

The influence of adsorbate concentration to the Fe adsorption

The results of treatment of the adsorbate concentration influence is presented in the figure 8.

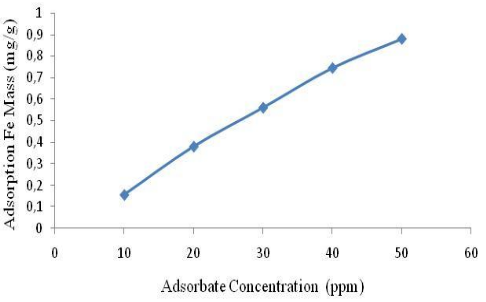


Figure 8. The curve of concentration variation to the % Fe adsorption.

Based on the figure 8, the amount of adsorbed Fe increase along with the increasing Fe that is from 10 to 20 ppm. It is caused by the shift of adsorbate from solution phase to the adsorbent surface is occurred continuously.

At the Fe concentration between 20-50 ppm, there is decrease of adsorption percentage so it is possible the occurrence of the adsorption equilibrium. In the equilibrium, then the adsorption rate proportional with the desorption rate.[14] After attainment of the equilibrium condition, then the use of higher concentration will decrease the adsorbed Fe. It is caused by the concentration addition at the solution phase cause the density of Fe ion increase.

The density increase cause the anion distance become shorter, so there is rejection force among ions. The rejection force of Fe that is not bound strongly to the adsorbent surface will release easily so the adsorbed Fe by fly ashes will be desorbed. The optimum condition of adsorption is attained at the adsorbate concentration of 20 ppm with adsorbed Fe amount of 94.41% . The determination of occurred interaction between adsorbent with adsorbate is determined by Langmuir and Freudlich model that is presented in the figure 9 and 10.

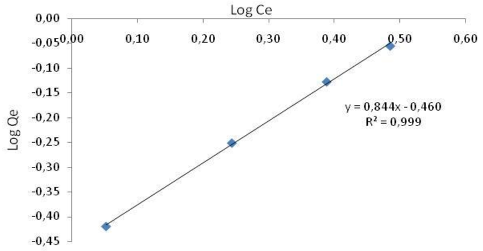


Figure 9. Isotherm graphic of Freundlich adsorption

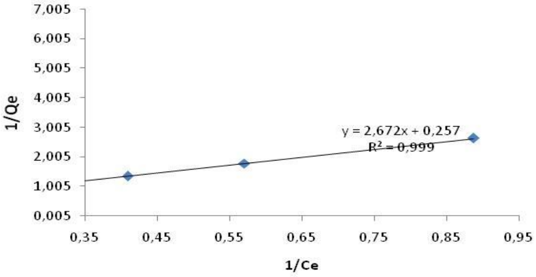


Figure 10. Isotherm graphic of Langmuir adsorption

Based on the comparison of the two modeling linearity of the adsorption is more in line with the modeling described Freundlich. Of modeling prices obtained Freundlich heterogeneity factor (n) of 1.183 mg/g, Freundlich constants of 0.264 L/mg. Freundlich constants indicate affinity adsorbent with adsorbate, ie how strong the interaction between the adsorbent with adsorbate. Freundlich adsorption is the occurred adsorption because of interaction physically that occurred between adsorbate with the adsorbent surface. When the adsorbent surface has been covered by adsorbate, then the non adsorbed adsorbate at the upper/single layer at the adsorbent surface, but also at the second layer and etc so produce multi layers.

Experiment with ground water samples

After get optimum condition from Fe adsorption at the synthesis solution, then it is done at the actual sample (ground water). Before adsorption process of Fe at the actual waste, ground water come from Balikpapan, at Kelurahan Lamaru where the location of sample collection can be seen in the figure 11 below.

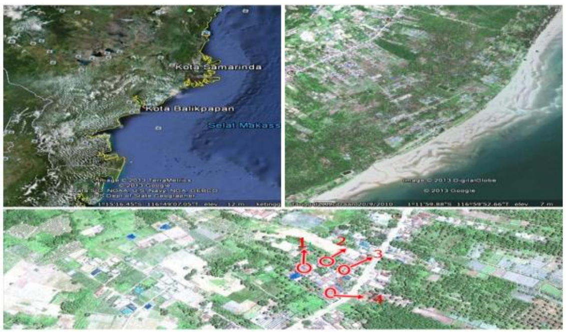
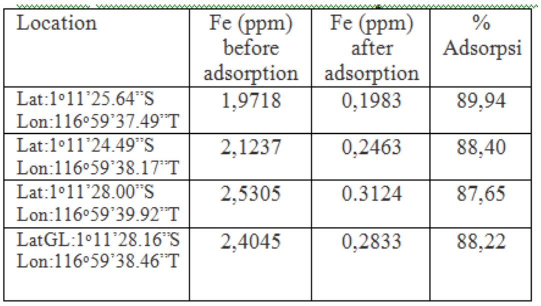


Figure 11. Location of ground water collection. From the figure 11, the sample of ground water are taken from four locations of Kelurahan Lamaru where the waste firstly observed the Fe composition through AAS. It can be seen in the table 3.

Table 3. The content of Fe before adsorption and after adsorption at various locations.



Location	Fe (ppm) before adsorption	Fe (ppm) after adsorption	% Adsorpsi
Lat:1°11’25.64”S Lon:116°59’37.49”T	1,9718	0,1983	89,94
Lat:1°11’24.49”S Lon:116°59’38.17”T	2,1237	0,2463	88,40
Lat:1°11’28.00”S Lon:116°59’39.92”T	2,5305	0.3124	87,65
LatGL:1°11’28.16”S Lon:116°59’38.46”T	2,4045	0,2833	88,22

If it is viewed from table 3, the fly ashes as adsorbent in the optimum condition, that is 2.5 gram, contact time 60 minutes, with stirring speed of 100 rpm able to adsorp Fe at ground water sample of 88.55%.

4. Conclusion

a. Activation of fly ash adsorbent using H_2SO_4 greatly affect the characteristics of the fly ash adsorbent with increasing percentage of 45.75% Si, the presence of silanol and siloxane groups on the adsorbent surface and the increase in adsorbent pore diameter of fly ash (566 nm - 761 nm) into (1.43 - 9.06 μm) and CEC increased from 0.6432 to 17.0448 mek/100 g.

b. The optimum conditions for Fe^{2+} ion adsorption using fly ash obtained adsorbent adsorbent mass of 2.5 grams, long contact time of 60 minutes, the pH optimum at pH 4, and the concentration of adsorbate at a concentration of 20 ppm.

c. Adsorption of Fe^{2+} ions in groundwater samples by an average of 88.55% with an average adsorption capacity of 0.0522 mg/g of lead water wells can be used as a drinking water standard.

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