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## Removal of Mn(II) from the acid mine wastewaters using coal fired bottom ash

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**Abstract.** Acid mine wastewater (AMW), the wastewater from mining activities which has low pH about 3-5 and contains hazardous heavy metals such as Cu, Fe, Mn, Zn, Pb, etc. Those heavy metals pollution is of prime concern from the environmental view point. Among the heavy metals, Mn occupies the third position in the AMW from one the iron ore mining company in Aceh, Indonesia. In this study, the possibility use of bottom ash from coal fired boiler of steam power plants for the removal of Mn(II) in AMW has been investigated. Experimental has been conducted as follows. Activation of bottom ash was done both by physical and chemical treatments through heating at 270 °C and washing with NaOH activator 0.5 and 1 M. Adsorption test contains two parts observation; preliminary and primary experiments. Preliminary study is addressed to select the best condition of three independent variables i.e.: pH of AMW (3 & 7), bottom ash particle size (40, 60 & 100 mesh) and initial Mn(II) concentrations (100 & 600 mg/l). AMW used was synthetics wastewater. It was found that the best value for NaOH is 1 M, pH is 7, particle size is 100 meshes and initial Mn(II) concentration is 600 mg/l from the adsorption efficiency point of view. The maximum adsorption capacity ( $q_e$ ) is 63.7 mg/g with the efficiency of 85%.

### 1. Introduction

One of the heavy metals pollution source is acid mine wastewater (AMW), such as iron core mining. The highest heavy metals contain in the AMW of iron core mining are iron (Fe) and manganese (Mn). Those heavy metals are hazardous and toxic materials. The heavy metals such as Fe and Mn when it accumulated in the human body will attach neural system, blood cell, kidney and bone-calcium content.

In this study, we developed a method for those heavy metals removal in order to solve the environmental problems cause by the AMW. The investigated method for the AMW's metals removal was adsorption, this method is a very usual method used in the wastewater treatment since the method is a lower in cost, without any further effect from hazardous materials and capable also to shift an organic material.

Patil et al. (2016) in their review on the Mn removal technologies both in the water and wastewater concluded that the chemical precipitation (degree of Mn(II) or  $Mn^{2+}$  ions recovery 99.5%),



oxidation/filtration (degree of Mn(II) shifting 95%) and adsorption (degree of Mn(II) removal up to 99.42%) can effectively be applied for that propose. The most promising technology is membrane filtration, with the degree of Mn(II) rejection almost 100%, however, this technology is still expensive. Others technology such as coagulation, flotation, ion exchange and electro-chemical treatment stand below the four technologies mentioned above.

In Mn(II) absorption by using hydrothermally modified bottom ash so that has a similar structure to zeolite (zeolite-like) and zeolite-like modified by dithizone, thermodynamics Mn(II) adsorption behavior by both adsorbent presented the change in Gibbs free energy is positive (endothermic reaction), which mean non-spontaneous chemical reaction. Meanwhile, its entropy change was negative that mean adsorption process occur spontaneously at low temperature. Optimum conditions of Mn(II) adsorption by zeolite-like were at pH 6, adsorption time 60 min, initial metal ion concentration 20 mg/L and temperature 50°C. Further, optimum conditions for adsorption of Mn(II) by zeolite-like modified were observed at pH 8, time 120 min, temperature 60°C and the same initial metal ion concentration (Putra et al., 2015).

Investigation on adsorption of Fe(II) AMW-contaminated ground water has been conducted by Orakwue et al. (2016) by using coal fly ash, bottom ash and bentonite. The highest adsorption capacity provided by bottom ash (~80 g/g), compare to fly ash and bentonite with adsorption capacity only at ~50 mg/g. Moreover, utilization of bottom ash as adsorbent for removing  $\text{Cu}^{2+}$  and  $\text{Ag}^{+}$  in the industrial wastewater has been examined by Kusmiyati et al. (2012). Maximum adsorption capacity occurred at initial metal concentration 25 ppm. Equilibrium state reached after 300 min.

Utilization of bottom ash and fly ash as activated carbon has also been performed by Damayanti et al. (2000). In the study, bottom ash and fly ash activated chemically were applied to reduce Fe and Mn concentrations in the AMW. It was obtained that degree of metal shifting was significant; about 93.6–95.9% for fly ash and about 55.9% for bottom ash.

This paper deal with utilization of bottom ash as an adsorbent for removal the  $\text{Mn}^{2+}$  ions in the AMW (used synthetic waste); to evaluate the effect of adsorbent particle size, pH of AMW, concentration of NaOH (as activator) and initial  $\text{Mn}^{2+}$  ions concentration on the adsorption capacity.

## 2. Experimental procedure

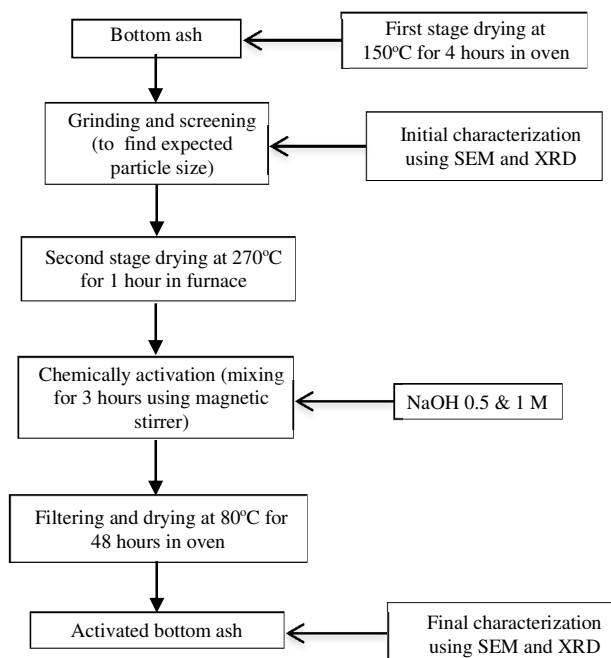
The experimental procedure comprises of materials and apparatus, adsorbent preparation and adsorption study as following.

### 2.1. Materials and apparatus

Material used in the experiment were  $\text{MnSO}_4$  [ $\text{Mn}^{2+}$  ions source], bottom ash from power plant, NaOH, and  $\text{H}_2\text{O}$ . Thus, apparatus needed were magnetic stirrer, pen stirrer, digital balance, 100 ml measuring jug/glass, 250 ml Erlenmeyer, 200 ml beaker glass, 10 ml pipette volume, filter paper, furnace, oven, ball mill, screen, SEM, XRD and AAS.

### 2.2. Adsorbent preparation

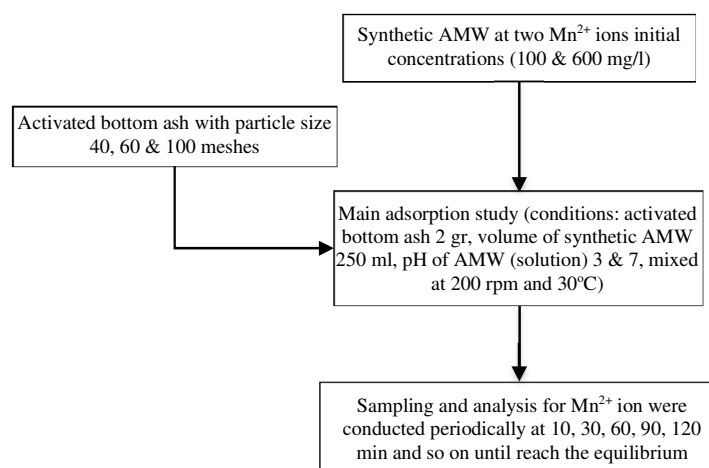
Adsorbent preparation procedure is presented in Figure 1. The chemical treatment was done at two activator (NaOH) concentrations, i.e. 0.5 and 1 M, respectively.



**Figure 1.** Scheme for adsorbent preparation.

### 2.3. Adsorption study

Main experimental was done for three independent variables (initial  $\text{Mn}^{2+}$  ion concentration, pH of synthetic wastewater and bottom ash particle size) as described in Figure 2.



**Figure 2.** Scheme for Mn(II) ion adsorption experimental.

Sampling and analysis for ion metal concentration were done at 10, 30, 60, 90, 120 min, etc. until reached the equilibrium state or  $t_e$  ( $t_e$  = equilibrium time). pH of solution was selected at acid condition (3) and neutral one (7), by considering the real condition in mining site. Most the heavy metal mining produce the AMW that has a lower pH, however, in rainy session the AMW become almost neutral since the lagoon is mostly in open site.

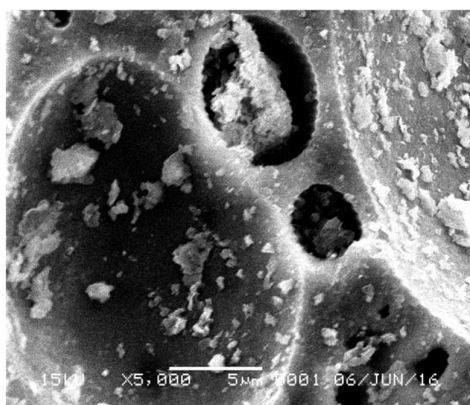
### 3. Results and discussion

The examination results will be provided in this section and discussion on them as well. Attention will be paid on the morphology and chemical constituents of adsorbent, followed by the discussion on the effect of the adsorbent particle size, initial Mn(II) concentration, pH of AMW and activator concentration on the adsorption capacity and efficiency.

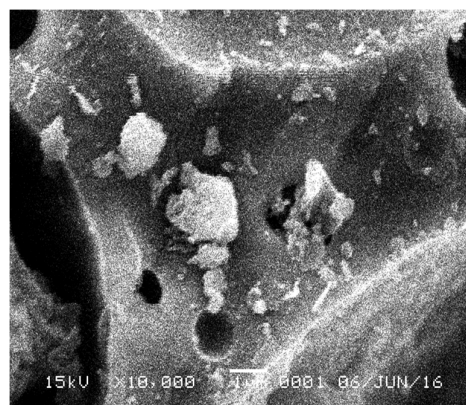
#### 3.1. Morphology of adsorbent

Figure 3 present the Scanning Electron Microscope (SEM) of adsorbent before and after activated at two magnifications 5.000x (diameter 5  $\mu\text{m}$ ) and 10.000x (diameter 1  $\mu\text{m}$ ) both for the adsorbent particle size 40 and 100 meshes.

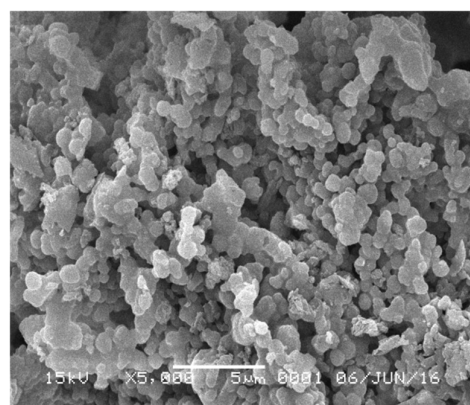
It is evident that the adsorbent before activation has small pore size and number of pore as well as many impurities trapped in the pore as presented in Figure 3(a), (b), (e) and (f). Meanwhile, after activation the size and number of pore increase significantly as shown by Figure 3(c), (d), (g), (h), (i) and (j), especially Figure 3(g) and (h). All the figures clearly reveal the surface structure, porous texture and porosity of the adsorbent. The bottom ash particles are in the form of indefinite shape and of a wide range of sizes. As shown in the images, many small holes are seen on the surface of activated bottom ash. Based on these photomicrographs, particles of the bottom ash can approximated as spheres (Gupta et al., 2004). It was also observed effect of the particle size on the cation exchange capacity (CEC) and weight fraction; it was found that decrease in the particle size caused increase of CEC and oppositely decrease of weight fraction (Gupta et al., 2005).



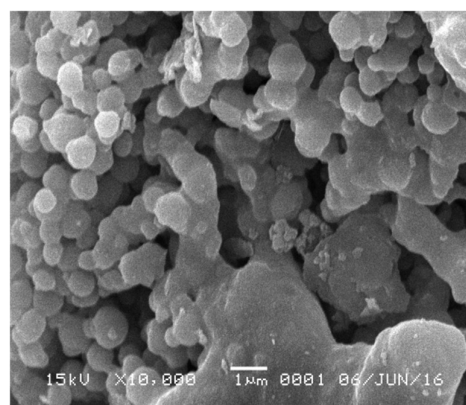
(a) Before activated (particle size 40 mesh; 5,000x)



(b) Before activated (particle size 40 mesh; 10,000x)

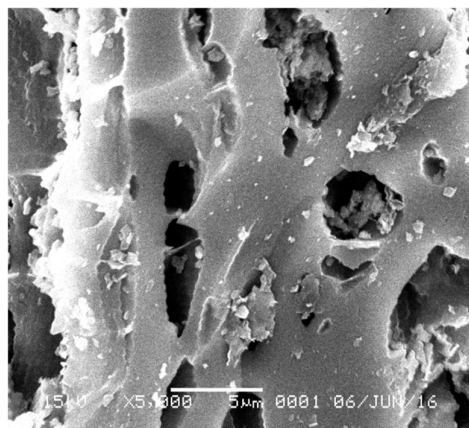


(c) After activated (particle size 40 mesh and NaOH concentration 1 M; 5,000x)

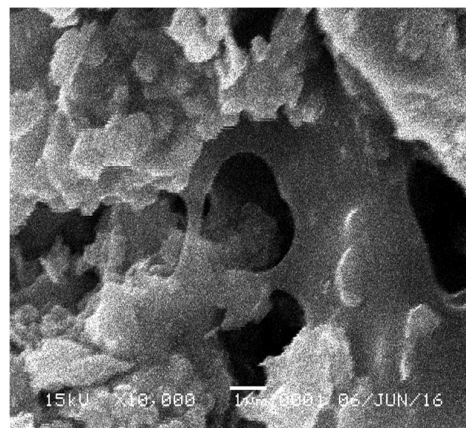


(d) After activated (particle size 40 mesh and NaOH concentration 1 M; 10,000x)

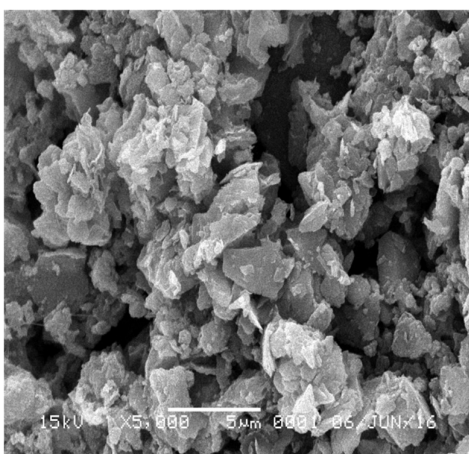




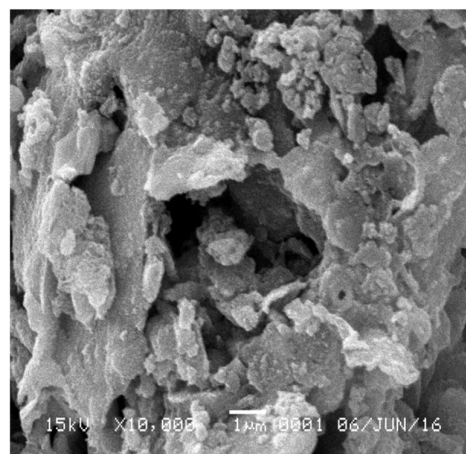
(e) Before activated (particle size 100 mesh; 5,000x)



(f) Before activated (particle size 100 mesh; 10,000x)



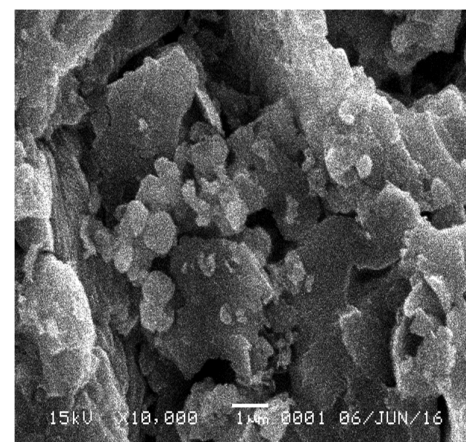
(g) After activated (particle size 100 mesh and NaOH concentration 0.5 M; 5,000x)



(h) After activated (particle size 100 mesh and NaOH concentration 0.5 M; 10,000x)



(i) After activated (particle size 100 mesh and NaOH concentration 1 M; 5,000x)



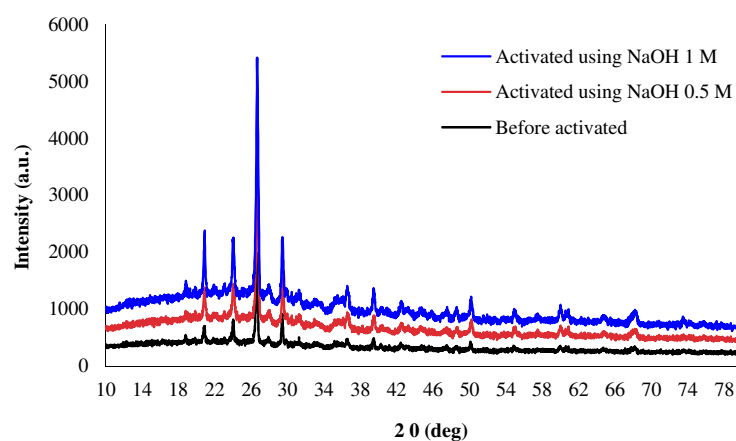
(j) After activated (particle size 100 mesh and NaOH concentration 1 M; 10,000x)

**Figure 3.** Morphology of bottom ash (40 and 100 meshes) before and after activated.

Bottom ash with particle size 100 mesh before activated has less pore and big pore diameter. Meanwhile, after activated was significantly changed; the number of pore greatly enhanced and the pore diameter significantly reduced. It is predicted that the NaOH activator plays an important role chemically to modify the surface and pore structure of bottom ash.

### 3.2. Chemical constituents content

Characterization by using the X-ray diffraction (XRD) was performed in order to identify chemical constituent in the adsorbent. Figure 4 shows that several peaks of bottom ash appear at  $2\theta$  around 10o-80o, 33 peaks for the raw bottom ash (before activated); for the activated bottom ash with NaOH 0.5 and 1 M the number of peaks are significantly increase to 41 and 40, respectively.



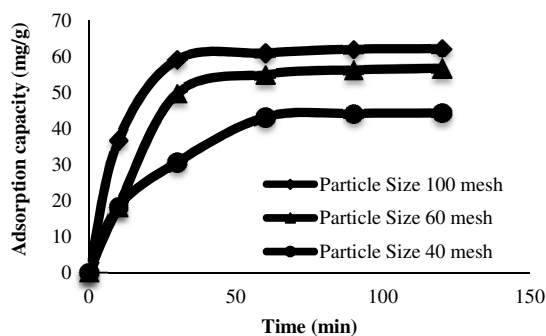
**Figure 4.** Wavelength of infrared spectra for adsorbent

For the raw bottom ash, the peak at  $26.597^\circ$  corresponds to a trigonal (hexagonal axes) crystal structure of  $\text{CaCO}_3$ , followed by others peaks at  $29.380^\circ$ , an orthorhombic crystal structure of C (graphite) and  $23.982^\circ$ , a trigonal crystal structure of  $\text{SiO}_2$  (quartz). Then, the sharp peaks for the activated bottom ash with NaOH 0.5 M occurred at  $26.712^\circ$  described a trigonal crystal structure of  $\text{SiO}_2$  (quartz), followed by others peaks at  $29.482^\circ$ , a trigonal crystal structure of  $\text{CaCO}_3$  (calcite) and  $24.093^\circ$ , also a trigonal crystal structure of  $\text{Fe}_3\text{O}_4$  (iron fluoride). Finally, the peaks for the activated bottom ash with NaOH 1 M appeared at  $26.598^\circ$  shows a trigonal crystal structure of  $\text{SiO}_2$  (quartz), followed by others peaks at  $20.853^\circ$ , a trigonal crystal structure of  $\text{CaCO}_3$  (calcium carbonate) and  $23.974^\circ$  with a cubic crystal structure of C.

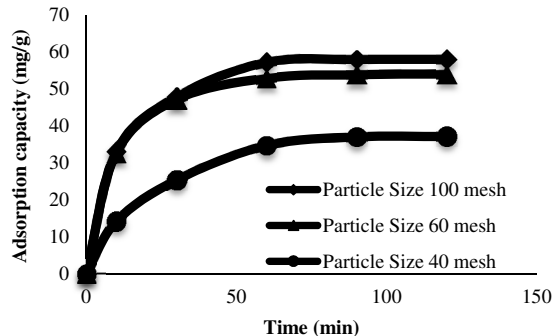
Based on above finding data, it can be postulated that the bottom ash contains the quartz component. In particular for the activated bottom ash, the sharp and higher peaks observed at around  $26^\circ$  correspond to the quartz component, so that the quartz ( $\text{SiO}_2$ ) intensity is the strongest as was investigated by Faridah et al. (2015) and Sutarno et al. (2004). This fact describes that the crystallinity level of the quartz is high. A similar characteristic was exhibited by fly ash which contains silica more than 44% (Sharma et al., 2007).

### 3.3. Effect of the adsorbent particle size, initial Mn(II) concentration, pH of AMW and activator concentration on the adsorption capacity

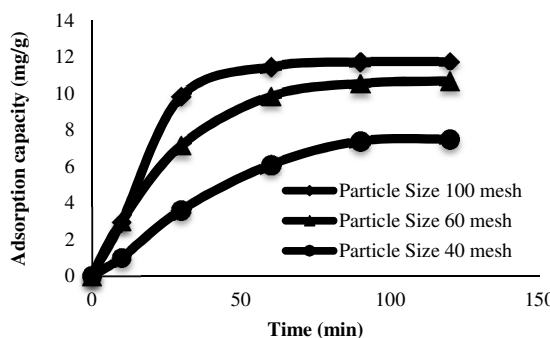
Figures 5 to 10 present the effects of the adsorbent particle size, initial Mn(II) ion concentration, pH of AMW and activator concentration on the adsorption capacity. It can be seen that the initial Mn(II) concentration strongly influences the adsorption capacity, whereas the adsorbent particle size, activator concentration and pH of solution (AMW) show the slightly effect only. This investigated fact correspond well with the result observed by Sharma et al. (2007), especially on the role of Mn(II) concentration.



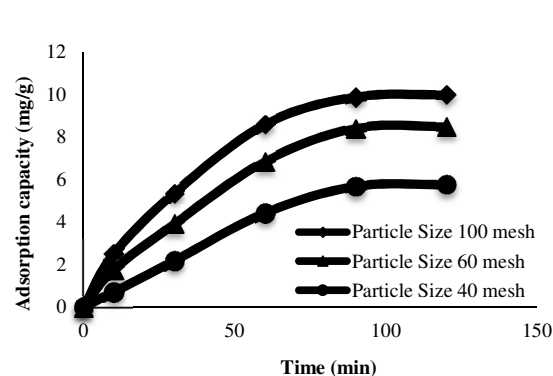
**Figure 5.** Adsorption capacity [initial Mn(II) ion concentration 600 mg/l; pH 7; NaOH 1 M].



**Figure 7.** Adsorption capacity [initial Mn(II) ion concentration 600 mg/l; pH 7 & NaOH 0.5 M].



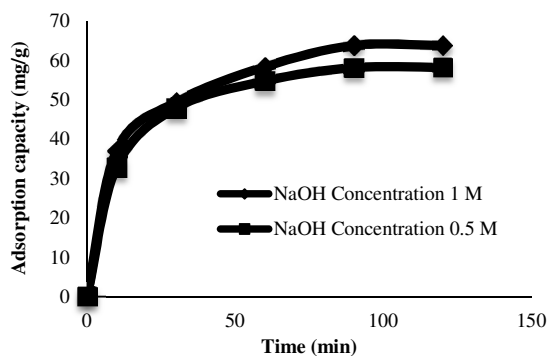
**Figure 6.** Adsorption capacity [initial Mn(II) ion concentration 100 mg/l; pH 7; NaOH 1 M].



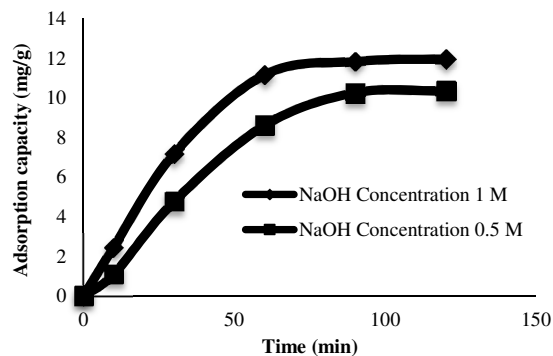
**Figure 8.** Adsorption capacity [initial Mn(II) ion concentration 100 mg/l; pH 7; NaOH 0.5 M]

It is clearly present by Figures 5 to 10 for the initial  $\text{Mn}^{2+}$  ions concentration of 600 mg/l provide the adsorption capacity up to 60 mg/g or more, while for the 100 mg/g ones reach only the level of 12 mg/g (max). As expected, at a small particle size the adsorption capacities are higher since it has big number of pore and small pore diameter compare to the large particle size one, consequently has higher surface area to ensure the contact between  $\text{Mn}^{2+}$  ions and adsorbent. In addition, pH of solution reflects a similar pattern to those parameters even not deeply influence the the adsorption capacity.





**Figure 9.** Adsorption capacity [initial Mn(II) ion concentration 600 mg/l; pH 3; particle size 100 mesh].

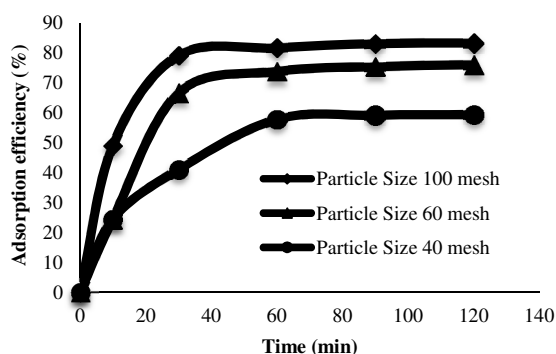


**Figure 10.** Adsorption capacity [initial Mn(II) ion concentration 100 mg/l; pH 3; particle size 100 mesh].

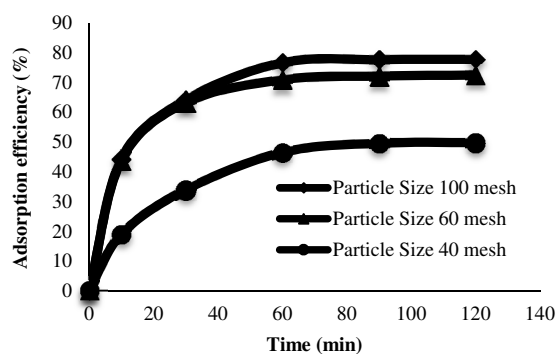
### 3.4. Effect of the adsorbent particle size, initial Mn(II) concentration, pH of AMW and activator concentration on the adsorption efficiency

It was found that the removal efficiency to be highly concentration dependent and higher removal efficiency was obtained at low concentrations of Mn(II) (Sharma et al., 2007). Figures 11 to 16 strongly support the previous observed facts. All the figures evidently describe that the higher efficiencies are detected at the lower initial  $\text{Mn}^{2+}$  ions concentration. The highest efficiency in this study is 85%, it is fantastic compare to the past result up only 74.2% (Sharma et al., 2007). McKay (1982) proposed that higher percentage removal in lower concentration ranges has lot of industrial significance as in most cases the wastewaters have been reported to have lower concentrations of metallic species including Mn(II).

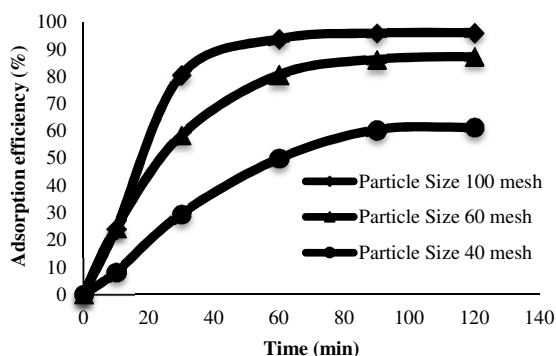
McKay (1982) and McKay and Sweeny (1980) also discusses the effect of adsorbent particle size. Higher external surface area in smaller particle sizes at a constant amount of the adsorbent is the reason for higher removal of Mn(II) at low particle sizes. Increase in removal does not have a 'directly proportional' relationship with particle size. Possible reason for this finding may be the lower free concentration of Mn(II) for smaller adsorbent particles is significantly less than that for the larger ones.



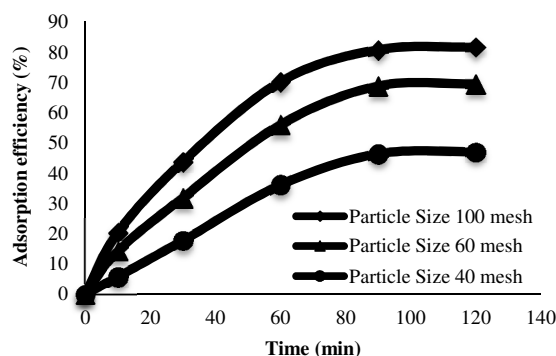
**Figure 11.** Adsorption efficiency [initial Mn(II) ion concentration 600 mg/l; pH 7; NaOH 1 M].



**Figure 13.** Adsorption efficiency [initial Mn(II) ion concentration 600 mg/l; pH 7; NaOH 0.5 M].

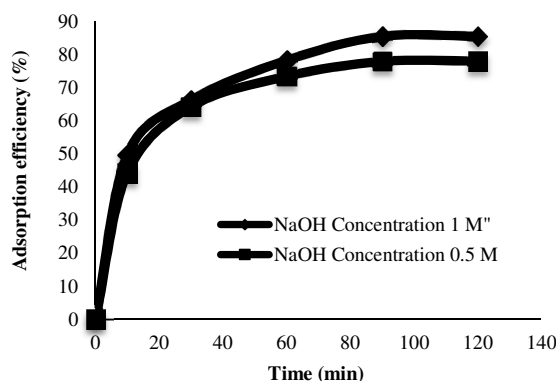


**Figure 12.** Adsorption efficiency [initial Mn(II) ion concentration 100 mg/l; pH 7; NaOH 1 M].

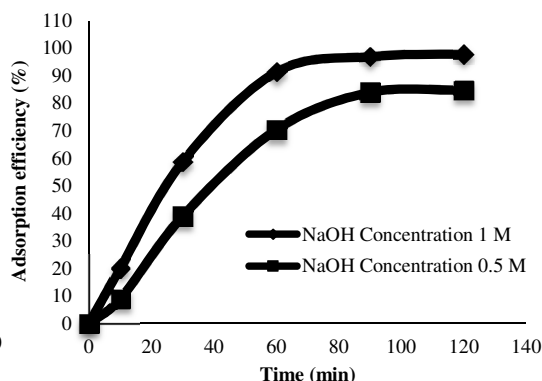


**Figure 14.** Adsorption efficiency [initial Mn(II) ion concentration 100 mg/l; pH 7; NaOH 0.5 M].

Furthermore, Sharma et al. (2007) and Taffarel and Rubio (2009) explained on pH influence. Sharma et al. examined effect of pH on removal of Mn(II) by adsorption on fly ash faced that removal was higher in alkaline range of pH. The removal increased from 41.7 to 92.2% by varying the pH of the solution from 3.0 to 8.5. Their experiment was performed at very low Mn(II) concentration of 1.5 mg/l and temperature of 25°C. That data is in good agreement with the present study. Taffarel and Rubio then wrote the medium pH influenced significantly the Mn<sup>2+</sup> ions adsorption capacity and best results were obtained at pH 6–6.8. In acid medium H<sub>3</sub>O<sup>+</sup> are competitive ions, similar to OH ions in alkaline medium. Those investigated data therefore further strengthen the present observation that the best pH is at 7 (neutral condition).



**Figure 15.** Adsorption efficiency [initial Mn(II) ion concentration 600 mg/l; pH 3; particle size 100 mesh].



**Figure 16.** Adsorption efficiency [initial Mn(II) ion concentration 100 mg/l; pH 3; particle size 100 mesh].

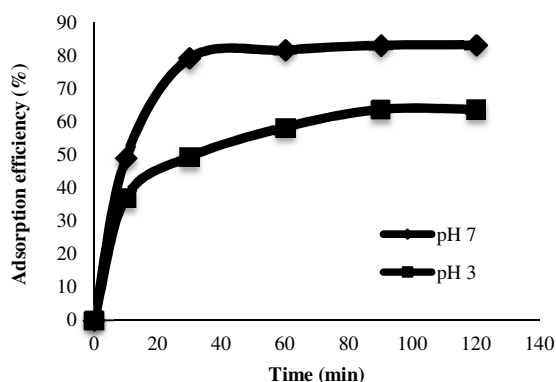
### 3.5. Comparison between pH 3 and 7

The pH of the solution is an important controlling parameter in the adsorption processes (Elliott and Huang, 1981) and metal ion removal usually increases with increasing pH values (Huang and Ostovic, 1978). According to those authors, the pH may affect the ionization degree (species formation) of the adsorbate and the surface property of the adsorbent (Lin and Yang, 2002).

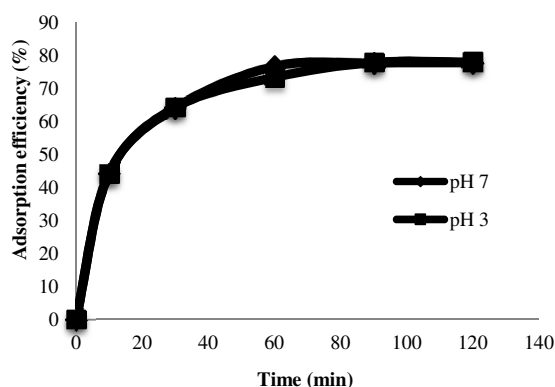
Figures 17 to 20 exhibited the adsorption efficiency as a function of pH. The experiment was conducted at the particle size 100 mesh. Figures 17 and 18 show that the amount of  $Mn^{2+}$  ions adsorbed on the adsorbent increases with the increase of the initial pH, but it is not for Figs. 19 and 20. This phenomenon appears to be due to the fact that bottom ash were highly selective for  $H_3O^+$  ions when the  $H_3O^+$  ions concentration was high (Taffarel and Rubio, 2009). At lower pH the  $H_3O^+$  ions compete with  $Mn^{2+}$  ions for the exchange sites in adsorbent leading to a low removal of  $Mn^{2+}$  ions (Shriver et al., 1990).

The increase in  $Mn^{2+}$  ion removal with the increases in pH can be explained on the basis of a decrease in competition between protons and  $Mn^{2+}$  cations for the same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between the surface and  $Mn^{2+}$  ions before ion-exchange. Adsorption results showed an optimum pH value of about 6 (equilibrium pH fluctuated between 6.0 and 6.8) which is also important in the disposal of the treated effluents (required for neutrality of the bodies ‘‘receivers’’ water or water reuse). The decrease in adsorption at higher pH (above pH 7), is probably due to the formation of insoluble manganese hydroxide  $Mn(OH)_2$  (Taffarel and Rubio, 2009).

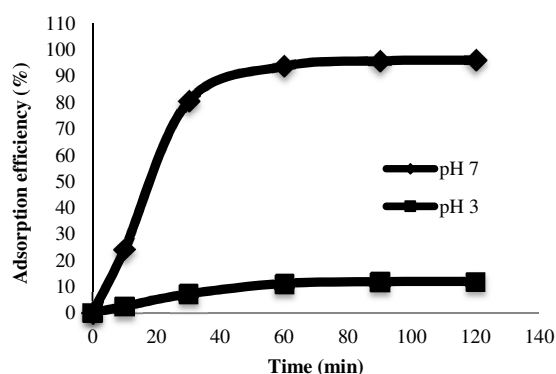
Unfortunately, the effect of pH in this study cannot be distinguished clearly from all points of view in overall.



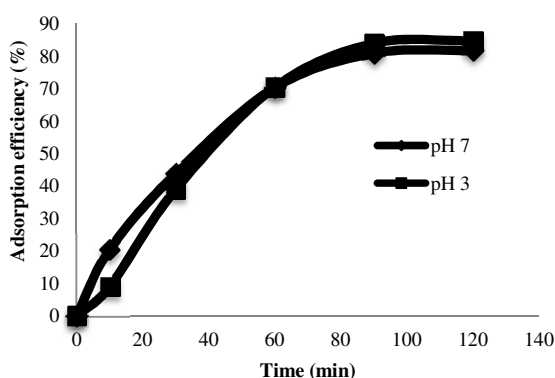
**Figure 17.** Adsorption efficiency [initial Mn(II) ion concentration 600 mg/l; NaOH 1 M].



**Figure 19.** Adsorption efficiency [initial Mn(II) ion concentration 600 mg/l; NaOH 0.5 M].



**Figure 18.** Adsorption efficiency [initial Mn(II) ion concentration 100 mg/l; NaOH 1 M].



**Figure 20.** Adsorption efficiency initial Mn(II) ion concentration 100 mg/l; NaOH 0.5 M].

#### 4. Conclusions

It concluded that the coal fired bottom ash can be applied as an adsorbent for the heavy metal removal (in this study was  $Mn^{2+}$ ). Higher initial  $Mn^{2+}$  ions concentration (of 600 mg/l) provide the higher adsorption capacities (up to 60 mg/g or more), however the higher adsorption efficiencies (up to 100%) are found at lower initial  $Mn^{2+}$  ions concentration (of 100 mg/l). The best recorded particle size, pH and NaOH concentration were 100 mesh, 7 and 1 M, respectively.

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