# THE EFFECT OF KCN ON GOLD ADSORPTION FROM HCl SOLUTION BY SYNTHESIZED MAGNETIC ACTIVATED CARBON COMPOSITE FROM IRON SAND

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***ABSTRACT***

*The composites of magnetic activated carbon has been successfully synthesized by utilizing the available materials abundant in the country such as iron sand, and other chemicals which are easily procured in local markets at low prices. The phase identification using X-ray diffraction technique showed that the magnetic part is $Fe_3O_4$ with crystallite size about 30 nm. The effectiveness of gold absorption from chloride solution by activated carbon magnetic composites are close to 100% and showed very dependent on pH. An addition of KCN in to the gold chloride solution can reduce effectiveness of activated carbon to adsorb gold by up to 20%. These might be caused by the formation of $Au(CN)_2^-$, in the solution, which could change the mechanism of adsorption of gold by the activated carbon. Based on these experimental results, by using chloride it is possible to recover valuable minerals from the ore processing of mining, which are economically,as well as environment friendly and safe.*

*Keywords : gold adsorption, composite, magnetic, activated carbon, iron sand*

## INTRODUCTION

Cyanidation is one of the processes that have been known quiet along time for the extraction of gold from ores. This technique is an economical, biodegradable process and it achieves excellent recoveries from a wide range of ores. However, in recent years, cyanide leaching has been banned in many regions due to environmental concerns. This is due predominantly to the acute toxicity of cyanide, effectively demonstrated by the recent Baia Mare tailings dam breach and subsequent pollution of the Tisza river in Romania (Andrew et al., 2003). Therefore many attempts have been done to replace cyanide by other reagents for the extraction of gold from ores which more environmental friendly. Chloride, thiosulfate, thiourea, ammonia and sulfite have been identified as low costs alternatives, the first two more beneficial in terms of health and safety issue and low environmental impact (Navarro et al., 2005 and Masiya et al., 2009).

Activated carbon is commonly used to remove any number of materials from liquids and gasses, for recovery of values or for purification of a wide range of substances. It is used in water, food, mining, automotive, chemicals, pharmaceutical and environmental industries. A common application of activated carbon is to adsorb ions, complexes and molecules from aqueous solutions, and the like. Accordingly, activated carbon has been used to extract dissolved metals, either to purify the water, nor to recover valuable metallic values.

Many techniques have been used to produce magnetic activated carbon such as mixing or coating carbon or a carbon precursor with a magnetic material, usually with magnetite, and treating to active or transform the carbon or carbon precursor (Ridwan, et al., 2010). These method has significant problem, that the coated magnetic in surface of activated carbon is easily break, braded or comminuted while stirred in the slurry and loss their magnet properties. These unmag-

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netic carbon can not be magnetically separated. An alternative method to produce homogenous magnetic activated carbon is throughout the precipitation of magnetic particle which diverse in to activated carbon particles, so that even a small fines carbon retain the magnetic property. In this paper, the study of synthesized magnetic activated carbon by using iron sand as source of iron through precipitation method followed by the gold adsorption from the chloride solution and the effects of potassium cyanide and pH to the adsorption of gold by magnetic activated carbon were carried out. In order to reduce the operation cost, the chemical reagents such as hydrochloric acid and natrium hydroxide used in this work were purchased from a local market in the form of technical grade.

## EXPERIMENTAL PROCEDURE

### Materials

The iron source used in this experiment was collected from the iron sand which abundantly found around south Yogyakarta beach. This is in accordance with government programs to increase the added value of local natural resources. The separation of iron sand from debris has been done by using magnetic bar and followed by subsequent washing with tap water. The clean iron sand was then dried in the oven at temperature around 90°C. Amount of 100 gram iron sand then poured in to the 250 ml hidrochloric acid of 30% technical grade while stirred by using magnetic stirrer in the temperature around 40°C. The solution of iron chloride was filtered to separate from the insoluble solid, and then keep for several hours to allow some fine particles separated from solution through sedimentation process. The insoluble part of iron sand then were dried and weighed, therefore the amount of iron in solution can be determined.

### Preparation synthesized of magnetic activated carbon

The iron chloride solution was mixed with activated carbon (particles size $\leq$ 100 μm procured from Merck) in amount proportional to the weight of iron soluble in the chloric acid. By using magnetic stirrer, the mixed solution was homogenized for two hours in the temperature keep around 80°C while adding small amount of water to compensate part of solution which was evaporated. The precipitation process of magnetic activated carbon was done by adding the sodium hydroxide solution to the solution of iron hydrochloride which mixed with activated carbon until pH of solution reach to the 12, while continuously stirred for another two hours in order to complete the reaction process. At the end of the reaction, dark black of magnetic activated carbon precursor was sedimented at the bottom of beaker glass and separated from solution by using magnetic bar. The precursor was then wash several time by using tap water until the normal pH was reached. In order to reduce water content in the precursor, at the end of process the precursor was then washed by using of ethanol. The powder of magnetic activated carbon was obtained by drying the precursor for overnight in the oven at 70°C which followed by pulverizing with manual grinding to get fine powder of magnetic activated carbon.

### Gold adsorption by magnetic activated carbon composite

The effectiveness of gold adsorption by magnetic activated carbon composite, in varied of pH solution were evaluated by preparing the stock gold solution of 1.0 g/l gold solution in 10 % HCl, diluted with distilled water untill the concentration of gold in solution was 10 mg/l. The adsorption of gold were done in the variation of pH solution of 8.5, 9.5, 10.5 and 11 adjusted by using potassium hydroxide with or without adding the potassium cyanide in to the gold solution. The gold adsorption were carried out with 30 mg of magnetic activated carbon in a 50 ml gold solution, while shaking continuously for 1, 3, and 5 hours.

## RESULTS AND DISCUSSION

### Characterization of synthesized magnetic activated carbon

The obtained magnetic activated carbon powders phase were characterized by X-ray diffraction (XRD) technique using Cu-Kα incident radiation target. The Retvield analysis of the measured diffracted X-ray pattern, confirmed that obtained constitutes iron oxide were crystallized in $Fe_3O_4$ or $\gamma$-$Fe_2O_3$ phases, as shown in Figure 1.

The size of crystallites were determined based on the full wave half maximum (FWHM) value obtained from refined X-ray diffraction data, calculated by using Scherrer formula (Scott A.

Speakman, http://www.fhi-berlin.mpg.de). The average size of $Fe_3O_4$ crystallite in the magnetic activated carbon powders were ≈ 30 nm. Where the morphology of the activated carbon and their composite magnetic, powders were determined by Scanning Electron Microscope (SEM) as shown in Figure 2 a,b.

Based on the SEM micrograph shown in Figure 2a and b, that the $Fe_3O_4$ particles were formed very likely to fill the pores of activated carbon. It is very possible, because the size of the $Fe_3O_4$ is crystallized in a very small size of about ≈ 30 nm.

The magnetic properties were measured using vibrating sample magnetometer (VSM) operating with the maximum external magnetic field of 10,000 Oe of room temperature. The magnetic measurement were carried out in the form of powder sample placed at stroke plastic tube in diameter of ≈ 1.0 mm. Figure 3a, show the hysteresis loop of magnetic activated carbon, measured at room temperature which shows that the magnetic saturation, Ms ≈ 16.0 emu/g while the intrinsic coercivity is Hci ≈ 191 Oe.

The weak saturation showed by magnetic activated carbon composite, were caused by the dilution effect of non-magnetic components fraction contained in the composite compound such as activated carbon, also the impurities which still take part during the synthesis of $Fe_3O_4$ from iron sand. The effect of impurities to the magnetic properties of synthesized of $Fe_3O_4$ from iron sand, was shown in the Figure 3b, Which shows the magnetic saturation of synthesized $Fe_3O_4$ from iron sand is lower compared to the measured magnetic saturation of $Fe_3O_4$ obtained from Aldrich. The magnetic activated carbon powders synthesized from iron sand in this work were used to study the KCN effect to the adsorption kinetic of gold from the solution.

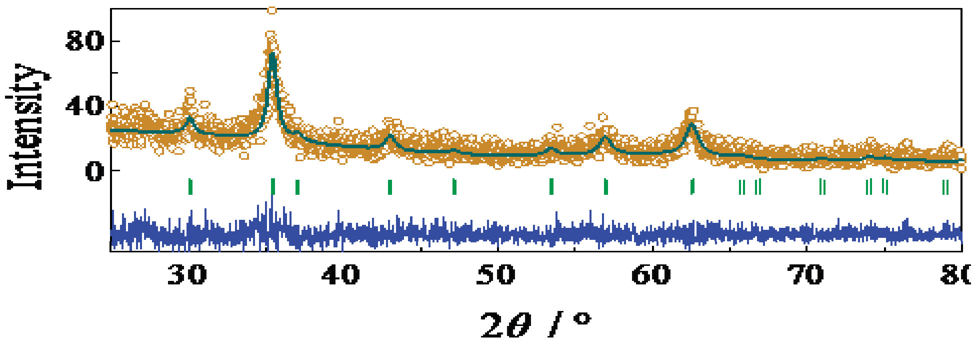


Figure 1. The data analyzed X-ray diffraction of $Fe_3O_4$ by Rietveld method

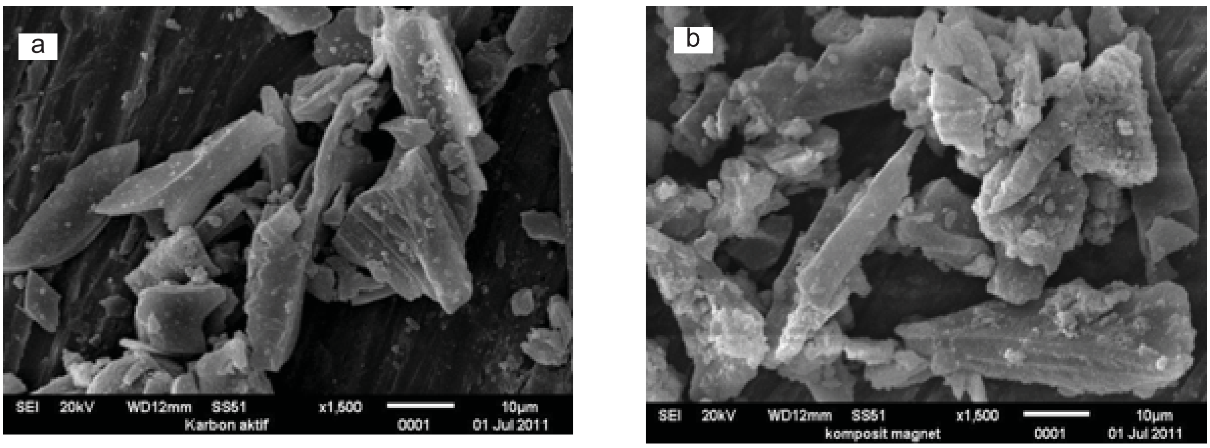


Figure 2. SEM micrograph of a) activated carbon b) synthesized magnetic activated carbon

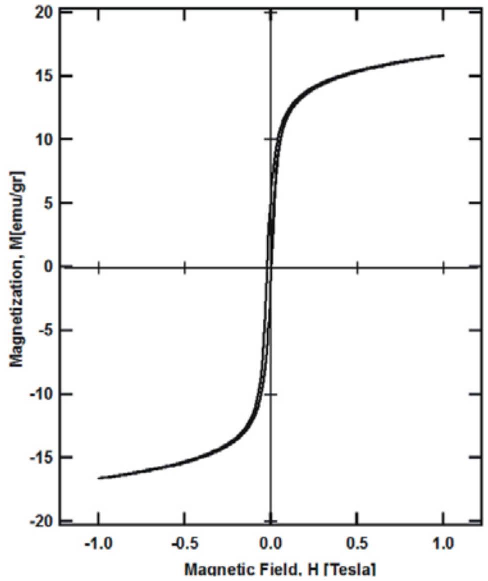


Figure 3a. The hysteresis loop of magnetic activated carbon synthesized by using iron sand.

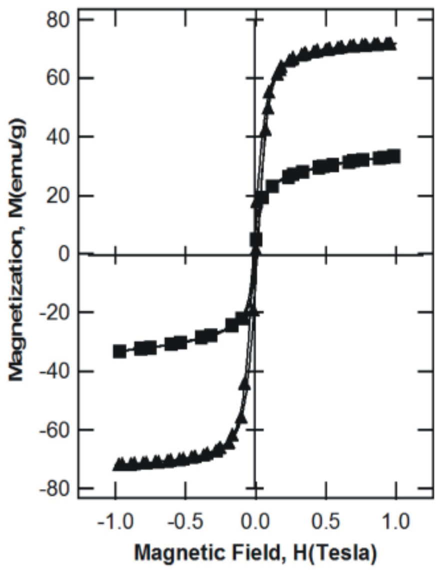


Figure 3b. The hysteresis loop $Fe_3O_4$ obtained from Aldrich (▲) and $Fe_3O_4$ synthesized by using iron sand (■)

### The adsorption of gold by composite magnet activated carbon in varied of pH solution

The effectiveness of gold adsorption was estimated from the percentage of gold adsorption, which was calculated by using the following equation :

$$A = [(C_o - C_t)/ C_o] \times 100$$

where Co is the initial concentration of gold in solution and Ct is the concentration at an elapsed time, t, after the addition of active carbon (Mini Namdeo et al., 2009). The concentration of gold in solution was determined by using AAS, where all the experiments were carried out in the room temperature.

Figure 4, shows the percentage of gold adsorption by magnetic activated carbon composite with variation of pH solutions, without adding KCN at the elapsed of time.

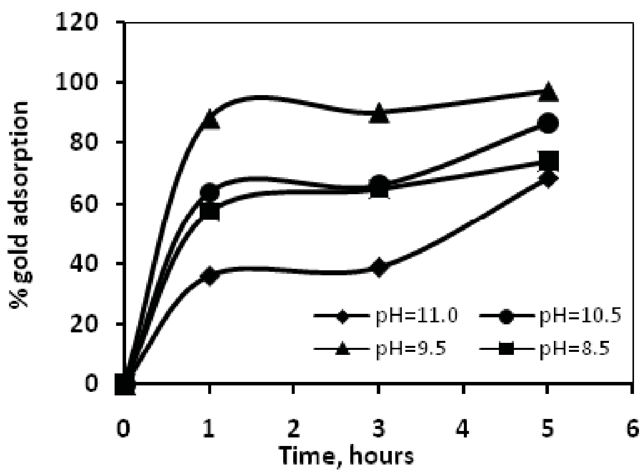


Figure 4. The percentage of gold adsorption on magnetic activated carbon at variation of pH solutions, with initial gold concentration Co ≈ 10ppm

It is shown in Figure 3, that the effectiveness of gold adsorption are strongly dependent on pH of solution. At the beginning, gold adsorption is increasing with the pH of solution and become monotonically decreases when the pH of solution is further increase, where the maximum adsorption at pH value of 9.5. The drop in adsorption rate with increasing pH can be explained by the competition of hydroxide and aurocyanide ions for active sites on the carbon[Davison, 1974]

### The adsorption of gold by magnetic activated carbon composite in varied of pH solution with addition of KCN 500ppm

The effect of KCN to the effectiveness of gold adsorption in varying of pH solution was also studied. The experiments were carried out by adding KCN with as much as 500 ppm into the as prepared gold stock solution of 10 mg/l. The pH of solution is adjusted by using potassium hydroxide to reach the values of 8.5, 9.5, 10.5 and 11. As it was shown, in Figure 5, the highest percentages of adsorbed gold by synthesized magnetic activated carbon composite were occurred at pH value of 8.5, and tend to decrease when the pH solution was increased. When the pH of gold solution adjusted by adding potassium hydroxide, then in the solution will have an additional cation $K^+$ besides anion of $Cl^-$ which may affected the adsorption of gold by activated carbon. The mechanism of adsorption of gold by activated carbon is basically very complex. Parameters such as pH, oxygen and cyanide concentrations, ionic strength and presence of competition between ions in solution-on will also affect the absorption of gold by activated carbon. However, only effect of addition of KCN to the solution of gold chloride to the mechanism of gold adsorption by the composite magnetic activated carbon was studied. While the effect of particle size and temperature of the reaction mechanism that can alter the absorption of gold by activated charcoal may be found in papers H.J. Burnet, 2001.

The results showed that, gold adsorption effectiveness by magnetic activated carbon composite significantly decreased around of 20% with an additional of KCN.

### The adsorption of gold by composite magnet activated carbon in varied of pH solution with addition of KCN, 50, 1000, 200 and 300ppm

For more further insight to understand the effect of KCN in the mechanism of gold adsorption by the magnetic composite, the other experiments were then performed by varying the concentration of KCN in the solution of 50, 100, 200 and 300 ppm while kept the pH of solution at 9.0 (see Figure 6).

In Figure 6, it shows that the effectiveness of gold adsorption with the concentration of KCN in the solution of 50, 100, 200 and 300 ppm at pH=9.0, are almost comparable to each others as well as

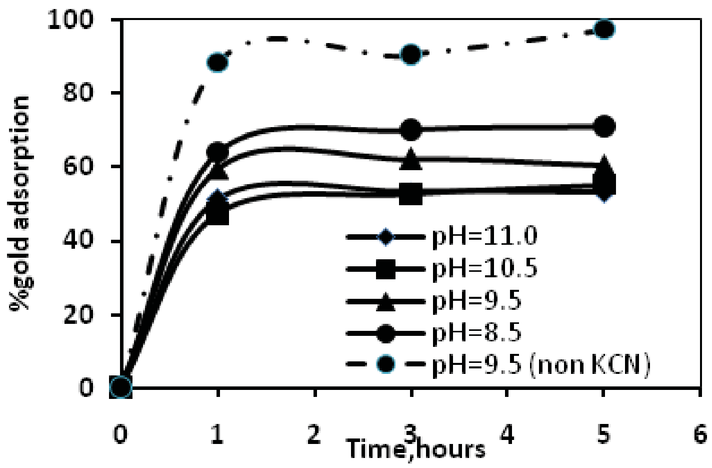


Figure 5. The percentage of gold adsorption on magnetic activated carbon at variation of pH solutions with an additional of 500 ppm KCN, which the initial gold concentration Co ≈ 10ppm

for the concentration of 500 ppm KCN at pH=8.5, see Figure 5. It means from these experiments confirmed that concentration of cyanide in the gold complex solution is not necessarily high for recovering gold from solution.

To study the kinetics of gold adsorption by activated carbon as the effect of the KCN addition to a gold chloride solution at pH= 9.0, the curve plots have been made between the amount of gold absorbed by activated carbon in a given time interval, $q_t$ to the value of the root of the time ($t^{0.5}$). The carbon absorption rate of gold in solution is determined from the slope of the curve $q_t = k_{id}t^{0.5}$, where the value of kid is very dependent on the absorption processes that occur intra-particle diffusion [Mini Namdeo et al., 2009, Lazaridis et al., 2003], as shown in Figure 7.

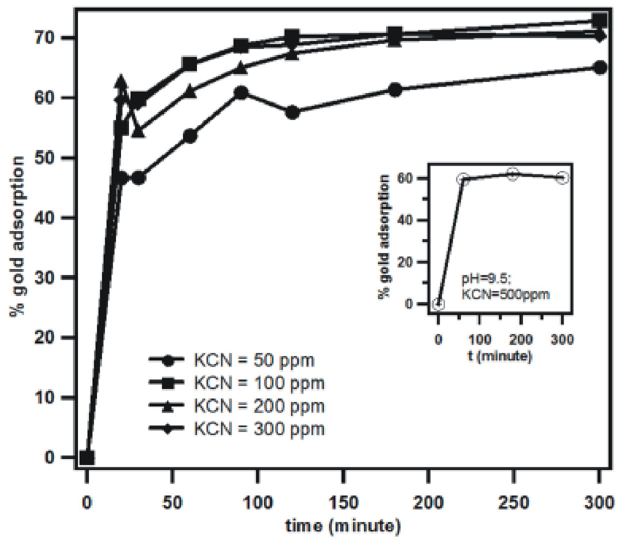


Figure 6. The percentage of gold adsorption on magnetic activated carbon at pH = 9.0 with an addition of KCN = 50, 100, 200 and 300 ppm where the initial gold concentration is Co ≈ 10ppm

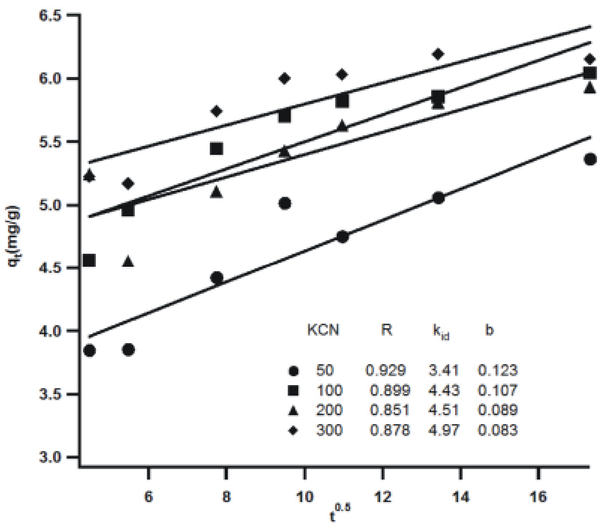


Figure 7. qt (mg g-1) versus t0.5 plot for determination of kid with an addition of KCN

It was shown at Figure 6, the adsorption rate of gold by the activated carbon increased with addition of KCN in solution. These results were agreed with the experiment done by McDougall et al. (1980) which shows that the adsorption rate of gold by the activated carbon was increased by the presence of a common cations such as $K^+$ or $Na^+$ at pH=9.0.

Based on these experiments, it can be concluded that the percentage of gold adsorb by the magnetic activated carbon composite is strongly influenced by the pH. Without the addition of KCN in the solution of gold chloride, the percentage of gold that has been absorbed by activated carbon composite magnet close to 100% at pH = 9.5 in a span of 3 hours, in accordance with the experimental results of Yen and Pindred (1989) . In the case of a solution of gold chloride, gold absorbed on the surface of activated carbon is likely to be a gold metal. This change is related to the transfer of electrons from a solid to the surface of activated carbon [McDougall et al., 1980]. Addition of KCN to a solution of gold chloride, allowing the reaction: $Au\,Cl_2^- + 2\,KCN \rightarrow Au(CN)_2^- + 2KCl$. $Au(CN)_2^-$ absorbed on activated carbon through the mechanism of precipitation into the pores of carbon, where the gold is absorbed not reduced to metallic gold.

## CONCLUSIONS

The absorption of gold from gold chloride solution by magnetic activated carbon composite is very high approaching to 100%. Absorption rate of gold by composite magnet depends strongly on the pH of the solution, with the highest amount of gold absorbed from solution occurred at pH = 9.5. The addition of a solution of KCN caused a decrease in absorption rate approaching 20% gold. This suggests there may have been ongoing reaction between $AuCl_2^-$ with KCN to form clusters $Au(CN)_2^-$, so the mechanism of absorption of gold by activated carbon composite magnets via a different route as well. Gold is absorbed by activated carbon magnetic composites from the solution of gold chloride, may be reduced to the metallic gold, so the process of recovering gold from activated carbon can be done mechanically. Therefore, this opened up an opportunity to be utilized in the process of gold recovering from ore to be more environmental friendly, i.e. without using cyanide solution. Moreover, considering the material used to make activated carbon magnetic composites, which are available in the country and can be obtained easily and cheaply, it is economically feasible to consider for application in the processing of valuable minerals produced from mining activities in the future.

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## REFERENCES

Andrew C. G., Greg W. D., Matthew J. S., Paul R. H., 2003. *Hydrometallurgy*, 69, Elsevier, p 1-21.

Burnett, H.J., *Equilibrium shift of gold adsorption in a batch reactor, Cape Technikon Theses & Dissertations*. (2001). http://dk.cput.ac.za/td_ctech/17.

Lazaridis, N. K., Karapantios, T.D., and Georgantas, D., 2003. *Water Research*, 37(2003) 3023-3033.

Masiya, T. T. and Gudyanga, F. P., 2009. Investigation of granular activated carbon from peach stones for gold adsorption in acidic thiourea, *Hydrometallurgy Conference 2009*, The Southern African Institute of Mining and Metallurgy, p. 465-474.

McDougall, G.J., Hancock, R.D., Nicol, M.J., Wellington, O.L., Copperthwaite, 1980. *Journal of The South African Institute of Mining and Metallurgy*, p. 344-356.

Mini Namdeo and S.K. Bajpai, 2009. EJEAF Che, 8, no.5(2009) 367-381.

Navarro, P., Vargas, C., Alonso,M., Alguacil,F.J., 2005. *Proceeding of the 9th International Conference on Environmental Science and Technology*, p. 1084-1089.

Ridwan, Mujamilah, and Fisli, A., 2010. S*ynthesized of Magnetic Activated Carbon Adsorbent by Wet Milling Method*, to be published.

Scott A. Speakman, 2012. *http://www.fhi-berlin.mpg*. de, February 01, 2012.

Yen, WT, Pindred, R.A., 1989. Pressure oxidation of refractory gold ore with sodium hypochloride, Precious Metals 1989, *Proc. Of the 13 IPMI Conf.*, Montreal, Quebec, June 1989, p 335-343.