

# Detoxification of Cyanide Wastewater using Sawdust and Charcoal pieces

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## Abstract

Cyanide, halides, thiosulphate, thiourea, and thiocyanate are some of the lixivants used in the mining and metallurgical industries for gold and silver extraction from their ores. Cyanide remains the universal ligand for gold extraction because it is less costly as compared with the above-mentioned lixivants. However, cyanide is toxic to plants, animals, aquatic life and humans, and hence, waste cyanide solutions need to be detoxified before disposal. Sawdust and waste charcoal pieces contribute immensely to waste disposal problems in Ghana, and there are efforts to remove them from the environment. This paper assesses the use of sawdust and charcoal pieces in the detoxification of cyanide wastewater in a bid to solve a two-fold problem; waste and environmental problems. Different masses (0 g, 2 g, 5 g and 10 g) of as-received sawdust and charcoal pieces were contacted with different concentrations of standard cyanide solutions (50, 100, 200 ppm) for up to 24 hours. The control experiment, which had no carbonaceous material in 1 L of 100 ppm of cyanide solution, recorded 20% detoxification, ascribed to natural decomposition of cyanide. On the contrary, 90% and 82% detoxification of cyanide were achieved when 2 g of sawdust and charcoal pieces respectively were contacted with 1 L of 100 ppm cyanide solution for 24 hrs. In general, over the 24-hr contact time, the extent of detoxification was not influenced extensively by the mass of carbonaceous material used, and the rate of detoxification was higher with higher concentration of cyanide solution. Sawdust performed generally better than the charcoal pieces, and this was attributed to the finer particle sizes of the as-received sawdust (80%-150  $\mu\text{m}$ ) as against charcoal pieces (10%-150  $\mu\text{m}$ ), though the initial detoxification rate was higher with the charcoal pieces. The result opens avenues for further research in the two-fold clean-up of liquid and solid waste from the environment.

**Keywords:** Cyanide wastewater, Sawdust, Waste charcoal, Detoxification

## 1 Introduction

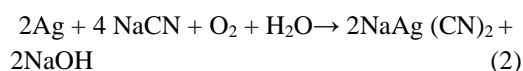
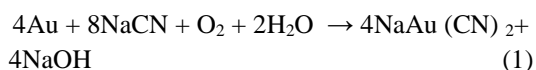
Cyanide generally refers to chemicals that have carbon (C) and nitrogen (N) which are joined together by a triple bond (Pekka, 2005; Francis *et al.*, 2007). Cyanide has the chemical formula as  $\text{CN}^-$  but is usually present as a single charged anion  $\text{CN}^-$ . Free cyanide ( $\text{CN}^-$ ) is a very strong ligand that can form complexes with most metals, and is very toxic even in small dosages (Giraldo and Moreno-Pirajan, 2010). Hydrogen cyanide gas (HCN) is a lethal and very reactive compound formed by cyanide. This gas prevents cells in the body from having access to oxygen thereby causing cell suffocation and can even lead to death. Other forms of cyanide include crystalline potassium cyanide (KCN) and sodium cyanide (NaCN). Cyanide

compounds can cause harm to human beings, animals, plants and aquatic life should they find their way into soil, groundwater and streams in the environment due to their toxic nature (Saarela and Kuokkanen, 2004).

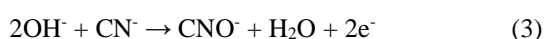
Cyanide is used in the mineral processing (for leaching and electroplating) and also illegally to capture live fish near coral reef for aquarium and seafood markets (Khodadadi *et al.*, 2005). It is used by the mining industry in tremendous quantities, with most being handled without the awareness of cyanide's obvious negative impacts. Apart from its usage in the extraction silver and gold from ores (Marsden and House, 2006; Asamoah *et al.*, 2014), cyanide is also used in low concentrations as an

activator in the flotation of minerals of base metals such as copper, lead and zinc.

Cyanidation involves the use of solutions such as sodium cyanide or potassium cyanide as lixiviants or leaching agents to solubilise and extract precious metals such as gold and silver from ore (Marsden and House, 2006), as depicted in Equations (1) and (2).



Cyanide is a toxic reagent and its effluents are a major source of toxic pollutants in the environment (Saarela and Kuokkanen, 2004; Dash *et al.*, 2009). Due to its toxicity and potentially disastrous environmental effects, there is a necessity to detoxify it before discharging its effluents into the environment. A lot of research has gone into finding pragmatic ways of detoxifying cyanide with major successes being chalked by researchers. Chemical treatment processes such as the  $\text{SO}_2$ /air process, hydrogen peroxide process, Caro's Acid process, Acidification-Volatilization-Recovery (AVR) process, Alkaline Chlorination process, Dilution, natural attenuation, adsorption by activated carbon, reverse osmosis, electrowinning and hydrolysis/distillation have been successful but with some associated problems and limitations (Dwivedi *et al.*, 2011). Biological treatment of cyanide waste is also yielding some good results although it is generally not used on a large scale (Akcil, 2003; Saarela and Kuokkanen, 2004). The fact that activated carbon can catalyse a lot of chemical reactions is known and established. The oxidation of cyanide to cyanate by molecular oxygen (Equation 3) has been achieved by passing cyanide through columnar beds of granular carbonaceous matter which act as a catalyst.



The reaction during this process is slow, and further studies have been done by introducing cupric ions into the water to accelerate and enhance the efficiency of such a process (Adams 1994). Carbonaceous matter such as sawdust and waste charcoal pieces used to be two of the major sources

of fuel for domestic appliances like braziers in Ghana. In recent times, the increase in the usage of LPG gas as an alternative source of fuel has led to a reduction of the dependency on these two products and that has created a surplus of the amount of sawdust and charcoal produced in Ghana. They are still produced in large quantities (from wood loggers and wood mills) with a lack of an expansive avenue for their usage to consume the surplus. This has led to indiscriminate disposal of charcoal and sawdust as wastes. The success of this paper, is to provide an option for using such waste products while solving the environmental and health problems associated with the use of cyanide.

## 2 Resources and Methods Used

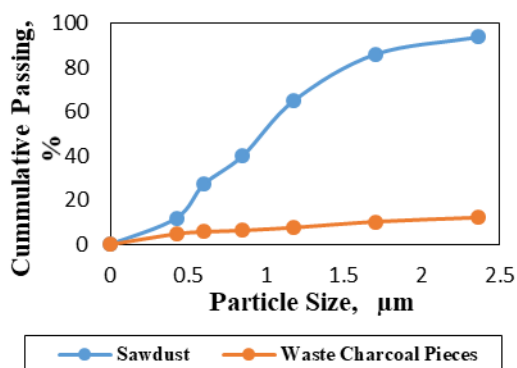
### 2.1 Resources Used

Sawdust was obtained from a local wood processing firm while waste charcoal pieces were acquired from local charcoal sellers. Cyanide, bottles, lime, silver nitrate ( $\text{AgNO}_3$ ), rhodanine, pipette, burette, filter paper and other reagents were obtained from the Minerals Engineering Laboratory in the University of Mines and Technology

### 2.2 Method

#### 2.2.1 Size Analysis

Sawdust and waste charcoal obtained from different sources were homogenized into composites and 100 g representative samples were drawn from each of them for particle size analysis. Sieves of aperture ranging from 2.36  $\mu\text{m}$  to 0.425  $\mu\text{m}$  were built for size analysis. Size analysis was done for 12 minutes using electronic shaker at an amplitude of 1.5 to obtain the particle size distribution for the sawdust and also for the waste charcoal pieces used. The various screen sizes of sawdust and waste charcoal pieces were weighed and recorded.



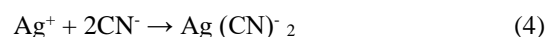
**Figure 1 Size Distribution of Sawdust and Waste Charcoal Pieces**

### 2.2.2 Preparation of Reagent Solutions and Detoxification Process

The reaction bottles were washed thoroughly with water. One litre of water was measured, poured into the bottles and conditioned with lime to a pH of 11 to prevent the formation of hydrogen cyanide gas upon contact with cyanide. Various concentrations of cyanide (50 ppm, 100 ppm and 200 ppm) were prepared by measuring 0.05 g, 0.1 g and 0.2 g of solid cyanide respectively and pouring them into bottles containing the conditioned water.  $\text{AgNO}_3$  was also prepared by weighing 1.73 g of silver nitrate ( $\text{AgNO}_3$ ) into 1-L of de-ionised water. Varying masses of 2 g, 5 g, and 10 g of sawdust and waste charcoal pieces were measured and poured into bottles containing 1-L cyanide solutions. A control solution of 100 ppm cyanide concentration was also observed with no contact of carbonaceous matter. The bottles were then placed on rollers to be rolled and agitated for 24 hours. Samples of cyanide solution in the bottles were taken on a two-hour interval basis for up to 24 hours. The samples were then filtered and 10 ml of the filtrate was titrated against silver nitrate ( $\text{AgNO}_3$ ) of concentration 0.0102 M using rhodanine as the indicator. Titre values obtained were recorded for calculation of cyanide concentration.

### 2.2.3 Calculation of Cyanide Concentration

The reaction between cyanide and silver nitrate has been given in Equation 4 while the formula for calculating cyanide concentration has been elaborated in Equation 5.



$$[\text{CN}^-] = \frac{2 \times [\text{Ag}^+] \times V_{\text{Ag}^+} \times \text{Molar mass of } \text{CN}^-}{V_{\text{CN}^-}} \quad (5)$$

Where  $[\text{CN}^-]$  is the concentration of cyanide in solution

$[\text{Ag}^+]$  is the concentration of silver nitrate

$V_{\text{Ag}^+}$  is the Titre value

$V_{\text{CN}^-}$  is the volume of filtrate containing cyanide used for titration

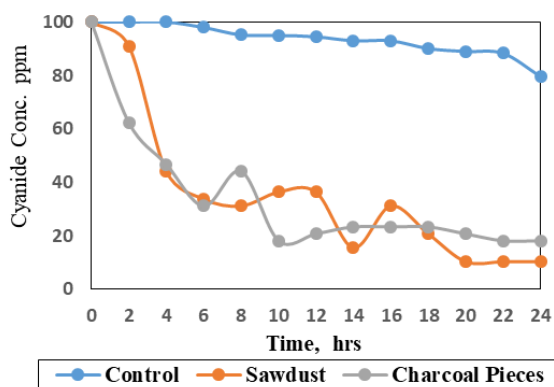
Equation 5 was used to ascertain the extent of cyanide detoxification using waste adsorbents.

## 3 Results and Discussions

This paper set out to ascertain the cyanide detoxification ability of sawdust and waste charcoal pieces and establish parameters that ensure optimum cyanide detoxification. Various concentration (50 ppm, 100 ppm and 200 ppm) of 1 L cyanide solutions were each contacted with 20 g, 50 g, and 100 g of sawdust and waste charcoal pieces. A control experiment of 100 ppm cyanide concentration was also set with no carbonaceous matter. The results are discussed in the following sections.

### 3.1 Cyanide Detoxifying Ability of Carbonaceous Materials

The ability of carbonaceous materials (sawdust and waste charcoal pieces) to detoxify cyanide is presented in Figure 2. From Figure 2, it can be seen that, the control solution which was not contacted with carbonaceous material reduced in concentration from 100 ppm to 87.6 ppm. This reduction can be attributed to the hydrolysis of cyanide to form aqueous hydrogen cyanide at a reduced pH. Aqueous hydrogen cyanide volatilizes easily as hydrocyanic gas with the process of volatilization being enhanced by agitation.



**Figure 2 Cyanide Detoxifying Ability of Sawdust and Charcoal Pieces**

When the cyanide solution was contacted with 2 g of sawdust, cyanide concentration reduced from 100 ppm to about 10.4 ppm after 24 hours as depicted in Figure 2. This drastic reduction in concentration cannot be associated with the hydrolysis of cyanide only but mainly to sawdust which played a major role in the reduction in cyanide concentration. It can also be observed that there was a major drop in cyanide concentration from 100 ppm to 18.2 ppm when the solution was contacted with waste charcoal pieces. This also implies that the waste charcoal pieces were the main reason for the reduction in cyanide concentration and not the formation and volatilization of hydrocyanic gas as was the case with the control solution. The role of the carbonaceous material in the detoxification process results in carbon-oxidative reaction with cyanide solution. The pores exhibited by these carbonaceous materials as a result of their graphitization during their production has oxygen attached to their structure. So when they are introduced in a system containing cyanide because of the oxygen present there is an oxidation reaction which leads to the conversion of cyanide to either cyanogen or cyanate (insoluble product) formation. This brings about the reduction in cyanide concentration. (Stenebraten *et al.*, 2000).

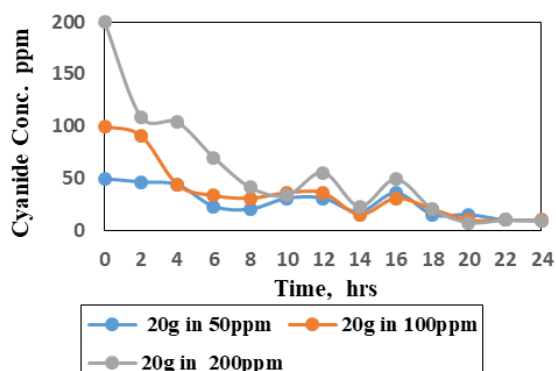
Also, sawdust has macropores and these pores require a longer time for the monomers of cyanide, cyanate or cyanogen to react to form larger polymers before it can be adsorbed into the macropores of the sawdust. The time taken for cyanide, cyanate or cyanogen to polymerize to form larger molecules to fill macropores accounts for the slower kinetics of cyanide adsorption at the early stages of the process. As the adsorption of

larger molecules of cyanide, cyanate or cyanogen occurs, the concentration of cyanide becomes low to a point where polymerization ion becomes very slow and the cyanide system hydrolyses due to the reduction in pH and follows the trend observed in the control (Jakob *et al.*, 2013). Similar process was observed when the cyanide solution was contacted with waste charcoal pieces. In this case the reduction in cyanide concentration is faster due to the micropores exhibited by the waste charcoal pieces. Waste charcoal pieces are partially activated due to the carbonization process. With these micropores present in charcoal, smaller molecules of cyanide, cyanate or cyanogen can be adsorbed without waiting for the molecules to polymerize. This accounts for the sharp reduction in cyanide concentration at the beginning of the curve for the adsorption process using charcoal waste. Charcoal is partially activated and hence the sections that are not activated would behave as if it were sawdust material. The adsorption occurs with the activated sites adsorbing first before non-activated sites. This explains the similarity in trend between the two materials as the adsorption period comes to an end. This process is faster as compared to the sawdust.

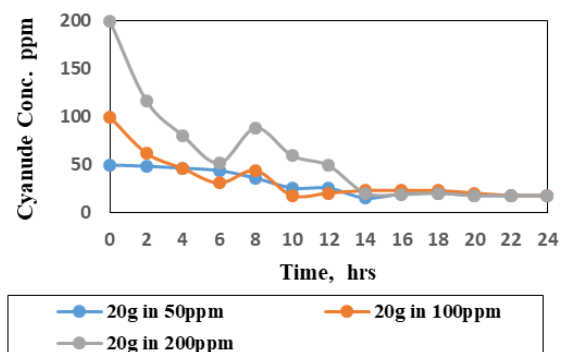
### 3.2 Effects of Cyanide Concentration on Detoxification

Both sawdust and waste charcoal pieces weighing 2-g each was used in the cyanide detoxification process. Figure 3a shows 79.2%, 68.8% and 58.4% detoxification of cyanide solution of concentration in 200 ppm, 100 ppm and 50 ppm respectively within the first 8 hours. After 24 hours, 95.3%, 89.6% and 80.2% of solution cyanide in 200 ppm, 100 ppm and 50 ppm was converted respectively during detoxification. Also from Figure 3b, it was observed that, within the first 6 hours of detoxification 74%, 68.8% and 11.6% of cyanide in 200 ppm, 100 ppm and 50 ppm cyanide solutions respectively were converted. After 24 hours 90.9%, 81.8% and 63.6% of solution cyanide in 200 ppm, 100 ppm and 50 ppm respectively was converted. These results show that the higher the cyanide concentration, the higher the level of cyanide detoxification per unit time. A higher concentration of cyanide means more cyanide ions in the solution is available for conversion and polymerisation. The rate of detoxification increases with increasing cyanide concentration. Furthermore, Figure 3a and

3b depicted slight increment and decrement within the process; 8-18 hours (Figure 3a) and 6-14 hours (Figure 3b).



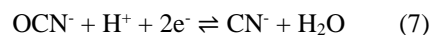
**Figure 3a Effects of Varying Cyanide Concentration on Detoxification with Sawdust**



**Figure 3b Effects of Varying Concentration of Cyanide on Detoxification with Waste Charcoal Pieces**

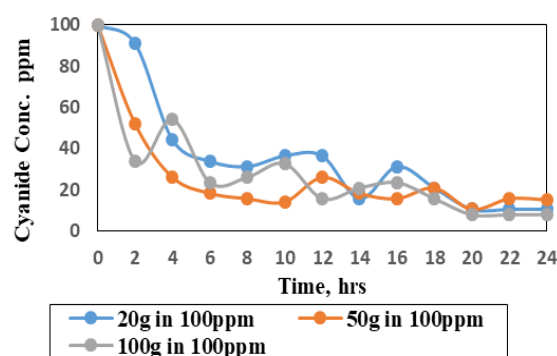
The rise and fall in the cyanide concentration during the process result from the hydrolysis of cyanide and the carbon-oxidative reactions. First, the increase in cyanide concentration can be attributed to two reversible processes that take place during cyanide detoxification as stated by Adams, 1990. The hydrolysis of cyanide to form aqueous hydrogen cyanide, where an increase in OH<sup>-</sup> ions in solution shifts the equilibrium to the left to favour the formation of free cyanide (Equation 6). Also, the conversion of cyanide to cyanate where a pH drop in the solution cyanide leads to deprotonation of H<sup>+</sup> ions and further reaction with cyanate to form free cyanide ions in solution (Equation 7). Moreover, the carbonaceous materials (sawdust and charcoal pieces) in the detoxification process results in polymerisation due to the micro and macro pores exhibited by them and also there is an oxidative reaction which occurs

in the cyanide solution. This reaction leads to the conversion of cyanide to either cyanogen or cyanate (insoluble product) formation which reduce the concentration of cyanide in the system (Senebraten *et al.*, 2000).



### 3.3 Effects of Varying Mass of Carbonaceous Materials.

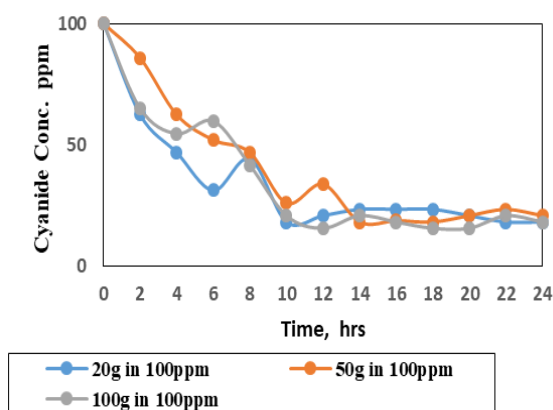
From Figure 4, it was observed that within the first two hours of detoxification with varying masses of sawdust, cyanide concentration reduced from 100 ppm to about 33.8 ppm, 52 ppm and 91 ppm using 10 g, 5 g, and 2 g of sawdust respectively. This could be because more sawdust was available in the 10 g as compared with the 5 g and 2 g. This resulted in the formation of more polymers in the 10 g. From 2 hours to 8 hours, there was a continuous reduction in cyanide concentration for the 5 g and 2 g but the 10 g recorded an increase and decrease in cyanide concentration within the same period. The extent to which the concentration of cyanide is decreased does not depend on the mass of sawdust. At the end of 24 hours, the concentration of cyanide for all the masses of sawdust were similar.



**Figure 4 Effects of Varying Mass of Sawdust on Cyanide Detoxification**

Similar concentrations of cyanide in solution were observed for the various masses of waste charcoal pieces after 10 hours of detoxification as shown in Figure 5. The rate of detoxification of cyanide was the same within the first 10 hours of detoxification for all masses of waste charcoal pieces. No major reduction in cyanide concentration was observed

from 10 hours to 24 hours. The extent to which cyanide was converted did not depend on the mass of waste charcoal pieces used.

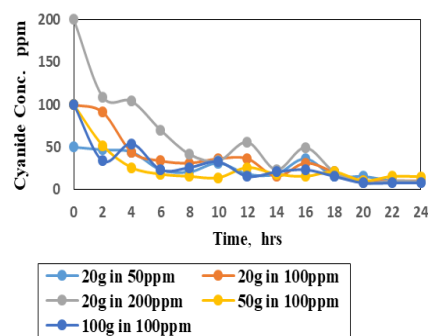


**Figure 5 Effects of Varying Mass of Waste Charcoal Pieces on Cyanide Detoxification**

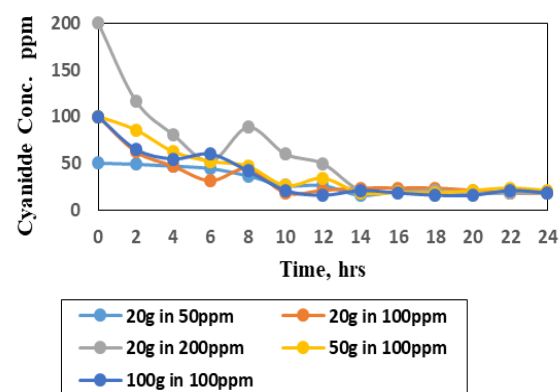
### 3.4 Effects of Time on Detoxification of Cyanide

Figure 6a and 6b show the effect of time on detoxifying cyanide with sawdust and waste charcoal pieces. Observing these figures, as the time for detoxification increases, concentration of cyanide decreases. This applies to all concentrations of cyanide used and all the different masses of sawdust and waste charcoal pieces used for detoxification until after 20 hours and 14 hours of detoxification for sawdust and waste charcoal pieces respectively. The drastic reduction in cyanide concentrations cannot be only attributed to the natural decomposition of cyanide as the time increases but mostly to sawdust and waste charcoal pieces which clearly played a major role in the detoxification process as explained earlier.

The results show that the higher the concentration of cyanide the higher the level of detoxification per unit time. From 20 hours to 24 hours, no significant change in concentration was observed for all samples in Figure 6a and also in Figure 6b from 14 to 24 hours. Cyanide is further reduced to about 10 ppm and 20 ppm after contacting with sawdust and waste charcoal pieces respectively for 24 hours as depicted in the figures.



**Figure 6a Effects of Time on Cyanide Detoxification with Sawdust**



**Figure 6b Effects of Time on Cyanide Detoxification with Waste Charcoal Pieces**

## 4 Conclusions

This paper evaluated the use of carbonaceous materials (sawdust and waste charcoal pieces) in the detoxification of cyanide waste water in a bid to solve a two-fold problem; waste and environmental problems. The results showed that sawdust and waste charcoal pieces can detoxify cyanide. About 90% and 82% detoxification of cyanide were achieved when 2 g of sawdust and charcoal pieces respectively were contacted with 100 ppm cyanide solution for 24 hr. Although the control experiment which had no carbonaceous material in 100 ppm of cyanide solution recorded 20% detoxification. This reduction was ascribed to the hydrolysis of cyanide to form aqueous hydrogen cyanide at a reduced pH. This paper therefore concludes that sawdust is a better detoxifier than waste charcoal pieces due to the finer particle sizes of the as-received sawdust (80%-150  $\mu\text{m}$ ) as against charcoal pieces (10%-150  $\mu\text{m}$ ). However detoxification was faster with the waste charcoal pieces than sawdust and this can also be attributed to the macropores and the activated portions of the waste charcoal pieces due

to the carbonisation process during their production. Also the extent of detoxification after the 24-hr corresponded positively with the mass of carbonaceous material used and negatively with the concentration of cyanide solution. Further research should be conducted to streamline the two-fold clean-up of liquid and solid waste from the environment. Adequate investigations should also be made into which of the two carbonaceous material will be easy to handle after adsorption and prudent ways of disposing of the final product, which is a cyanide-contaminated organic residue.

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