# Adsorption potential of Blast Furnace Granulated slag towards removal of aqueous cyanide

**Dr. Kalpataru Rout[1], Manoj Kumar Sahoo[2], Dr. CR Sahoo[3]**

[1]Sr. Manager, Quality Control, Neelachal Ispat Nigam Limited, Duburi, Odisha
[2]Research Scholar, Dept of Civil Engg, IGIT, Saranga, Odisha
[3]Associate Professor Dept of Civil Engg, IGIT, Saranga, Odisha

---

**Abstract:** *The present work focuses the removal of cyanide present in industrial waste water using granulated BF slag (generated as waste material in steel industry). Cyanide is acutely toxic to humans. Liquid or gaseous hydrogen cyanide and alkali salts of cyanide can enter the body through inhalation, ingestion or absorption through the eyes and skin.*

*The study will help us to assess self adsorption characteristics in plant generated solid waste Vs in plant toxic effluents. In the study shows that granulated BF slag is an efficient adsorbent for the removal of cyanide from industrial waste water.*

***Key Words:* Adsorption column, BF Flue Dust, Cyanide, Equilibrium Isotherms, Equilibrium Kinetics, Granulated BF Slag, Sorption, Wastewater.**

## 1. Introduction:

Cyanide is a carbon-nitrogen chemical unit which combines with many organic and inorganic compounds. It may cause health problems if found in amounts greater than the health standard set by the United States Environmental Protection Agency (EPA). The Maximum Contaminant Level (MCL) has been set at 0.2 ppm.

The steel industry produces waste materials as much as or even more than any other manufacturing industries [1]. Million tons of steel are produced per year and this in return, produces million tons of wastes in the form of slag, dust, sludge, effluents and other pollutants. Some the wastes generated are recycled in the process like sintering and water harvesting, but certain pollutants are very much threat to biological organisms.

Cyanide is the priority pollutant since it is toxic and harmful to organisms even at low concentration. Surface and ground waters are contaminated by cyanide as a result of the continuous release of these compounds from petrochemical, coal conversion and cyanide producing industries. Therefore, the wastewaters containing cyanide compounds must be treated before their discharging into the water streams [2, 3].

Removal of Cyanide from waste water by using banana peel was conducted by Mohammed Nsaif Abbas, Firas Saeed Abbas, Suha Anwer Ibrahim, The University of Mustansiriyah, College of Engineering, Engg department and concluded that banana peels showed a good ability to remove Cyanide ion by using fixed bed adsorption unit.

Conventional methods for the removal of cyanide pollutants in aqueous solutions can be divided into three main categories: physical, chemical and biological treatment [4]. Among them, physical adsorption method is generally considered to be the best, effective, low cost and most frequently used method for the removal of cyanide pollutions. Therefore, the search for low cost and easily available adsorbents has led many researchers to search more economic and efficient techniques of using the natural and synthetic materials as adsorbents. Recently, using the inorganic materials as adsorbents has become one hot research field.

Adsorption as a simple and relatively economical method is a widely used techniques in removal of pollutants. Although the adsorbent used may vary due to the change in adsorption condition depending on the type of pollutants.

## 2. Material & Methods:

Adsorbent - Granulated Blast furnace slag collected from NINL stack yard. The chemical composition of GBFS is given in table 1.

**Table: 1** Chemical Composition:

| Parameters (%) | GBFS |
|---|---|
| $SiO_2$ | 31.00 % |
| $Al_2O_3$ | 23.21 % |
| CaO | 32.64 % |
| MgO | 10.33 % |
| FeO | 0.32 % |
| MnO | 0.33 % |
| S | 0.76 % |
| Basicity (CaO/SiO2) | 1.05 |

### 2.1 Adsorption unit:

Fixed bed column of continuous mode experiment is conducted in order to test cyanide ion removal with the various bed heights of the adsorbent media, at various pH, varying time and varying initial concentration. The representation of sorption unit shown in the figure 1, where the flow direction is down ward by gravity. Glass column has 40 mm internal diameter and 250 mm height and below which a valve is fitted. The heights of adsorbent media at adsorption packed bed were (50, 75, 100, 150, 200 mm).

Before starting the experiments the adsorption column was washed with down flow DM water.

The granulated BF slag is packed in the column to the desired depth, to fed to it as slurry by mixing the slag with DM water, in order to avoid the formation of air bubbles inside the media. After the packed bed sorption column was accommodation and putting the required amount of adsorbent media, the adsorption process started by allowing the cyanide ion of required concentration and pH down flow the sorption column from inlet container by gravity at precise flow rate in experiment which is adjusted by valve. To determine the best operational conditions, the experiments were carried out at temperature at (20 – 55$^{o}$ C), various pH values which are (1- 8) and initial concentration varies between (10 - 50 ppm) and flow rate 5ml/min, for cyanide ion initial feed concentration. Outlet samples after samples after treatment in each experiment were collected every 10 minutes from the bottom of packed column and the unabsorbed concentration of cyanide ion was analyzed.

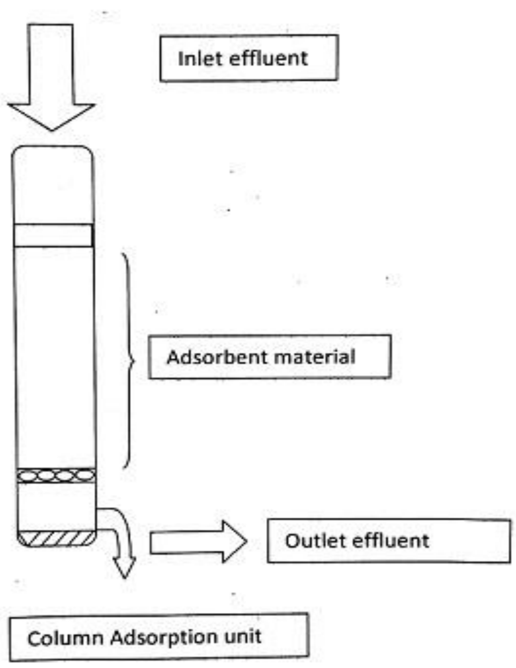


**Fig 1:** Adsorption unit

### 2.1.1 Chemicals used for Cyanide Determination

1. Magnesium Chloride ($MgCl_2$)
2. $H_2$ $SO_4$ (1:1)
3. Sodium Hydroxide (NaOH) (1:1)
4. Lead Acetate
5. Rhodenine indicator
6. Silver Nitrate ($AgNO_3$)

### 2.1.2 Apparatus Used: Distillation Apparatus

### 2.1.3 Procedure for determination of cyanide from waste water

50 ml of waste water sample was taken in a round bottom flask. 20 ml of $MgCl_2$ (51%), 10 ml of $H_2SO_4$ (1:1) was added to it. Then taking the sample in a distillation apparatus, distillation was done for one hour and the distillate was collected in a receiver containing 50 ml NaOH ( 1 N) and few crystal of lead acetate.

Then the receiver solution was filtered and titrated against 0.02 N $AgNO_3$ using rhodanine indicator till colour changes from yellow to salmon red [5].

$$AgNO_3 + NaCN = AgCN + NaNO_3$$

Calculation:
Cyanide in ppm = Burette Reading X dilution factor

### 2.2 Column Study of Cyanide

Adsorbent material: Granulated BF slag
Adsorbate used: Cyanide aqueous solution (NaCN)

### 2.2.1 Adsorption of Cyanide with varying initial CN concentration:

pH = 7.5 (kept fixed)
Height of Bed=200 mm (kept fixed),
Time=60 min (kept fixed)

**Table 2** with varying initial concentration

| Initial concentration (mg/lt) | Cyanide remain (mg/l) | Cyanide Adsorbed (mg/l) | % Remove |
|---|---|---|---|
| 10 | 2 | 8 | 80 |
| 20 | 5 | 15 | 75 |
| 30 | 9 | 21 | 70 |
| 40 | 12.8 | 27.2 | 68 |
| 50 | 17.5 | 32.5 | 65 |

### 2.2.2 Adsorption of Cyanide with varying Bed height:

Cyanide concentration 5 mg/l (kept fixed)

**Table 3** with varying bed height

| Bed Height in (mm) | Cyanide remain (mg/l) | Cyanide Adsorbed (mg/l) | % Remove |
|---|---|---|---|
| 50 | 3 | 2 | 40 |
| 75 | 2.75 | 2.25 | 45 |
| 100 | 2.25 | 2.75 | 55 |
| 150 | 2.4 | 3.6 | 72 |
| 200 | 1.0 | 4 | 80 |

### 2.2.3 Adsorption of Cyanide with varying time of adsorption:

Bed Height=200 mm (kept fixed)
Cyanide concentration=5mg/l (kept fixed)

**Table 4** with varying Time

| Time (min) | Cyanide remain (mg/l) | Cyanide Adsorbed (mg/l) | % Remove |
|---|---|---|---|
| 10 | 3.25 | 1.75 | 35 |
| 20 | 2.9 | 2.10 | 42 |
| 30 | 2.1 | 2.9 | 58 |
| 40 | 1.9 | 3.1 | 62 |
| 50 | 1.45 | 3.55 | 71 |
| 60 | 0.85 | 4.15 | 83 |

### 2.2.4 Adsorption of Cyanide with varying pH:

Cyanide concentration=5 ppm (kept fixed)
Temperature=400 C (kept fixed)
Time=60 min (kept fixed),
Bed Height=200 mm (kept fixed)

**Table 5** with varying pH

| pH | Cyanide remain (mg/l) | Cyanide Adsorbed (mg/l) | % Remove |
|---|---|---|---|
| 1 | 2 | 3 | 60 |
| 2 | 1.5 | 3.5 | 70 |
| 3 | 1.25 | 3.75 | 75 |
| 4 | 1 | 4 | 80 |
| 5 | 0.75 | 4.25 | 85 |
| 6 | 0.65 | 4.35 | 87 |
| 7 | 0.44 | 4.56 | 91.20 |
| 8 | 0.35 | 4.65 | 93 |
| 9 | 0.42 | 4.58 | 91.6 |

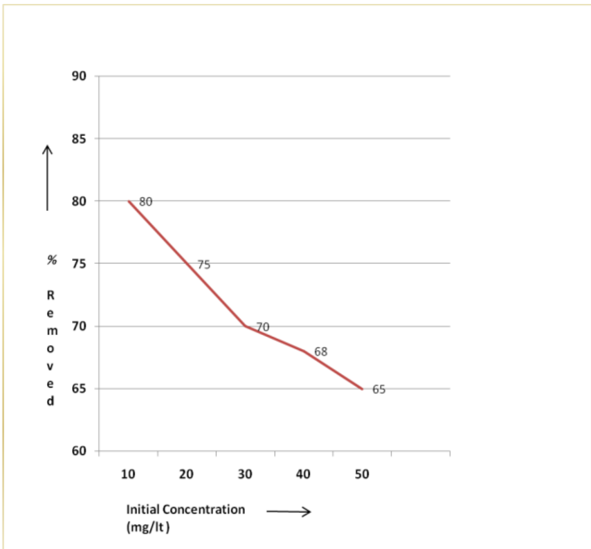


**Fig 2**: Initial Concentrations % cyanide removed

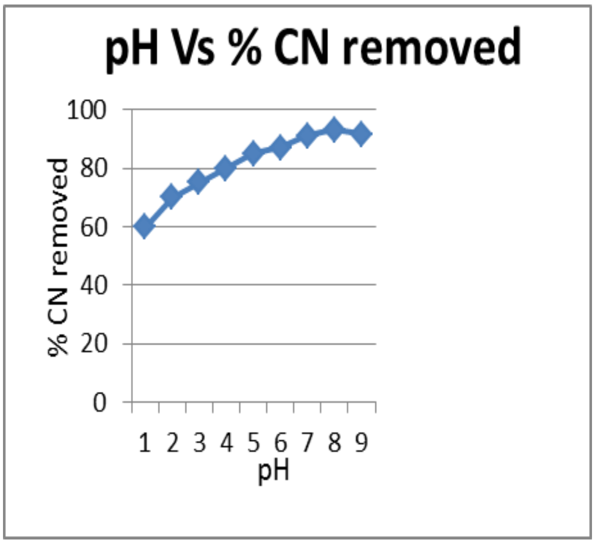


**Fig 3**: pH Vs % cyanide removed

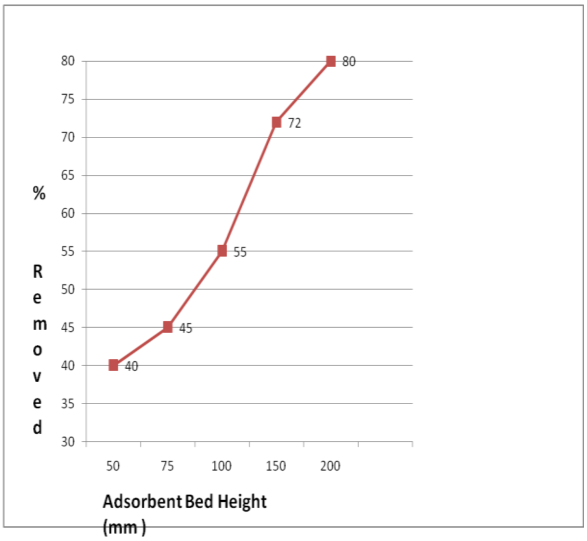


**Fig 4**: Adsorbent Bed Height Vs % cyanide removed

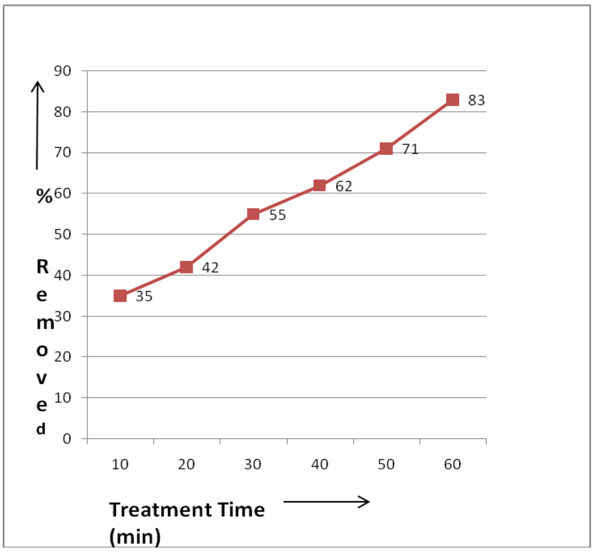


**Fig 5**: Treatment time (min) Vs % cyanide removed

## 3. Results and Discussions:

### 3.1 Initial Concentration Effect

The results in table 2 and figure 2 showed that using adsorbent material, granulated BF slag, the percentage removal of cyanide ion was decreased when the initial concentration of cyanide ion was increased. This can be explained by the fact that the initial concentration of cyanide ion had a restricted effect on cyanide ion removal capacity; simultaneously the adsorbent media had a limited no of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the no of cyanide ion and molecules competing for the available function groups on the surface of adsorbent material. Since the solution of lower concentration of small amount of cyanide ion than the solution of higher concentration of it, so the percentage removal was decreased with increasing initial concentration of cyanide ion.

### 3.2 Effect of pH

The results in table 5 and figure 3 showed that using adsorbent material granulated BF slag, the percentage removal of cyanide ion was increased when the pH of cyanide ion increased, at constant other variable. This growing in removal efficiency can be elucidated as above, the pH of the solution influence the adsorbent surface charged and the ionization degree with speciation of different pollutants. The effect pH was very less pronounced in adsorption but had a marked effect on the stability of cyanide ion. HCN presents at low values of pH which is a weak acid and highly soluble in water. This tendency to water at low pH in habits the adsorptions onto granulated BF slag adsorbent. Also at a higher pH the de-protonation on slag surface provides functional groups, for chemisorptions, on its surface that undergoes ion exchange type of interaction with cyanide ion. In the alkaline pH free cyanide is existed mostly in neutral HCN form. Equilibration adsorption between granulated BF slag and cyanide indicates that extend of adsorption is not dependent on pH range of 7 to 10. Thus the optimum pH for removal of cyanide from the adsorbate is 8.

### 3.3 Adsorbent Media Bed Height Media

The results in table 3 and figure 4 elucidated that when the adsorbent media bed height was increased, the percentage removal of cyanide was increased too. At constant other variables. The increased of bed height meaning increased in the amount of adsorbent media BF granulated slag, thus increasing the surface area of adsorbent material, hence increased the no of active sites in the adsorbent materials i,e increased the availability of binding sites for adsorption and consequently increased the cyanide ion removal capacity on granulated BF slag. This leads to increase the ability of absorbent media to adsorb greater amount of cyanide ion at different initial concentration and ultimately the percentage removal of cyanide ion increased.

### 3.4 Treatment Time Effect

The results in table 4 and figure 5 demonstrated that when the treatment time of cyanide ion increased the percentage removal of cyanide ion increased at constant other variable. This may be due to the fact that when the time of treatment of cyanide increasing and the velocity of cyanide ion in the column packed with the adsorbent material was remaining constant, the solution spend longer time than that spend it when the time of treatment decreased, so the adsorbent material uptake more amount of cyanide ion, therefore the percentage removal of cyanide ion was increased.

## 4. Conclusion

It is inferred from the above observation that granulated BF slag shows good adsorption capacity to remove cyanide from wastewater. The result indicated that the percentage removal of cyanide was considerably affected by initial cyanide concentration, amount of adsorbent dose and mixing contact time. In adsorption of cyanide by using granulated BF slag as adsorbent, it has been studied that the efficiency was decreased with increasing concentration; efficiency was increased with increase the bed height of adsorbent, increase the contact time and increase the pH range. Maximum removal efficiency was 93% for cyanide at pH 8.

The study shows that granulated BF slag may be used as efficient adsorbent material for the removal of cyanide from the industrial waste water, thus reduce pollution.

### Reference:

[1] https://en.wikipedia.org /wiki / iron and steel industry in the united states

[2] LiZ. Butt T. and Bowman R.S. “Sorption of ionizable organic solute by Surfactant modified Zeolite”. Environmental Science Technology 34, (2000), 3756 – 3760

[3] Akcay M., “Characterization and determination of The Thermodynamic and Kinetic properties of P-cP Adsorption unto organophilic Bentonite Aqueous Solution”, J Colloid Interf. Science, Vol 280 (2004) 299/304.

[4] Hao O. J., Kim H. and Chiang P. C., “Decolorization of Wastewater”, Crit. Rev. Environmental Science and Technology, Vol. 30(2000) 449-505.

[5] EPA 815-B-16-012 Aug 2016 - CHEMICAL ANALYSIS OF MUNICIPAL AND INDUSTRIAL WASTEWATER METHOD CYANIDE.

[6] Camps F.E., Robinson A., Lucas Bernard G.B. Volatile poisons and corrosives In Gradwhol‟s Legal Medicine. 3rd Edition, 1976. John Wright & Sons Ltd, Bristol: pp.647-649.

[7] Ludwig J. Current Methods of autopsy practice, 2nd ed., W.B. Saunders Co., Philadelphia: 1979, p529.

[8] Polson C.J., Green M.A., Lee M.R. Clinical Toxicology, J.B.Lippincott Co. Philadelphia: 1983, pp162-196.

[9] Knight B., Saukko P. Corrossive and metallic poisoning In Knight‟s Forensic Pathology. 3rd edition, 2004.Hodder Arnold publications, London: pp585-587.

[10] Andrews J.M., Sweeny E.S., Grey T.C., Wetzel T. The biohazard potential of Cyanide Poisoning during postmortem examination." Journal of Forensic Sciences, JFSCA.vol 34 No: 5 Sept.1989: 1280-1284.