



Adsorption Studies of Cyanide (CN)⁻ on Rice Husk Ash (RHA)

S. Naeem^a, U. Zafar^b and T. Amann^c

^{a,b}PCSIR Laboratories Complex, Lahore, Pakistan and ^cKinnaird college for women, Lahore

Abstract

In this investigation, adsorption of cyanide has been studied by means of batch-technique. Percentage of adsorption was determined for Rice Husk Ash (RHA)-Cyanide solution system as a function of i) contact time, ii) pH, iii) adsorbate concentration and iv) temperature. Adsorption data has been interpreted in terms of Freundlich and Langmuir equations. Thermodynamics parameters for the adsorption system have been determined at three different temperatures. The value of $\Delta H^{\circ}=38.326\text{KJ/mole}$ and $\Delta G^{\circ}=6.117\text{KJ/mole}$ at 283^oK suggest that the adsorption of cyanide on RHA is an endothermic and a spontaneous process.

Key words: Cyanide, Rice husk ash (RHA), Adsorption Isotherms

Introduction

Although cyanides themselves are useful industrial materials, but as a component of waste water certain forms of cyanide are undesirable, having been found to be offensive to the aquatic environment. Examples of the undesirable forms of cyanide are HCN and CN⁻(Tsoung,1992). As an environmentally protective measure, the Environmental Protection Agency (EPA) has placed strict limits on the allowable cyanide levels of industrial waste water effluent streams. Industrial sources of undesirable forms of cyanide are waste water, from electroplating industries. Cyanides are used extensively in metal finishing processes and heat treatment of steel, and are a significant constituent of wastes from coke oven and blast furnace operations. The toxic effect of cyanide is severe and it is established that cyanide at a concentration level of <0.1mg/l is toxic (Anonymous 2005). Therefore waste treatment efforts by industry need persistent analytical procedures and a better understanding of the various cyanide complexes that may be encountered (ASTM 2006).

Substantial elimination of cyanide from waste water by current analytical techniques has been reported by (Tsoung, 1992). Adsorption and biodegradation are two significant methods for treatment of waste water bearing cyanide compounds, either operated separately or simultaneously (Roshan Darh *et al.*, 2006), but the selection of the treatment methods is based on the concentration of waste and the cost of treatment. The process of adsorption is a well established and powerful technique for treating domestic and industrial effluents. Activated carbon which has been the most used adsorbent however it is relatively expensive, other specific

examples of materials which are used as adsorbents include both the naturally occurring materials such as the minerals, zeolites of different types, clays and synthetic materials which include Al₂O₃, SiO₂⁻(Tsoung,1992). Adsorption of cyanide from aqueous solutions at pyrophyllite surface as well as iron-cyanide adsorption on to gamma Al₂O₃ (Sona Saxena *et al.*, 2001, Huang & Cheng 1997) have also been reported.

Various biomass materials and agricultural by-products also have been utilized in the removal of heavy metals and toxic materials from waste water such as walnut waste, maize cobs, peanut shell, cassava waste, wheat bran, maize husk, coconut shell and bagasse (Thomas *et al.*, 2008). The objective of this work was to explore the feasibility of rice husk as an adsorbent for the removal of cyanide from aqueous solution. The pertinent parameters that influence adsorption such as initial cyanide (CN⁻) concentration, agitation time, pH and temperature were investigated. Adsorption isotherms at three different temperatures (i.e.283^oK, 313^oK, 343^oK) have been studied. The adsorption data have been interpreted using Freundlich and Langmuir isotherms. Various thermodynamic parameters including the mean energy of adsorption have been calculated.

Materials and Methods

Preparation of Adsorbent

The rice husk used was obtained from Daroghewala Rice Mill, Lahore. The rice husk was crushed and sieved with 80 mesh sieve. Then the husk was thoroughly washed with dis-

* Corresponding author: E-mail:

tilled water to remove all dirt and then it was dried at 100°C to constant weight. The rice husk was stored in desiccator until used. The rice husk ash (RHA) was prepared from washed and dried by the incineration of rice husk at 750°C in Muffle Furnace, which was ground to -200 mesh and was used without any heat or chemical treatment for the adsorption studies reported here. A complete chemical analysis Table I and (SEM) S2700 Hitachi-JAPAN (Fig-1) of rice husk ash is given showing the presence of SiO₂ which is >90%.

Table I: Chemical analysis of Rice Husk Ash (RHA)

Metal Oxides	Wt. %
SiO ₂	94.7520
Fe ₂ O ₃	0.9000
MgO	0.6400
CaO	0.4980
Na ₂ O	1.0852
K ₂ O	2.0300



Fig. 1: Scanning Electron micrograph of Rice Husk Ash (RHA) at 750 °C

Chemicals

All reagents used in the experimental work were of analytical grade (E. MERCK)[®]. Argentometric (largely AgNO₃) titrations were employed for CN⁻ determination (Vogel, 1961). Stock solution of cyanide (1000 mg l⁻¹) was prepared by dissolving Sodium Cyanide in distilled water. The concentration range of cyanide prepared from stock solution varied between 10 to 80 mg l⁻¹.

Instrumentation

The pH of the solution was measured using micro processor pH meter model HI 8417 by Hanna instruments. A Gallenkamp thermostated automatic shaker model BKS 305-166, UK was used for the batch experiments. The centrifugation was done with Wirowka Type WE-1 centrifuge machine at 4500 rpm.

Adsorption Studies

The adsorption of CN⁻ on Rice Husk Ash (RHA) was studied by batch-technique (Mahvi *et al.*, 2005). The general method used for these studies is described below:

A known weight (i.e., 0.5g of the RHA) was equilibrated with 25cm³ of the spiked cyanide solution of known concentrations in Pyrex glass flasks at a fixed temperature in a thermostated shaker water bath for a known period of time. After equilibrium the suspension was centrifuged in a stoppered tube for 5 minutes at 4500 rpm, was then filtered through Whatman 41 filter paper. All adsorption experiments except where the pH was varied were done at pH 7.20, which was obtained naturally at solution to adsorbent ratio of 50:1. To study the effect of pH, in one set of experiments the pH of the suspensions was adjusted by using NaOH/NH₄OH and HNO₃. The pH of solution was that of supernatant, which was obtained after equilibration. The amount of cyanide adsorbed, 'X' and the equilibrium cyanide concentration in the solution, 'Ce' was always determined volumetrically with standard silver nitrate solution. Adsorption of cyanide on RHA was determined in terms of percentage extraction. Amount of Cyanide ions adsorbed per unit weight of the RHA, X/m was calculated from the initial and final concentration of the solution. Adsorption capacity for the adsorption of cyanide species has been evaluated from the Freundlich and Langmuir adsorption isotherms at three different temperatures (i.e., 10 ± 0.5 °C, 40 ± 0.5 °C and 70 ± 0.5 °C). The cyanide concentration studied was in the range of 10 ppm to 80ppm for 50:1 solution to RHA ratio.

Results and Discussion

The adsorption of cyanide on the RHA was studied as a function of shaking time in water Bath shaker (Gallenkamp-England), pH, adsorbate concentration and temperature for known cyanide concentration at 40±0.5°C. The results are interpreted in terms of percentage adsorption as shown in (Table II A, II B, II C). Adsorption of cyanide on the RHA is rapid at 40±0.5°C; equilibrium reached instantaneously after mixing, indicates that surface precipitation as well as ion exchange may be the possible adsorption mechanism. Similarly adsorption of cyanide as a function of its concentration was studied by varying the metal concentration from 10ppm to 80ppm, percentage adsorption values decreases with increasing metal concentration, which suggests that at least two types of phenomena (i.e. adsorption as well exchange) taking place in the range of metal concentration studied, in addition less favorable lattice positions or exchange sites become involved with increasing metal concentration. The adsorption is pH dependent, a much greater adsorptive capacity for cyanide was observed in neutral solution i.e., pH 7~ 8.0 (Table II A.). Because when the pH is

reduced, surface charge of the particles becomes increasingly positive and because of the competition of the hydrogen ions for the binding sites, metal ions tend to desorb at low pH region, as well a small decrease in cyanide adsorption was observed at pH higher than 9.0. This behavior may be due to

calculated from the distribution constant K by using the following relations:

$$\Delta G^{\circ} = -RT \ln K \quad (1)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \quad (2)$$

$$\text{And } \ln K = -\Delta H^{\circ} / RT + \text{Constant} \quad (3)$$

Table II A: Effect of pH on adsorption of CN⁻ on RHA at 40 ± 0.5°C.

pH	Amount of CN ⁻ taken	Amount of CN ⁻ in soln. at equilibrium	Amount of CN ⁻ adsorbed	Adsorption
	(ppm)	(ppm)	(ppm)	(%)
3.02	10.00	3.707	6.293	62.93
6.25	10.00	3.105	6.895	68.95
7.34	10.00	2.512	7.488	74.88
9.05	10.00	3.207	6.793	67.93
12.08	10.00	3.905	6.095	60.95

Table II B: Effect of temperature on adsorption of CN⁻ on RHA at pH= 7.34

Temperature	Amount of CN ⁻ taken	Amount of CN ⁻ in soln. at equilibrium	Amount of CN ⁻ adsorbed	Adsorption
°C	(ppm)	(ppm)	(ppm)	(%)
10 ± 0.5	10.00	2.512	7.488	74.88
40 ± 0.5	10.00	2.400	7.600	76.00
70 ± 0.5	10.00	2.347	7.653	76.53

Table II C: Dependence of adsorbate concentration relative to CN⁻ on RHA at 40 ± 0.5 °C at pH 7.34.

Amount of Adsorbent Taken	Amount of CN ⁻ taken	Amount of CN ⁻ in soln. at equilibrium	Amount of CN ⁻ adsorbed	Adsorption
	(ppm)	(ppm)	(ppm)	(%)
500.00	10.00	2.400	7.600	76.00
500.00	20.00	6.930	13.07	65.38
500.00	40.00	16.97	23.03	57.56
500.00	60.00	32.70	27.30	45.50
500.00	80.00	52.88	27.12	33.90

the formation of soluble cyanide complexes, which remain in solution as dissolved component.

The adsorption isotherms at three different temperatures (10±0.5 °C, 40±0.5 °C and 70±0.5 °C) were obtained by plotting the amount of cyanide adsorbed on RHA (g/g) against metal at equilibrium concentration (Fig. 2). Adsorption of cyanide increases with increasing temperature. The straight lines were obtained for Freundlich isotherms (Fig. 3), which gave the comparable values of Freundlich constant i.e. 1/n= 0.8321, 0.8338 and 0.8429. Similarly straight lines were obtained for Langmuir adsorption isotherms. (Fig. 4).

Calculations of Thermodynamic Parameters:

Thermo-dynamic parameters such as Gibbs free energy ΔG° (KJ/mol), change in enthalpy ΔH° (KJ/mol) and change in entropy ΔS° (KJmol⁻¹K⁻¹) for cyanide adsorption were

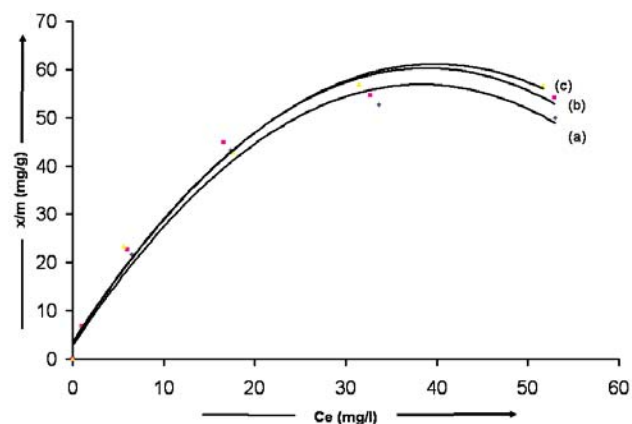


Fig. 2: Adsorption isotherms of CN⁻ on Rice Husk Ash at different temperatures (a) 283°K, (b) 313°K, (c) 323°K

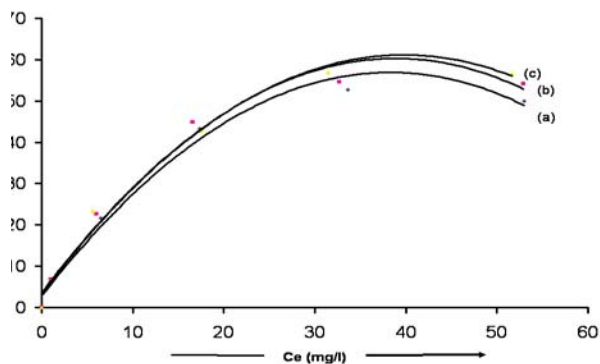


Fig. 3: Freundlich plots of CN⁻ adsorption on rice husk ash at different temperatures (a) 283^oK, (b) 313^oK, (c) 323^oK

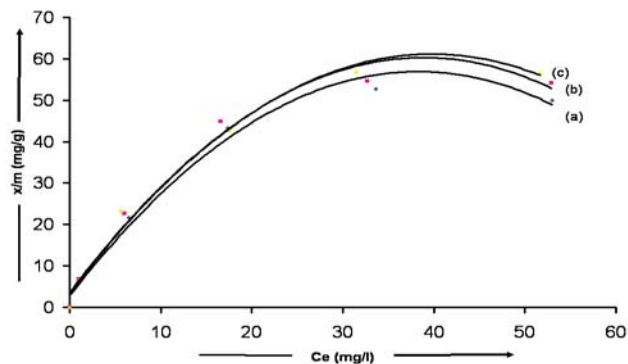


Fig. 4: Langmuir plots of CN⁻ adsorption on Rice Husk Ash at different temperatures (a) 283^oK, (b) 313^o K, (c) 323^oK

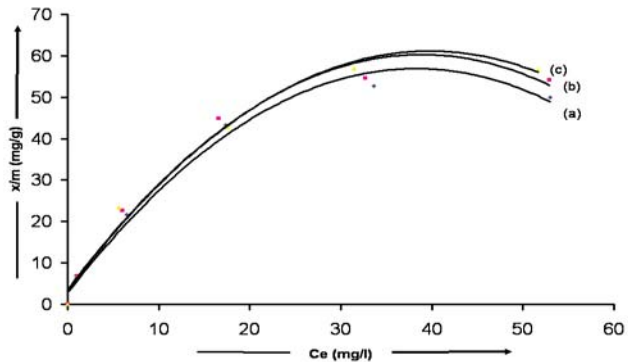


Fig. 5: Plot of lnK Vs.1/T for CN⁻ adsorption on Rice Husk Ash

Table III shows the values of thermodynamics parameters ΔH° ΔS° ΔG° . The positive value of $\Delta H^\circ=38.326\text{KJ/mole}$, which is calculated from equation (3) and Fig. 5, confirms the endothermic nature of the overall adsorption process. The positive value of ΔS° suggests increased randomness at the solid/solution interface with some structural change in the adsorbate and adsorbent and also affinity of the RHA towards CN⁻. A negative value of ΔG° indicates the feasibility and spontaneity of the adsorption process, where higher negative value reflects a more energetically favorable adsorption process.

Table III: Values of Thermodynamic Data for adsorption of CN⁻ on RHA

Temperature K	ΔH° (KJ/mole)	ΔG° KJ/mole	ΔS° (KJK ⁻¹ mol ⁻¹)
283	38.326	-6.117	0.157
313	38.326	-9.037	0.151
323	38.326	-13.46	0.150

Conclusion

Rice husk ash (RHA) is proven to be potentially good scavenger and low-cost adsorbent for the removal of cyanide from aqueous solution, at optimum parameters more specifically pH, as adsorption of cyanide was highly pH dependent. The optimum pH was found to be 7.34, at which cyanide exists mostly as the most easily adsorbed form. In the isotherm studies the experimental adsorption data fitted reasonably well the Langmuir and Freundlich isotherms.

References

Anonymous (2006). Standard Test Methods for Cyanides in Water, American Standards for Testing Materials(International), ASTM D2036-06 pp.82-101.

Hang C. P. and Cheng W. P. (1997). Thermodynamics parameters of iron-cyanide adsorption on to gamma Al₂O₃. *J Colloidal and Interface Sci.* **188**(2): 647-648.

Mahvi A. H., Alavi N. and Maleki A. (2005). Application of rice husk and its ash in cadmium removal from aqueous solution. *Pak. J Biological Sci.***8** (5): 721-725.

Anonymous Ministry of Health, the Govt.of Pakistan. (2005). Quality Drinking Water: Guidelines and Standards for Pakistan.

Roshan R. D., Balomajumder C. and Kumar A. (2006). Cyanide removal by combined adsorption and biodegradation process. *Iran J. Environ. Health. Sci. Eng.***3** (2): 91-96.

Sona S., Prasad M., Amritphale S. S. and Navin C. (2001). Adsorption of Cyanide from aqueous solutions at pyrophyllite surface. *Separation and Purification Technology.***24** (2): 263-270.

Thomas A. J., Niveta J., Joshi H. C. and Prasad S. (2008). Agricultural and agro-processing wastes as low cost adsorbents for metal removal from wastewater: A review. *J Scientific & Industrial Research.* **67**: 647-658.

Tsoug Y. Y. (1992). Removal of cyanide from water. United states Patent No.5112494 May 12.

Vogel A. I. (1961). A Text-Book of Quantitative Inorganic Analysis. 3rd Ed. (Richard Clay and Company, Ltd. Great Britain) pp.271-272.

Received : October 14, 2009;
Accepted : February 18, 2010