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Adsorption Studies of Cyanide $(CN)^-$ on Alumina

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Abstract

In this investigation, adsorption of cyanide on to alumina has been studied by means of batch-technique. Percentage adsorption was determined for Alumina-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 ΔH^o=5.448kJ/mole and ΔG^o=-7.162kJ/mole at 283K suggest that the adsorption of cyanide on Alumina is an endothermic and spontaneous process.

Keywords: Cyanide, Alumina, 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^-[1]. As an environmentally protective measure, the Environmental Protection Agency (EPA) has placed strict limits on the allowable cyanide levels of industrial wastewater 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 effects of cyanide are so severe to cause thyroid glands malfunctioning and nerve damage and established toxicity level so low (<0.1mg/l) [2] that waste treatment efforts by industry need persistent analytical procedures for a better understanding of the various cyanide complexes that may be encountered [3].

Substantially elimination of cyanide from waste water by current analytical techniques has been reported by Tsoung [1]. Adsorption and biodegradation are two significant methods for treatment of wastewater bearing cyanide compounds, either operated separately or simultaneously [4] 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 Al_2O_3, SiO_2 [1]. Iron-cyanide adsorption on to gamma Al_2O_3 [5] as well adsorption of cyanide from aqueous solutions at pyrophyllite surface [6] have also been reported by different workers. Likewise batch and column tests were performed with various soils yielded significant removal of free cyanide at near-neutral pH values [7].

The objective of this work is to explore environment friendly material like Alumina 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.283K, 313K, 323K) 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.

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Materials and Methods

All reagents used in the experimental work were of analytical grade (E.MERCK)® Argentmetric (largely $AgNO_3$) titrations were employed for CN^- determination [8]. Stock solution of cyanide (1000mgl^-) was prepared by dissolving Sodium cyanide in distilled water. The concentration range of cyanide prepared from stock solution varied between 10 to 80mgl^-.

Adsorbent

α- Alumina (E.MERCK)™, with a BET area of 100±30m^2g^{-1}, density 3.970g/cm^3 and a mean particle size 20nm was used as an adsorbent without any heat and chemical treatment.

Instrumentation

The pH of the solutions 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 4500rpm.

Adsorption studies

The adsorption of CN^- on α-Alumina was studied by batch-technique [9]. The general method used for these studies is described below:

A known weight (i.e., 0.5g of the Alumina) was equilibrated with 25cm^3 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 (i.e. 30 minutes). 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 $NaOH/NH_4OH$ and HNO_3.The pH of solutions was in the range of 3.0-12. 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 Alumina was determined in terms of percentage extraction. Amount adsorbed per unit weight of the Alumina, 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 were studied at three different temperatures (i.e. 283K, 313K, 323K). The cyanide concentration studied was in the range of 10pmm to 80ppm for 50:1 solution to Alumina ratio.

Results and Discussion

The adsorption of cyanide on the Alumina was studied as a function of shaking time in water Bath shaker (Gallenkamp-England), pH, adsorbate concentration and temperature for known cyanide concentration at 313K. The results are interpreted in terms of percentage adsorption. The variation of %adsorption with different intervals of time ranging from 5 minutes to 24 hours is illustrated by Fig.1 which shows that the adsorption of cyanide at 10ppm as well as 40 ppm concentration on alumina is rapid at 313K and equilibrium reached instantaneously after mixing cyanide solution with alumina. No significant change in %adsorption values was observed up to 24 hours, which indicates that surface precipitation as well as ion exchange may be the possible adsorption mechanism. Therefore, equilibrium time of 30 minutes was selected for all further studies. The adsorption is pH dependent, a much greater adsorptive capacity for cyanide was observed in neutral solution i.e., pH 7- 8.0 Table-1A,. 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 desorbs 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 the formation of soluble cyanide complexes, which remain in solution as dissolved component. Similarly adsorption of cyanide as a function of its concentration was studied by varying the metal concentration from 10ppm to 80pmm, %age adsorption values decreases with increasing metal concentration Table-1B, which suggest that at least two types of phenomena (i.e. adsorption as well ion-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 isotherms** at three different temperatures (i.e.283K, 313K, 323K) were obtained by plotting the amount of cyanide adsorbed on alumina (mg/g) against metal at equilibrium concentration 'Ce' (mg/l) Fig. 2 and Table-1C. Adsorption of cyanide decreases with increasing temperature. Two models, Langmuir and Freundlich equations, were used to describe experimental data for adsorption isotherms.

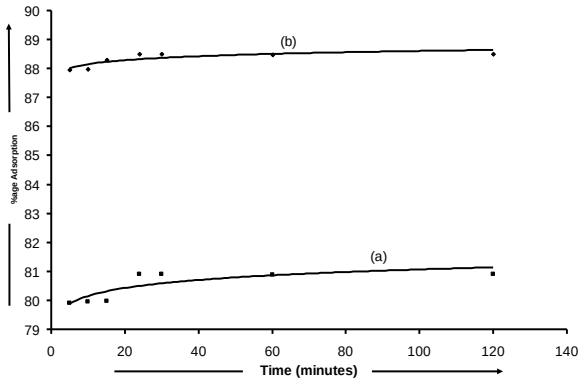

Figure 1. **Effect of shaking time on %age Adsorption at (a) 10ppm, (b) 40 ppm for CN^- adsorption on Alumina.**

Table-1-A: **Effect of pH on Adsorption of CN^- on Alumina at 313K.**

pH	Amount of CN^- Taken	Amount of CN^- in Soln. at Equilibrium	Amount of CN^- Adsorbed	Adsorption
	(ppm)	*(ppm)*	*(ppm)*	*(%)*
3.02	10.00	2.46	7.54	75.40
6.25	10.00	1.60	8.40	84.00
7.34	10.00	1.15	8.85	88.50
9.05	10.00	2.02	7.98	79.80
12.08	10.00	2.70	7.30	73.00

Table-1-B: **Dependence of Adsorbate concentration relative to CN^- on Alumina at 313K at pH 7.34.**

Amount of Adsorbent Taken	Amount of CN^- Taken	Amount of CN^- in Soln. at Equilibrium	Amount of CN^- Adsorbed	Adsorption
(mg)	*(ppm)*	*(ppm)*	*(ppm)*	*(%)*
500.00	10.00	1.15	8.85	88.50
500.00	20.00	2.80	17.20	86.00
500.00	40.00	7.640	32.60	80.90
500.00	60.00	12.60	47.40	79.00
500.00	80.00	20.80	59.20	74.00

The linear form of the Freundlich isotherm model is given by the following relation:

$$\log X/m = \log K_F + 1/n \log Ce \quad (1)$$

Where X/m is the amount adsorbed at equilibrium (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/l), and K_F and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity respectively, of the sorbent. The values of K_F and 1/n can be obtained from the intercept and slope respectively, of the linear plot of experimental data of logX/m versus logCe.

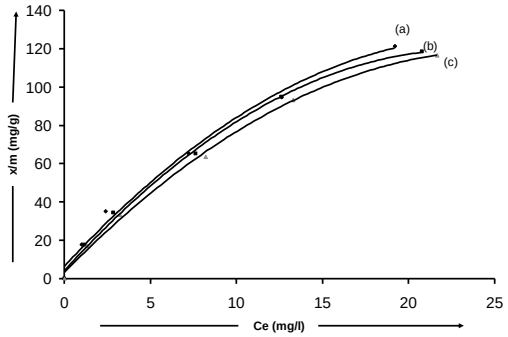

Figure 2. **Adsorption isotherms of CN^- on Alumina at different temperatures: (a) 283K, (b) 313K, (c) 323K.**

Table-1-C: **Effect of Temperature on Adsorption of CN^- on Alumina at pH= 7.34.**

Temperature	Amount of CN^- Taken	Amount of CN^- in Soln. at Equilibrium	Amount of CN^- Adsorbed	Adsorption
K	*(ppm)*	*(ppm)*	*(ppm)*	*(%)*
283	10.00	1.10	8.90	89.00
313	10.00	1.15	8.85	88.52
323	10.00	1.30	8.70	87.00

The linear form of the Langmuir isotherm model can be represented by the following relation:

$$Ce/X/m = 1/K_L Vm + Ce/Vm \quad (2)$$

Where Vm and K_L are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and slope of the linear plot of experimental data of Ce/X/m versus Ce. The linearized Freundlich and Langmuir adsorption isotherms are shown in Fig. 3 and Fig. 4. The related parameters of Langmuir and Freundlich models are summarized in Table 2. The results reveal that both the Langmuir and Freundlich isotherm models can adequately describe the adsorption data.

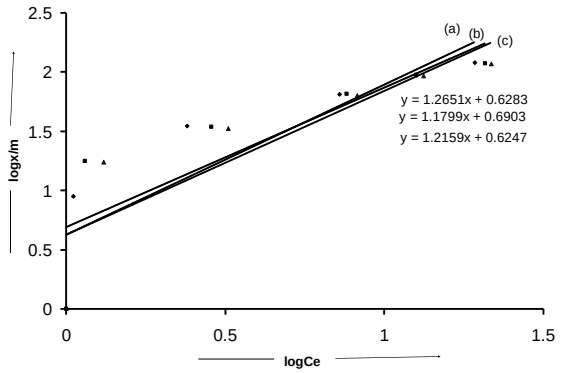

Figure 3. **Freundlich plots of CN^- adsorption on Alumina at different temperatures: (a) 283K,(b) 313K,(c)323K.**

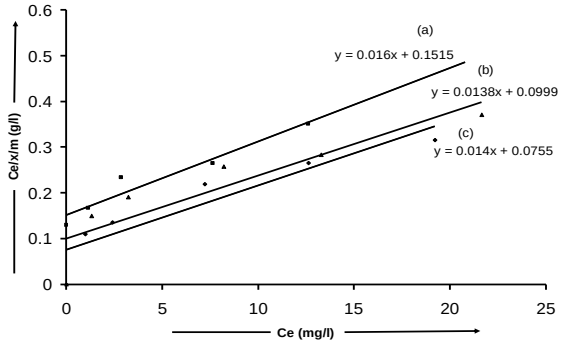

Figure 4. **Langmuir plots of CN^- adsorption on Alumina at different temperatures : (a) 283K, (b)313 K, (c)323K.**

Table-2. **Freundlich and Langmuir Isotherm parameters for Adsorption of CN^- on α-Alumina.**

Temperature	Freundlich isotherm			Langmuir isotherm		
K	***1/n***	K_F	R^2	V_m	K_L	R^2
283	1.26	0.20	0.75	62.50	1.00	0.94
313	1.20	0.20	0.77	72.46	1.00	0.80
323	1.22	0.20	0.75	1.42	1.00	0.85

Calculations of thermodynamic parameters:

Thermodynamic parameters such as Gibbs free energy ΔG^O(kJ/mol), change in enthalpy ΔH^O(kJ/mol) and change in entropy ΔS^O ($J^-K^-mol^-$) for cyanide adsorption were calculated from the distribution constant K [10] by using the following relations:

$$\Delta G^O = -RT\ln K \quad (3)$$

$$\Delta G^O = \Delta H^O - T\Delta S^O \quad (4)$$

$$\text{And } \ln K = -\Delta H^O/RT + \text{Constant} \quad (5)$$

Table 3 shows the values of thermodynamics parameters ΔH^O, ΔS^O ΔG^O. The positive value of ΔH^O=5.448kJ/mole, which is calculated from equation (5) and Fig. 5, confirms the endothermic nature of the overall adsorption process. The positive value of ΔS^O suggests increased randomness at the solid/solution interface with some structural change in the adsorbate and adsorbent and also affinity of the Alumina towards CN^-. A negative value of ΔG^O indicates the feasibility and spontaneity of the adsorption process, where higher negative value reflects a more energetically favorable adsorption process.

Table-3. **Values of Thermodynamic Data for Adsorption of CN^- on Alumina.**

Temperature	ΔH^0	ΔG^0	ΔS^0
K	(kJ/mole)	kJ/mole	($JK^{-1}mol^{-1}$)
283	5.448	-7.162	0.0445
313	5.448	-5.329	0.0344
323	5.448	-10.67	0.0470

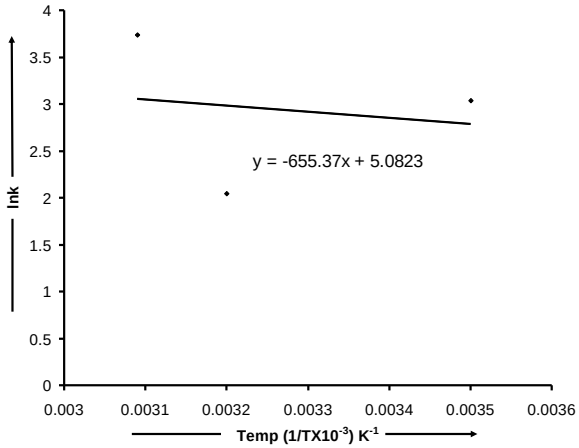

Figure 5. **Plot of lnK Vs.1/T for CN^- adsorption on Alumina.**

Conclusion

Keeping the adsorptive nature of alumina in view it is felt desirable to select batch adsorption process for removal of Cyanide from the industrial wastewater using alumina. The main advantages of the procedure are:

i. Cost of process as alumina is an indigenous material and easily available in country.
ii. Ease and simplicity of preparation of the sorbent due to non-corrosive and non-poisonous nature of alumina.

iii. Rapid attainment of phase equilibration and good enrichment as well fitting of adsorption data with Freundlich and Langmuir isotherms.

iv. The positive value of ΔH^O and negative values of ΔG^Oindicate the endothermic and spontaneous nature of the adsorption process.

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