

Batch Equilibrium Adsorption of Cyanides from Aqueous Solution onto Copper- and Nickel-Impregnated Powder Activated Carbon and Clay

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Abstract

The present paper reports the removal of cyanide ions from aqueous solutions using Cu/PAC, Ni/PAC, Cu/Clay and Ni/Clay adsorbents at pH=11. At this pH, the cyanide is completely dissociated into its ions. Equilibrium data fitted Langmuir and Freundlich isotherms well. The applicability of the isotherm equation to describe the adsorption process was judged by the correlation coefficients, R^2 , values. The Langmuir model yielded the best fit with R^2 values equal to or higher than 0.960, as compared to the Freundlich model. The fact that $1/n$ values range from 0.20 to 0.58 indicates that the adsorption of cyanide ions onto these metal supported adsorbents is also favored by the Freundlich model.

Keywords: Adsorption, metal-cyanide complex, correlation coefficient, activated carbon, clay

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1. Introduction

Waste waters from industrial operations transport many chemicals that have adverse effects on the environment. Ammonia and amine compounds from carcass-processing, and sewage-treatment plants [1], phosphates and nitrates from paper mills, fertilizer plants, and detergent industries [2], cyanide and its compounds from electroplating and mining (extraction of gold, silver, etc.) industries [3, 4] end up in lakes, creeks, and rivers. These chemicals may be toxic and are more so when they are associated with heavy metals (Cd, Cu, Ni, Zn, Co, Au, Fe, Ag, etc.) leached from the earth [5-7]. These, of course, will adversely affect aquatic and land biota. It is therefore necessary to develop new technologies for the pre-treatment of these harmful chemicals at their point source before they are released into the environment.

Cyanide and its compounds from electroplating and mining industries are responsible for the contamination of lakes, creeks, and rivers. From the environmental and economic point of view, the

management of such a contaminating but valuable resource is very important.

Cyanide is a highly toxic species. Short-term exposure can cause rapid breathing, tremors, and other neurological effects. Long-term exposure can cause weight loss, thyroid deficiency, and nerve damage [8]. The mean lethal dose for the human adult is 50-200 mg/L, but for freshwater invertebrates it is only 0.028-2.295 mg/L [8]. Thus, cyanide-contaminated effluents should not be discharged into the environment without detoxification to meet cyanide statutory limits.

In the literature, treatment methods for cyanide removal from wastewater containing cyanide compounds comprise physical, adsorption, complexation, and/or oxidation methods [9]. The physical process and adsorption methods are used to purify effluents by separation processes, which consist of concentrating and recovering the cyanide. On the other hand, oxidation processes are used to destroy the cyanide and include various biological,

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catalytic, electrolytic, chemical, and photolytic methods. These processes can be cumbersome, especially when large volumes of effluent are to be treated. In this paper, we report the results of our studies on the removal of cyanide from aqueous solution by Cu(II)- and Ni(II)-impregnated powder activated carbon (PAC) and kaolinitic clay from Cameroon at pH=11. These two metals were used in order to increase surface adsorption and adsorption capacities of the cyanide ion [10]

2. Materials and Methods

2.1 Adsorbents

PAC was provided by CHEMVIRON S.A. of Bruxelles. Kaolinitic clays were samples from the Nkolafane region (Yaoundé, Cameroon). The particle size of the PAC sample is less than 0.12 nm, with a BET surface area of 1,200 m²/g [2]. The kaolinitic clay material has a particle size less than 10⁸ nm, with a specific surface area of 42 m²/g.

The adsorbents were heated in an oven at 120°C for 24 hours before being used in the impregnation reaction. The adsorbents (activated carbon and clay) used in this work were impregnated by small amounts of Cu(NO₃)₂·3H₂O and Ni(NO₃)₂·3H₂O salt solutions according to procedures described in the literature [10-12]. Concentrations of these salt solutions ranged from 5 to 15×10⁻² mol/L. The weight of the adsorbents used in the adsorption process refers to the total weight of the supported metal adsorbents as distinct from the weight of the metals used. Thermolysis of these adsorbents/salt mixtures at around 230°C converts the salts into Cu₂O and NiO respectively. At 400°C, the metal oxides are reduced to metallic Cu and Ni, resulting in Cu/PAC, Ni/PAC, Cu/Clay, and Ni/Clay samples. Some of these metallic particles have the tendency to aggregate under heat treatment, resulting in a uniform distribution in the adsorbents. These samples were analysed by using a Perkin-Elmer Atomic Adsorption Spectrometer (AAS) model 2380, at wavelengths of 324.8 nm and 232.0 nm, in order to titrate for copper and nickel, respectively.

2.2 Batch equilibrium experiments

The batch equilibrium experiments of the adsorption studies were conducted at room temperature (25°C) in a 100-mL screw-cap conical flask. For each run, 1 g of the adsorbent was weighed and placed in the flask containing 30 mL solution of NaCN of the desired concentration (ranging from 0.01 to 0.15 mol/L) at pH=11 for each run. The suspension was stirred for 1 hour using a magnetic stirrer. To measure the residual concentration of the cyanide, 5 mL of the filtrate was placed in a 100-mL Erlenmeyer flask and analyzed using the LIEBIG DENIGES method [13]. In the filtrate, 5 mL of 1 M ammonia solution was added to allow the formation of soluble silver cyanide complex. Potassium iodide is then added,

and this mixture is titrated, while stirring with 0.1 M standard solution of silver nitrate until the appearance of a whitish to yellowish color. Each experiment was duplicated under identical conditions and the average of the results obtained is reported.

The amount of cyanide adsorbed at equilibrium, q_e (mol/g), was calculated by the equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e (mg/L) are the initial and equilibrium liquid-phase concentration of cyanide respectively; V (L) is the volume of the solution; and W (g) is the mass of the dry adsorbent used. The equilibrium data were then fitted on the Langmuir and Freundlich adsorption isotherm models.

3. Results and Discussion

3.1 Adsorption isotherms

The adsorption isotherm usually shows how the molecules are distributed between the liquid and the solid phases, at equilibrium during the adsorption process. The analysis of the isotherm data by fitting them to the different adsorption isotherm models is an important first step to finding a suitable model that can be used for design purposes [14]. An adsorption isotherm is important in describing how solutes interact with adsorbents. The adsorption isotherm study was carried out on two isotherm models: Langmuir and Freundlich.

3.2 Langmuir adsorption isotherm

The Langmuir adsorption isotherm assumes monolayer coverage onto a surface containing a finite number of adsorption sites of uniform capacities of adsorption with no transmigration of adsorbate in the plane of surface [15]. The linear form of the Langmuir adsorption isotherm equation is as follows:

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o K_L} \times \frac{1}{C_e} \quad (2)$$

where C_e (mol/L) is the equilibrium concentration of the cyanide, q_e (mol/g) is the amount of cyanide adsorbed per unit mass of adsorbent, and K_L and q_o are Langmuir constants related to the adsorption capacity and the rate of adsorption, respectively.

The suitability of the isotherm equation to describe the adsorption process was judged by the correlation coefficient, R^2 , values shown in Table 1. When C_e/q_e is plotted against C_e , for the Langmuir isotherm, a straight line with slope of $1/q_o$ is obtained. The correlation coefficient, R^2 , of at least 0.960 indicated that the adsorption data of cyanide ions on the supported metal adsorbents were well

fitted to the Langmuir isotherm. The Langmuir constants K_L and q_0 were calculated from equation 2 and are shown Table 1. The Langmuir model yielded the best fit with R^2 values equal to or higher than 0.960, as compared to the Freundlich model.

Table1: Adsorption Equilibrium Constants for Cyanide Uptake from Aqueous Solutions

Supports	Sample	Langmuir parameters			Freundlich parameters		
		q_0 (mol/g)	K_L (L/mol)	R^2	K_F $\times 10^3$	$1/n$	R^2
Powder Activated Carbon (PAC)	PAC	25.46	1.93	0.9478	1.16	0.310	0.9641
	9% Cu/PAC	134.83	3.93	0.9617	1.54	0.210	0.5842
	12.5% Cu/PAC	177.80	5.76	0.9774	2.90	0.225	0.7069
	18.5% Cu/PAC	438.64	5.86	0.9348	4.20	0.260	0.7525
Clay	PAC	25.46	1.93	0.9478	1.16	0.310	0.9641
	8.9% Ni/PAC	36.17	0.41	0.9930	1.02	0.580	0.9936
	12% Ni/PAC	35.00	0.25	0.9930	1.00	0.570	0.9942
	18% Ni/PAC	59.06	0.57	0.9575	1.70	0.470	0.9296
Clay	Clay	18.38	0.52	0.7352	2.95	0.416	0.8522
	1.5% Cu/Clay	129.31	0.41	0.9878	3.06	0.460	0.8962
	1.9% Cu/Clay	131.03	1.12	0.9997	3.50	0.400	0.9303
	3.2% Cu/Clay	190.02	1.13	0.9397	3.92	0.350	0.8035
	Clay	18.38	0.52	0.7352	2.95	0.416	0.8522
	3.5% Ni/Clay	26.70	0.01	0.7957	3.57	0.560	0.6440
	6.2% Ni/Clay	28.96	0.11	0.8564	3.31	0.490	0.6932
9.2% Ni/Clay	28.76	0.13	0.8280	3.40	0.460	0.6682	

Conformation of the experimental data with the Langmuir isotherm equation indicates the homogeneous nature of the adsorbant-adsorbent surface, that is, each adsorbate-adsorbent adsorption has equal adsorption activation energy [16]. These results represented in Fig. 1 also demonstrate monolayer coverage of the cyanide ion on the surface of the metal-supported PAC and clay materials. Similar observations have been reported in the literature [17].

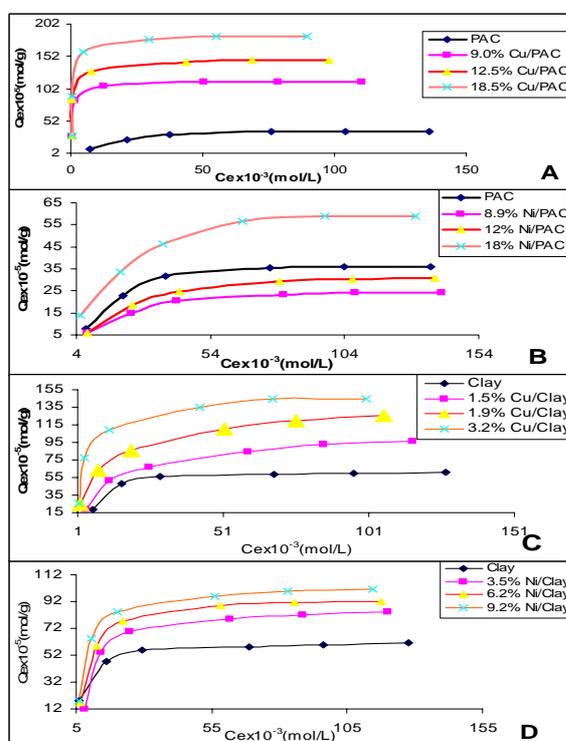


Figure 1: Adsorption Isotherms of Cyanide on Cu and Ni-Impregnated Adsorbents

3.3 Freundlich adsorption isotherm

On the other hand, the Freundlich adsorption isotherm assumes heterogeneous surface energy in which the energy term varies as a function of the surface coverage [15]. The Freundlich adsorption equation is given in the logarithm form as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

C_e (mol/L) is the equilibrium concentration of the cyanide; q_e (mol/g) is the amount of cyanide adsorbed per unit mass of adsorbent; K_F and n are Freundlich constants; n gives an indication of how favorable the adsorption process is; and K_F is the adsorption capacity of the adsorbent, which can be defined as the adsorption or distribution coefficient and represents the quantity of cyanide adsorbed onto the PAC or clay for a unit equilibrium concentration. The slope $1/n$, ranging from 0 to 1, is a measure of adsorption intensity or surface heterogeneity that becomes more heterogeneous as its value gets closer to zero [18]. A value for $1/n$ below 1 indicates a normal Langmuir adsorption isotherm, while $1/n$ above 1 is indicative of cooperative adsorption [19]. However, the R^2 values do not seem to indicate a good fit.

For the Freundlich isotherm, the plot of $\log q_e$ versus $\log C_e$ gives a straight line with slope of $1/n$ value ranging from 0.20 to 0.50, as shown in Table 1. This indicates that the adsorption of cyanide ions onto these metal-supported adsorbents is favorable as well. K_F and $1/n$ are related to adsorption capacity and energetic heterogeneity, respectively. Accordingly, Freundlich constants K_F and n were calculated from equation 3 and are listed in Table 1. The fact that $1/n$ values are less than 1 suggests that the equilibrium data truly follow the Freundlich mechanism and, therefore, that the active sites are energetically heterogeneous.

Experimental data for cyanide ion adsorption onto Cu/PAC, Ni/PAC, Cu/Clay and Ni/Clay adsorbents at 298 K are shown in Figure 1. In the low concentration region, the amount of cyanide adsorbed on these adsorbents sharply increased with an increase in equilibrium concentration, giving an indication of the high affinity of the binding sites for cyanide ions [12]. This is a good attribute of the materials tested in this study since there is high cyanide uptake at low equilibrium concentration. This will enable the treatment of large volumes of effluent before replacement or regeneration of the adsorbents. At high concentrations, the increase in quantities adsorbed is gradual, as a result of an almost full occupation of the active sites. It appears Cu-impregnated materials perform much better than Ni-impregnated materials.

The cyanide is a singly-charged anion containing unimolar amounts of carbon and nitrogen atoms triply-bonded together: $C \equiv N^-$ or CN^- . It is a strong ligand capable of complexing with

virtually any heavy metal at low concentrations [20]. Metal-complexed cyanides are classified according to the strength of the metal-cyanide bond. There are weak-acid dissociables (WADs) that refer to cyanide complexes with metals such as cadmium, copper, nickel, and zinc. There are strong-acid dissociables (SADs) that refer to cyanide complexes with metals such as cobalt, gold, iron, and silver. Thus, although activated carbons have high porosity and a high surface area, adsorption capacities and rates can be high. Adsorption, however, is not very selective: cations, anions, and neutral species can be adsorbed simultaneously at various sites via ion exchange, and coulombic interactions. Therefore, the cyanide's strong affinity for metals requires that the adsorbents used in this work be impregnated with Cu and Ni metals (WADs). Cyanide wastewater treatment has been shown to be very efficient at dilute cyanide concentrations [17,21] with increased adsorption for WADs as compared to the un-impregnated adsorbents.

4. Conclusions

Cyanide (CN⁻) is a toxic species found predominantly in industrial effluents generated by metallurgical operations. The present investigation showed that Cu(II)- and Ni(II)-impregnated activated carbon and kaolinitic clay found in Cameroon are promising adsorbents for the uptake of cyanide from aqueous solutions. Equilibrium data were fitted to Langmuir and Freundlich isotherms and both models best described these results, with maximum monolayer adsorption capacity, q_0 , of 438.64 mol/g for the 18.50% Cu/PAC and 190.02 mol/g for the 3.20% Cu/Clay adsorbents at room temperature. The maximum monolayer adsorption capacities found for Ni-impregnated activated carbon and clay were 59.06 mol/g and 28.76 mol/g for 18% Ni/PAC and 9.2% Ni/Clay, respectively. The results were much lower for the Ni-impregnated adsorbents than for the Cu-impregnated adsorbents. The maximum monolayer adsorption capacity, q_0 , decreased with decreasing percent metal loading and from Cu(II) to Ni(II). The technique of copper and nickel impregnation optimises the existing properties of the metal unsupported activated carbons and clay giving greater cyanide removal capacities.

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6. References

1. Tsutomu I, Takashi A, Kuniaki K and Kikuo O. (2004) Comparison of Removal Efficiencies for Ammonia and Amine Gases between Woody Charcoal and Activated Carbon. *J. Health Sci.*; 50:148-153.
2. Ketcha Mbadcam J, Manga Ngomo H, Kouotou D and Tchoua Ngamou PH. (2007) Kinetic and Equilibrium Studies of the Adsorption of Nitrates Ions in Aqueous Solutions by Activated Carbons and Zeolite. *Res. J. Chem. Environ.*; 11(3):47-51.
3. Kapa U, Stanczyk-Mazanek E and Stepniak L. (2008). The use of the advanced oxidation process in the ozone-hydrogen peroxide system for the removal of cyanide from water. *Desalination*; 223:187-193.
4. Roshan Dash R, Balomajumder CH and Kumar A. (2006). Cyanide Removal by Adsorption and Biodegradation Process. *Iran. J. Environ. Health. Sci. Eng.*; 3(2):91-96.
5. Igwe JC and Abia AA. (2007). Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk. *Electronic Journal of Biotechnology*; 10(4):536-548.
6. Sengorur B, Ogleni O. and Ogleni N. (2006). Removal of Copper and Zinc from Automobile Wastewater by Purolite C-104 Ion Exchange Resin. *Fresenius Environmental Bulletin*; 15(3): 182-185.
7. Murathan A. (2005). Removal of Heavy Metal Ions from Aqueous Solutions in Fixed Beds by using Horse Chestnut and Oak Valonia. *Fresenius Environmental Bulletin*; 14(4): 296-299.
8. Huiatt JL, Kerrigan JE, Olson FA and Potter GL. (1983). Cyanide from mineral processing: proceedings of a workshop. Utah Mining and Mineral Industries, Salt Lake City, Utah, Chapter 2-4, pp.
9. Young CA and Jordan TS. (2000). Cyanide remediation; current and past technologies. *Proceedings of the 10th Annual Conference on Hazardous Waste Research*, 104-129.
10. Adhoum N and Monser L. (2002). Removal of Cyanide from Aqueous Solution using Impregnated Activated Carbon. *Chem. Eng. Processing*; 41: 17-21.
11. Ryu SK, Lee WK and Park SJ. (2004). Thermal Decomposition of Hydrated Copper Nitrate [Cu(NO₃)₂·3H₂O] on Activated Carbon Fibers. *Carbon Science*; 5(4): 180-185.

12. Jackson SD, Willis J, Kelly GJ, et al. (1999). Supported nickel catalysts: Preparation and characterisation of alumina-, molybdena-, and silica-supported nickel, and the identification of reactive oxygen on these catalysts by exchange with isotopically labelled carbon dioxide. *Phys. Chem. Chem. Phys.*; 1: 2573-2580.
13. Deniges G, (1893). Titration of cyanide with silver using potassium iodide as indicator. *Compt. Rend.*; 177: 1078-1080.
14. El-Guendi M. (1991). Homogeneous surface diffusion model of basic dyestuffs onto natural clay in batch absorbers. *Adsorp. Sci. Technol.*; 8(2): 217-225.
15. Weber TW and Chakkravorti, R.K. (1974). Pore and diffusion models for fixed-bed adsorbers. *AIChE J.*; 20: 228.
16. Bansal RC, Donnet JB and Stoeckli F. (1988). *Active Carbon*, Marcel Decker, New York.
17. van Weert G and de Jong I. (1992). Trace Cyanide Removal by Means of Silver Impregnated Active Carbon. *Proc. Emerging Process Technologies for a Cleaner Environment*, SME, Littleton, CO, pp. 161-168.
18. Haghseresht, F. and Lu, G. (1998). Adsorption characteristics of phenolic compounds onto coal-derived adsorbents. *Energy Fuels*, 12, 1100-1107.
19. Fytianos K, Voudrias E and Kokkalis E. (2000). Sorption-desorption behaviour of 2,4-dichlorophenol by marine sediments. *Chemosphere*; 40: 3-6.
20. Marsden J and House I. (1992). *The Chemistry of Gold Extraction*, Ellis Horwood, New York.
21. Huff JE and Bigger JM (1980). Cyanide Removal from Refinery Wastewater Using Powdered Activated Carbon. RS Kerr, Environmental Research Laboratory, Ada, OK, EPA-600/2-80-125.