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Adsorption of Ferricyanide Ion on Activated Carbon and γ-Alumina

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Abstract: Iron-cyanide complexes are present in soil and ground water due to anthropogenic inputs. We compared the adsorption of ferricyanide ion, on two commercial activated carbons (COM3 and COM4) and γ-alumina (A1G) in aqueous solution. Isotherm parameters obtained from batch experiments of iron-cyanide complex adsorption on these adsorbents were carried-out. The mass of the adsorbents were varied at 40 mg, 60 mg and 100 mg and the inorganic ion initial concentrations, C_o also varied between $3.04x10^{-4}$ and $2.43x10^{-3}$ mol/L. The equilibrium data obtained were tested by using the Langmuir and Freundlich isotherm models. These data fit well with the Langmuir and Freundlich isotherm models at this low inorganic ion initial concentration.

Keywords: Ferricyanide ion, Activated carbon, γ-Alumina, Adsorption isotherms.

Introduction

Cyanide in the form of the iron-cyanide complexes *i.e.* ferricyanide, ($[Fe(CN)_6]^{3-}$) and ferrocyanide, ($[Fe(CN)_6]^{4-}$), are from anthropogenic sources are present in natural soil environment or drinking water[1]. The potential sources of these small amounts of iron-cyanide complexes in soil and aquifers are industrial wastes from coal gasification[2], blast furnace sludge from pig iron production[3], paper de-inking sludge from paper recycling[4] and road salt which contains Berlin Blue, $Fe_4[Fe(CN)_6]_3$ or $Na_4[Fe(CN)_6]$ as anti caking agents[5,6].

The iron-cyanide complexes, with iron in the oxidation states +3 and +2 respectively are very stable[7]. However, they are potentially hazardous because they are converted to free cyanide ion, $CN^-_{(aq)}$ and hydrogen cyanide, $HCN_{(g,\ aq.)}$ when transported to surface water and exposed to sunlight[8]. Free cyanides are defined as the form of molecular and ionic cyanide released into solution by the dissolution and dissociation of cyanide compounds and complexes[9]. Free cyanides are extremely toxic to higher animals and humans[10]. Cyanide inactivates cytochrome oxidase, an enzyme which is essential for the fixation of oxygen. This inactivation leads to cellular asphyxiation and cellular death and therefore to the suspension of all vital functions and subsequent death.

The main objectives of drinking water treatment are to produce high quality water that is safe for human consumption, has aesthetic appeal, conforms to world standards and is economical in production[11,12]. One of the ways to achieve these goals is adsorption on activated carbon or any good adsorbents. The reason why these adsorbents are effective is that they are porous and thus have very large surface areas available for adsorption or chemical reaction[13]. Adsorption is the process by which adsorbents such as activated carbon, gamma alumina, clays, *etc.* remove selected substances from solution by binding to an adsorbent surface by either chemical or physical attraction[14].

The adsorption of iron-cyanide complexes ferricyanide, ($[Fe(CN)_6]^{3-}$) and ferrocyanide, ($[Fe(CN)_6]^{4-}$) on goethite, alpha-FeOOH, as a model adsorbent in the soil was investigated in a batch experiments[15,16]. In this study, it was proposed that the adsorption mechanism between ferrocyanide and the goethite was a combination of inner-sphere surface complexation and surface precipitation of a Berlin Blue-like phase. As for the adsorption of ferricyanide on the goethite, it is an outer-sphere and weak inner-sphere surface complexation adsorption mechanism. Similar studies using batch as well as column experiments of adsorption and desorption on other adsorbents such as soils, acid soils containing large amounts of Al and Fe oxides, clay minerals and soils containing organic matters have been reported[1,17-19]. The most important properties that control adsorption of these Fe-cyanide complexes are pH and clay mineral and iron oxide contents. A similar study indicated that both the dissolution of Berlin Blue and the desorption of Fe-cyanide complexes were rate-limited[20]. It has been shown in the literature that both iron-cyanide complexes formed outer-sphere surface complexes[21,22] on γ–Al_2O_3. The adsorption of potassium hexacyanoferrate(III) on three commercial alumina samples, studied by IR, neutron activation and visible absorption spectroscopy, reported[23] that above pH = 7, the extent of adsorption was small and the uptake of iron-cyanide complex increased with decreased pH and reaches a plateau near pH = 5.

The sorption of iron-cyanide complexes on goethite in the presence of sulphate and its desorption in the presence of phosphate and chloride have been studied[24]. From the results obtained, high sulphate concentration does not diminish the uptake of the iron-cyanide complex. Both iron-cyanide complexes adsorbed on goethite were desorbed by phosphate solutions adjusted to pH ≥ 5. This competitive sorption of ferrocyanide and sulphate and of its desorption using chloride and phosphate solutions suggested strong sorption, which may be explained by inner-sphere surface complexation of ferrocyanide and partial precipitation as a Berlin Blue-like phase at low pH.

Whereas, the outer-sphere surface complexation is caused by electrostatic attraction and is relatively weak, the inner-sphere surface complexation is more stable. The adsorbent becomes part of the surface and a covalent bond can be formed via ligand exchange[25,26].

The objective of this work was to investigate the adsorption of potassium ferricyanide, ($K_3Fe(CN)_6$) at very low concentrations in aqueous solution on two commercial activated carbons (COM3 and COM4) and on a γ-alumina (A1G) in batch experiments. The extent of adsorption was investigated by varying the mass (m) from 40, 60 to 100 mg and the inorganic ion initial concentrations, C_o also varied between $3.04x10^{-4}$ and $2.43x10^{-3}$ mol/L.

Experimental

COM3, COM4 and A1G were obtained from CHEMVIRON S.A., Bruxelles. The pH values recorded for these three adsorbents in aqueous solution were pH = 3.6 for COM3, pH = 2.8 for COM4 and pH = 7.5 for A1G. The BET surface areas specified for these adsorbents ranged between 900 and 1200 m^2/g. The adsorbents were heated in an oven at 105 °C for 24 hours before use in the batch experiments.

The batch equilibrium experiments of the adsorption studies were carried out at room temperature in a 100 mL conical flask. For each run, 40, 60 or 100 mg of the adsorbent was introduced into the flask containing 20 mL of the potassium ferricyanide at very low initial concentrations (C_o) ranging from 3.04×10^{-4} to 2.43×10^{-3} mol/L. The mixture was stirred using a magnetic stirrer for 2 hours. The solution was then filtered by using a filter paper. The residual concentration at equilibrium (C_e) of the ferricyanide ion was determined with a UV-visible spectrophotometer (model HITACHI U-2000). The quantity of ferricyanide ion (mg/g) adsorbed at equilibrium (q_e) was calculated from the equation:

$$q_e = \frac{(C_{o-}C_e)}{W} V \tag{1}$$

Where C_o and C_e (mg/L) are the initial and equilibrium liquid-phase concentration of ferricyanide ion 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 to the Langmuir and the Freundlich adsorption isotherm models.

Results and Discussion

Two important independent physicochemical aspects for the evaluation of the adsorption process are the equilibrium of adsorption and the kinetics. Equilibrium studies give the adsorption capacity of the adsorbent. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and the residue in solution at equilibrium at a given temperature. There are two types of adsorption isotherms: the Langmuir and the Freundlich. Linear regression was applied on the linear transforms of these isotherms in order to determine[27] the coefficients R^2. The Langmuir adsorption equation is one of the most common isotherm equations for modelling equilibrium data in solid-gas and solid-liquid systems. The general linearised form of the Langmuir equation is,

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o K_L} x \frac{1}{C_e} \tag{2}$$

where q_e is the quantity of ferricyanide ion adsorbed at equilibrium (mg/g), C_e is the equilibrium liquid-phase concentration of ferricyanide ion (mol/L), q_o is the quantity of ferricyanide ion adsorbed to form a monolayer (mg/g) and K_L is the Langmuir adsorption constant (L/mol). The values of q_o and K_L are obtained from the plot of $1/q_e$ *versus* $1/C_e$ of equation 3.

The Freundlich model is represented by the equation,

$$q_e = K_F C_e^{1/n} \tag{3}$$

Where K_F and n are Freundlich constants, n gives an indication of how favourable 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 ferricyanide ion adsorbed onto the absorbent for a unit equilibrium concentration. In order to fit the experimental data, the Freundlich model was linearised as follows by taking logs of equation (3):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{4}$$

In Figure 1, the isotherms observed for COM3 were the L-type but for COM4 and AlG, S-type isotherms observed. S-type isotherms are usually characterised by very weak adsorption at low initial adsorbate concentration. However, the adherence of adsorption isotherms does not provide evidence of the actual adsorption mechanism. The adsorption isotherms are linear over a wide range of the equilibrium concentration, C_e; saturated plateaus are observed at large concentrations[19].

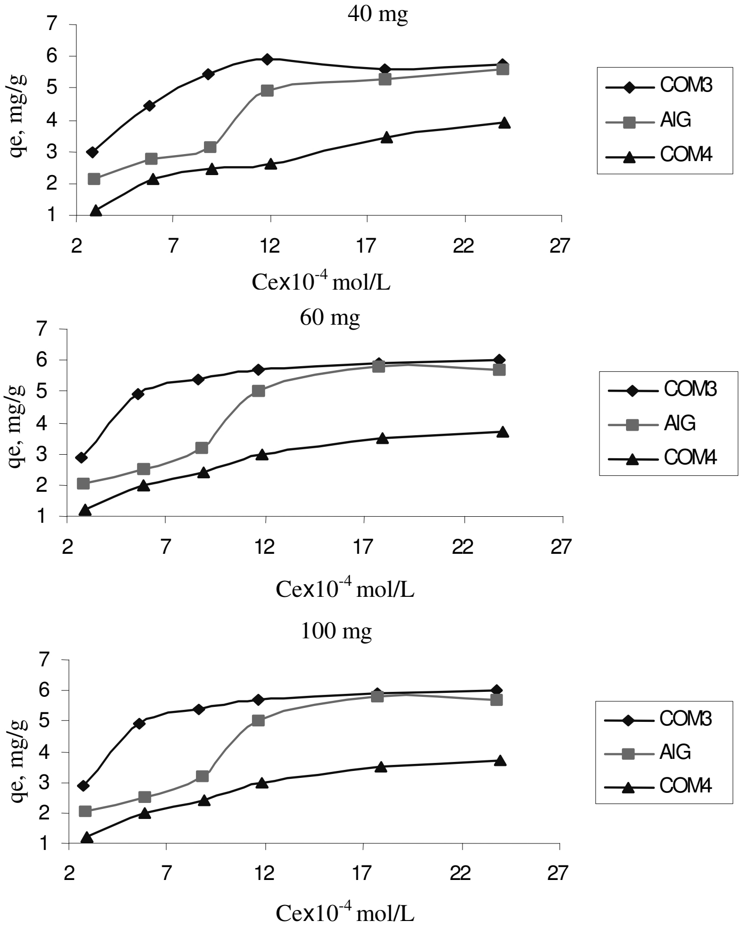

Figure 1. Adsorption isotherms of ferricyanide ions on COM3, AlG and COM4 for 40, 60 and 100 mg of adsorbent.

The values of the correlation coefficient, R^2 observed in Table 1 range from 0.845 to 0.999 for the Langmuir model and from 0.800 to 0.979 for the Freundlich model. In cases where coefficients of determination are used to treat experimental results, it was observed that both models yielded the best fit at low inorganic ion initial concentrations, thus confirming other reported work in the literature[27]. As observed earlier, the mechanism by which the ferricyanide ion, is adsorbed on these adsorbents depends on the nature of the adsorbate-adsorbents. Whereas the Langmuir model refers to the homogeneous nature of the adsobateadsobent surface with each adsorbate-adsorbent surface having equal adsorption activation energy, the Freundlich mechanism refers to surface active sites that are energetically heterogeneous[10]. The two adsorption mechanisms associated with the adsorption of iron-cyanide complexes in general, are the inner-sphere and the outer-sphere mechanisms. Whereas the outer-sphere surface complexation is caused by electrostatic attraction and is relatively weak, the inner-sphere surface complexation is more stable. The adsorbent becomes part of the surface and a covalent bond can be formed via ligand exchange[25,26]. The pH values recorded for the three adsorbents used in this work were as follows: pH=3.6 for COM3, pH=2.8 for COM4 and pH=7.5 for AlG, indicating that these adsorbents have either acidic or neutral surfaces. At low pH values, the surfaces of the adsorbents (COM3 and COM4) become protonated and can adsorb large anion complexes such as ferricyanide ion, through an inner-sphere type mechanism. In the case of the neutral adsorbent, AlG, an outer-sphere surface complexation through electrostatic attraction could be operating.

Table 1. Values of K_L, q_o, K_F, 1/n and R^2 of COM3, AlG and COM4 for 40 mg, 60 mg and 100 mg of adsorbent.

Adsorbent	Mass	Langmuir			Freundlich		
		K_Lx 10^5	q_o,mg/g	R^2	K_F x 10^{-4}	1/n	R^2
COM3	40 mg	2,45	7,33	0,962	1,27	0,31	0,802
	60 mg	2,21	7,83	0,946	1,47	0,32	0,800
	100 mg	2,19	8,19	0,965	1,65	0,33	0,934
AlG	40 mg	1,59	6,44	0,900	3,61	0,50	0,928
	60 mg	1,40	6,84	0,866	5,31	0,55	0,913
	100 mg	1,78	6,44	0,845	4,00	0,50	0,917
COM4	40 mg	0,87	5,69	0,985	3,60	0,56	0,963
	60 mg	0,98	5,36	0,999	3,36	0,55	0,979
	100 mg	1,35	5, 56	0,988	2,39	0,47	0,951

Conclusion

The present work evaluated the removal of ferricyanide ion, from aqueous solution using activated carbons (COM3 and COM4) and γ-alumina as adsorbents. The equilibrium adsorption data agrees well with both the Langmuir and Freundlich isotherms with high correlation coefficients. The adsorption capacity of ferricyanide ion, was the highest for COM3 followed by AlG and COM4 at all initial concentrations of the adsorbate. The values of Freundlich exponent, n are greater than one (since the values of 1/n range between 0.31 and 0.56) for all three adsorbents used, confirming the adsorption of the ferricyanide ion by activated carbons (COM3 and COM4) and γ-alumina as a significant mechanism of removal.

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References

1 Fuller W H, Cyanides in the environment with particular attention to the soil. In: van Zyl D. (Ed.), Cyanide in the Environment: Colorado State University, Fort Collins, Co, 1985, 19-44.

2 Shifrin N S, Beck B D, Gauthier T D, Chapnick S D and Goodman G, *Regul. Toxicol. Pharm.*1996, **23,** 106-116.

3 Mansfeldt T and Dohrmann R, *J Environ Qual.,* 2001, **30**, 1927-1932.

4 Mansfeldt T, *J Plant Nutr Soil Sci.,* 2001, **164**, 637-641.

5 Paschka M G, Ghosh R S and Dzombak D A, *Water Environ Res.,* 1999, **71**, 1235-1239.

6 Ohno T, *Environ Pollut.* 1990, **67**(2)**,** 123-132.

7 Sharpe A G, The A. G. Chemistry of Cyano Complexes of the Transition Metals, Academic Press, London, 1976.

8 Meeussen J C L, Keizer M G and de Haan F A M, *Environ Sci Technol.*, 1992, **26**, 511-516.

9 Smith A and Mudder T, The Chemistry and Treatment of Cyanidation Wastes, Mining Journal Books, London, 1991.

10 Ketcha Mbadcam J, Manga Ngomo H, Tcheka C, Ntieche Rahman A, Djoyo H S and Kouotou D, *J Environ Protect Sci.*, 2009, **3**, 53-57.

11 WHO/UNICEF, Meeting the MDG Drinking Water and Sanitation: A Mid-Term Assessment of Progress, Geneva: WHO/UNICEF. ISBN 2004, 92 4 1562781.

12 De Zuane J P E, Handbook of Drinking Water Quality, John Wiley & Sons: New York, 1997.

13 Gregg S I and Sing K S, Adsorption, Surface Area and Porosity, 2nd Ed., Academic Press, New York, 1982.

14 Brunauer S and Copeland L E, Handbook of Physics, Condon E U and Odishaw H Eds., McGraw-Hill, New York, 1967, **2**, Chapt. 7.

15 Rennert T and Mansfeldt T, *Eur J Soil Sci.,* 2001, **52**, 121-128.

16 Rennert T and Mansfeldt T, *J Environ Qual.,* 2002, **31**, 745-751.

17 Theis T I, Iyer R and Kaul W, *Environ Sci Technol.,* 1988, **22**, 1013-1017.

18 Ghosh R S, Dzombak D A, Luthy R G and Nakles D V, *Water Environ Res.,* 1999, **71**, 1205-1216.

19 Rennert T and Mansfeldt T, *Soil Sci Soc Am J.,* 2002, **66(2)**, 437-444.

20 Weigand H, Totsche K U, Mansfeldt T and Kogel-Knabner I., *J Plant Nutr Soil Sci.* 2001, **164**, 643-649.

21 Cheng W P, Huang C and Pan J R, *J Colloid Interface Sci.,* 1999, **213**, 204-207.

22 Cheng W P and Huang C, *J Colloid Interface Sci.* 1996, **181**, 627-637.

23 Hipps K W, Dunkle E and Mazur U, *Langmuir*, 1988, **4**, 463-469.

24 Rennert T and Mansfeldt T, *J Environ Qual.,* 2002, **31**, 745-751.

25 Hingston F J, Posner A M and Quirk J P, *J Soil Sci.,* 1972, **23**, 177-193.

26 Tejedo-Tejedo M I and Anderson M A, *Langmuir*, 1990, **6**, 602-611.

27 Ho Y-S, *Polish J Environ Stud.*, 2006, **15(1)**, 81-86.