

Adsorption Studies of Silver (+1) on Bentonite

U. ZAFAR*, I. KHAN,
F. JAMSHAD AND S. NAEEM

*Minerals and Metallurgy Research Centre
Pakistan Council for Scientific and Industrial Research Laboratories Complex
Lahore, 54600, Pakistan*

(Received 27th July, 2001, revised 4th April, 2002)

Summary: Adsorption of silver on bentonite has been studied by using batch-technique. Distribution Co-efficient (K_d 's) were determined for bentonite silver solution system in natural water as a function of contact time, pH, adsorbent & adsorbate concentration and temperature. Adsorption data have been interpreted in terms of Freundlich and Langmuir equations. Thermodynamics parameters for the adsorption have been determined at three temperatures. The value of $\Delta H^\circ = -3.62$ KJ/mol and $\Delta G^\circ = 3.61$ KJ/mol at 298K suggests that the adsorption of silver on bentonite is an exothermic process. The desorption studies at low given silver loading on bentonite shows that significant %age of the element is irreversibly adsorbed due to the fixation of the silver by isomorphous replacement in the crystal lattice of the adsorbent.

Introduction

Concern about trace metals in natural water and soils has generated interest in sources, mode of aqueous transport; retention times in the water column and sediment burial rates. Adsorption and Ion-Exchange is one of the fundamental and significant process that control the mobility of metals in the soil environment, helps in predicting the migration of these metals in the geological formations [1] and for evaluating the feasibility of a particular material for the disposal/recovery [2]. All soils naturally contains trace levels of metals. The average concentration of silver (Ag) in soil is 0.05mg/kg [3]. Photography, recycling of photographic waste and other silver bearing waste; other waste streams containing silver halides are considered to be the origin of waste [4].

Published data concerning the interaction of silver with soil, chemical forms, mode of transport and toxicity are rare, while it is commonly accepted that the free form of monovalent silver, is quite toxic to microorganisms and algae. It is also true that silver is quite reactive towards commonly occurring ligands and solids in natural waters [5] and very strongly adsorbed by clay and organic matter and precipitates of silver, AgCl, Ag₂SO₄ and Ag₂CO₃ are highly insoluble, silver is highly immobile in the soil environment [3]. Adsorption characteristics of silver in natural waters on to common sediment material via batch-technique has been studied [6]. Most previous work on silver partitioning to solids have focussed on amorphous iron and manganese oxides at much higher concentrations than found in natural waters. In

*To whom all correspondence should be addressed.

this present work we measure adsorption coefficients for environmental levels of silver on to Bentonite. Bentonite, commonly used to construct clay liners at waste sites, is a type of clay composed of primarily Smectite mineral produced by the alteration of volcanic ash in situ [7]. Because of its physical and chemical properties it is considered as one of the most promising candidates for use as buffer material in the geological disposal systems [8,9]. Therefore, under all pertinent parameters the adsorption of Ag on local Bentonite is investigated as a contaminant.

Results and Discussion

Effect of Shaking Time

The sorption of silver on Bentonite was studied as a function of shaking time at known silver concentrations (*i.e.*, $1 \times 10^{-2}N$ and $1 \times 10^{-3}N$) at temperature (*i.e.*, $24 \pm 0.5^\circ C$ and $40 \pm 0.5^\circ C$). 10 cm^3 of stock silver solution was shaken with 0.5g of Bentonite for different intervals of time ranging from 5min to 24 hrs. Fig. 1. Shows the variation of distribution Co-efficient, K_d and %adsorption, P with shaking time, and that the rate of sorption of bentonite is rapid at both temperature, equilibrium is reached instantaneously after mixing. No significant change in K_d values was observed up to 24hrs. Therefore, equilibrium time of 30 min was selected for all further studies. The instantaneous uptake of silver on bentonite indicates that ion-exchange may be the adsorption mechanism.

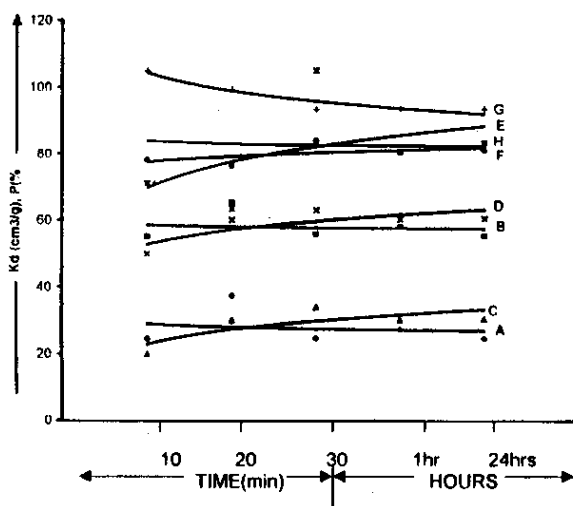


Fig.1: Variation in K_d and Percentage adsorption of silver concentration, temperature and shaking time. (A,B): 298K & (C,D): 318K for Ag conc. $1 \times 10^{-2}N$, (E,F): 298K & (G,H): 318K for Ag conc. $1 \times 10^{-3}N$.

Effect of pH

The effect of pH on sorption of $10^{-3}N$ silver on Bentonite was studied at $25 \pm 0.5^\circ C$ by varying the pH of silver solution-clay suspension from pH 1.5 to pH 11. The results are shown in Fig. 2. The adsorption of silver on bentonite increases with increasing pH. Both K_d and percent extraction increases with an increase in pH with in the pH range studied. However, a much greater increase in K_d values are observed when pH of the suspension change from 5 to 9. At low pH the lesser K_d values are due to relatively small number of available sites. This is because of solubility of different constituents of Bentonite in acidic solutions; therefore relatively small number of calcium sites, which is one of the major exchangeable cation, will be available for the adsorption of silver. In addition to this, metal ions may also be adsorbed on sandy sediment grains, by exchange with proton, which are present in the outer part of the electric double layer. The extent of adsorption will, therefore, depend upon experimental parameters that could affect the surface charge. Similar results have been reported for adsorption of cesium on bentonite [11]. The natural pH 7.3 obtained by mixing silver solution with clay in 20: 1 ratio was used in all the subsequent experiment, until otherwise mentioned.

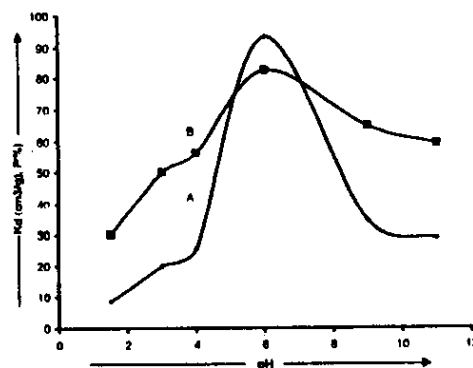


Fig.2. Influence of pH on silver sorption on bentonite (A): K_d and (B): Percentage adsorption.

Effect of Sorbent Concentration

The dependence of silver adsorption on Bentonite concentration was studied at $25 \pm 0.5^\circ C$ and ($1 \times 10^{-2}N$ and $1 \times 10^{-3}N$) concentrations of the metal solution by varying the adsorbent amount from 0.1 to 1.0gram while keeping the volume, 10 cm^3 of the metal solution constant. The results are shown in Fig. 3. The uptake of silver increases with the increasing amount of the Bentonite because of the

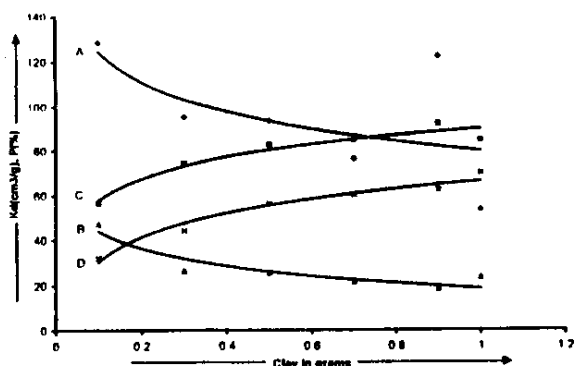


Fig. 3: Dependence of silver sorption on the amount of bentonite (A,B); and (C,D):Percentage adsorption for silver concentration (A,C): $1 \times 10^{-3}N$, (B,D): $1 \times 10^{-2}N$

greater availability of the exchangeable sites at higher concentration of the adsorbent.

Effect of Adsorbate Concentration

The adsorption of silver as a function of its concentration was studied at $25 \pm 0.5^\circ C$ at two different solution to clay ratio (i.e., 40:1 and 100:1) by varying the metal concentration from $2.5 \times 10^{-4}N$ to $1 \times 10^{-2}N$. The results are shown in Fig. 4. Both K_d and P values decrease with increasing metal concentration. The shape of K_d curve is of L-type, this suggest that at least two types of phenomena (i.e., adsorption as well as exchange) are taking place in the range of silver concentration studied. The removal of silver by the latter process may be due to isomorphous replacement or by ion-exchange. This suggest that energetically less favorable lattice positions or exchange sites become involved with increasing cobalt concentration.

Adsorption Isotherms

The adsorption isotherm at three different temperatures were obtained by plotting the amount of silver adsorbed on Bentonite(g/g) against metal concentration. Range of silver solution concentration studied was from $1 \times 10^{-3}N$ to $2 \times 10^{-1}N$. These isotherms are shown in Fig. 5.

Freundlich adsorption isotherm was used for the study of silver sorption on bentonite.

The linear form of the equation is written as :

$$\log X/m = \log K + 1/n \log C_e, \quad [4]$$

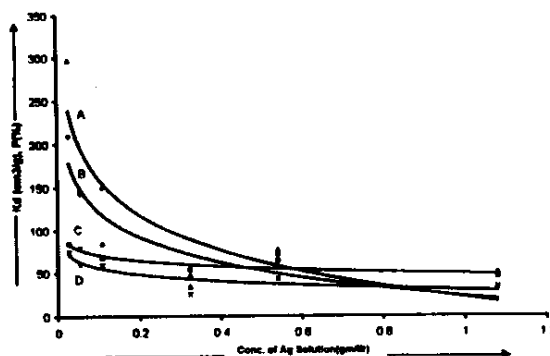


Fig. 4: Effect of silver concentration on its sorption on bentonite (A,B): K_d and (C,D): Percentage adsorption for solution/bentonite ratio.(A,C): 40:1, (B,D): 100:1

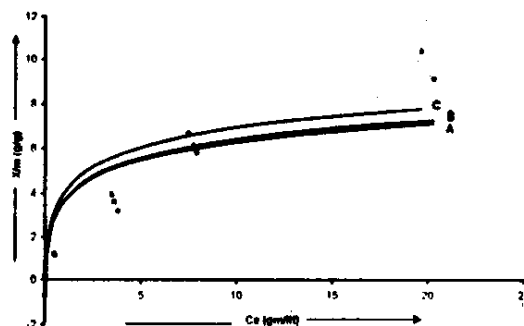


Fig. 5: Sorption isotherms of silver on bentonite at different temperatures. (A): 283K, (B): 298K, (C): 318k

Where X/m is the amount adsorbed per gram of the adsorbent, C_e is the equilibrium concentration, K and $1/n$ are constants. The equilibrium concentration of silver studied was in the range of $2.5 \times 10^{-4}N$ to $1 \times 10^{-2}N$ for 40:1 and 100:1 solution to Bentonite ratio, respectively. A plot of $\log X/m$ against $\log C_e$ give a straight line, the slope and intercept of which corresponds to $1/n$ and $\log K$, respectively, Freundlich plots for silver adsorption on Bentonite are shown in Fig. 6. The values of the Freundlich constant $1/n$ are 0.591 and 0.845 at solution to Bentonite ratio 40:1 and 100:1 respectively, these values are comparable with these found in other studies (i.e., 0.52-0.75) on montmorillonite clay [12]. Although the Freundlich isotherm does not take the adsorbent finite capacity for adsorption at high concentration into account, it often describes adsorption of trace amount of adsorbing species satisfactorily.

Linear regression of Freundlich plots, Fig. 6. gives slopes of less than 1, indicating a concentration dependent (*i.e.*, nonlinear) adsorption of silver in the concentration range used.

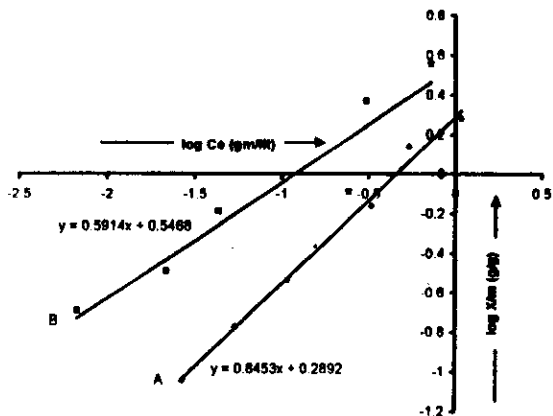


Fig. 6: Freundlich plot of silver sorption on bentonite at solution/bentonite ratio.(A): 40:1 , (B): 100:1

Langmuir's adsorption equation was used for the adsorption of silver on bentonite. The linear form of the equation is written as:

$$C_e/X/m = 1/KV_m + C_e/V_m, \quad [5]$$

Where X/m is the amount adsorped per unit mass of adsorbent, C_e is the equilibrium concentration of adsorbate in solution, V_m is the monolayer capacity, and K is the binding constant that is related to the heat of adsorption by equation:

$$K = K_0 \exp(-q/RT), \quad [6]$$

Where q is the heat of adsorption. The equilibrium concentration of silver used was in the range of 1×10^{-3} N to 2×10^{-1} N in these studies. A straight line is obtained by plotting $C_e/X/m$, against C_e Fig. 7.

Calculations of Thermodynamic Parameters

Thermodynamic parameters such as free energy and enthalpy of silver adsorption were calculated from the binding constant K obtained from Langmuir's equation by using the following relations:

$$\Delta G^\circ = -RT \ln K, \quad [7]$$

$$\ln K = -\Delta H^\circ/RT + \text{Constant}, \quad [8]$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \quad [9]$$

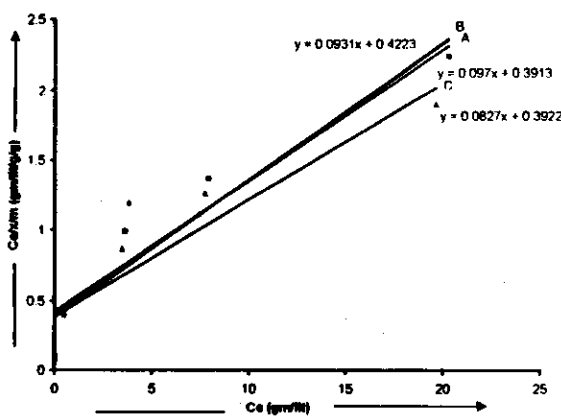


Fig. 7. Langmuir plots of silver sorption on bentonite at different temperatures. (A): 283K, (B): 298K, (C): 318k

The value of ΔH° is calculated from the slope of the linear variation of $\ln K$ versus $1/T$ Fig. 8. The value of ΔS° are calculated by using the well known equation:

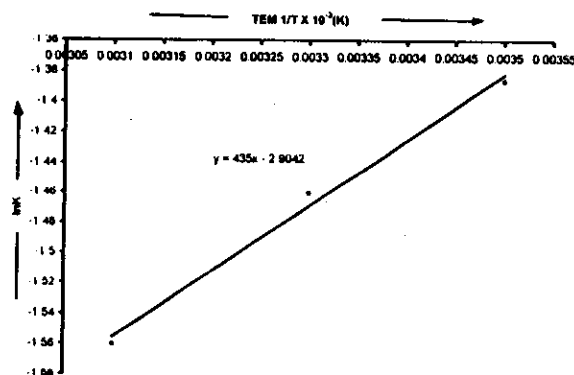


Fig. 8. Plot of $\ln K$ vs. $1/T$ for silver sorption on bentonite.

The values of ΔH° , ΔS° and ΔG° for the silver Bentonite system calculated from binding constant are given in Table :1. The value of ΔH° show that the process of silver adsorption on Bentonite is exothermic and extent of adsorption increases with increasing temperature; this is what that has experimentally been observed *i.e.*, Fig. 5.

Desorption of Silver

Desorption studies were carried out for various silver loading concentrations at given

Table-1: Values of the Thermodynamic Parameters for Silver Adsorption on Bentonite.

Temp. (K)	ΔH° (KJ/mol)	ΔG° (KJ/mol)	ΔS° (KJ K ⁻¹ mol ⁻¹)
283	-3.62	3.26	0.024
298	-3.62	3.61	0.024
318	-3.62	4.13	0.025

temperature (i.e., $25 \pm 0.5^\circ\text{C}$). This was done by carefully decanting the remaining solution. After adsorption the loaded Bentonite was resuspended in 10cm³ of Deionized water and was shaken for 30 min at fixed temperature. Percent desorption was determined volumetrically. The results are shown in Table 2. The extent of desorption does not change with time up to 24 hrs

Table-2: Effect of Silver Bulk Concentration on the Sorption and Bentonite Loading on the Desorption of Silver on Bentonite

Ag concentration in solution (gm/lit)	% Sorption (Mean \pm SD)	Loading of Ag on Bentonite (gm/lit)	% Desorption with ground water (Mean \pm SD)
10.788	26.40 \pm 0.005	2.849	28.8 \pm 0.4
5.3940	35.20 \pm 0.006	1.898	15.40 \pm 0.3
1.0788	51.61 \pm 0.05	0.557	13.95 \pm 0.1
0.5394	66.82 \pm 0.1	0.360	8.32 \pm 0.05
0.3240	72.82 \pm 0.4	0.241	11.20 \pm 0.04
0.10788	81.79 \pm 0.3	0.088	16.72 \pm 0.67

Experimental

Locally available clay, characterized as Bentonite on the basis of XRD and chemical analysis Table.3 has been used for the present study. Processed Bentonite sample was sieved through -200 mesh screen and was used without any heat or chemical treatment for the sorption studies reported here.

Table-3: Chemical Analysis of Local Clay Characterized as Bentonite

Metal oxides	Chemical analysis(%)
Silica (SiO ₂)	63.96
Alumium (Al ₂ O ₃)	25.68
Lime (CaO)	3.03
Iron Oxide(Fe ₂ O ₃)	4.28
Magnesia(MgO)	1.84
Potassium Oxide(K ₂ O)	0.71
Sodium Oxide(Na ₂ O)	0.47
Titanium Oxide(TiO ₂)	-

All the chemicals were of analytical grade [WINLAB.UK.].N/10 AgNO₃ stock solution was prepared by standard procedure [10]. Various spiked standard solutions of silver were prepared by taking a known aliquot of the silver stock solution in

measuring flasks, making the volume to the mark with deionized water.

The adsorption of silver on bentonite was studied by batch-technique [11]. The general method used for these studies is described below:

A known weight of Bentonite was equilibrated with known concentration in a stoppered Pyrex flask (25 cm³) at a fixed experimental temperature in a thermostated shaker water bath for a known period of time. All of the adsorption experiments, except where the pH was varied, were pH 7.3, which was obtained naturally at solution to clay ratio of 20:1. The pH of the suspension in one set of experiments was adjusted by using NaOH and HNO₃. The pH of the solution was that of the supernatant, which was obtained after equilibration.

After equilibration the suspension was centrifuge in a stoppered tube for 5 min at 4500 rpm then filter it. The amount of silver adsorbed 'X' and equilibrium silver concentration in the solution 'Ce' was always determined volumetrically by Volhard's Method [10]. Adsorption of silver on the walls of glass flasks and centrifuge tubes were determined by running the blank experiment, this was found to be negligible.

Adsorption of silver on bentonite was determined in terms of distribution Co-efficient K_d , Percentage extraction 'P' or amount adsorbed per unit weight of the adsorbent, " X/m (g/g). These are described below:

The distribution Co-efficient ' K_d ' is defined as the concentration of a species sorbed per gram of the adsorbent divided by its concentration per cm³ in the liquid phase

$$K_d = \frac{ms/M}{me/V}, \text{ cm}^3/\text{g} \quad [1]$$

Where ' ms ' and ' me ' are the masses of metal ion adsorbed and in solution respectively, M is the mass of the adsorbent in gram, and V is the volume of the solution in cm³. In the present study K_d values were determined volumetrically by using the following equation.

$$K_d = \frac{A_i - A_e}{A_e} \times V/w, \text{ cm}^3/\text{g} \quad [2]$$

Where A_i and A_e are the concentrations of metal compound in

Solution at the beginning and at the end of adsorption, respectively, V is the volume in cm^3 of the solution used for equilibrium, and W is the weight of adsorbent in grams.

The percentage adsorption, P , was calculated from K_d by using following equation:

$$P = \frac{100 \times K_d}{K_d + V/W} \quad (\%) \quad [3]$$

Amount adsorbed per unit weight of the Bentonite x/m , was calculated volumetrically from the initial and final concentration of the solution.

Conclusions

The present study is a mathematical model (*i.e.*, metal-ion adsorption) based on experimental data for adsorption of metals on to clay minerals, which can be used to remove poisonous metals from the waste products of industries and to have a pollution free environment.

References

- Mattigod, S.V., Sposito, G and Page, A.L. Factors affecting the solubilities of trace metals in soils. In D.E. Baker (Ed.). Chemistry in the soil environment. ASA Special publication No.40. Amer.Soc.Agronomy, Madison, WI. (1981).
- E. H. Cho and C.H. Pitt, *Metall. Trans. B.*, **10B**, 159, (1979)
- Lindsay, W.L. Chemical equilibria in soils. John Wiley and Sons; New York. 1979.
- R. Rhodes and M. Rubin. *Radiol Manage.* **20**, 19, (1998)
- U.S. EPA. Ground Water issue: Behavior of Metals in Soils. EPA/540/S-92/018, U.S. Environmental Protection Agency, Washington, DC. (1992).
- Andren, A.W., Phillips, H. A. Silver adsorption characteristics in natural waters. The National Association of Photographic Manufacturers (Publisher), San Francisco, CA. (1992).
- M. A. Takashi, M. Muroi, A. Inoue, M. Aoki, M. Takizawa, K. Ishigure and N. Fujita, *Nuclear Technology USA.* **76**, 24 (1987).
- G. Berket, A. Z. Aro. and M. Z. Ouml, *J Colloid Interface Sci.*, **187**, 338 (1997).
- B.S. Krishna, D.S. Murty and B.S. Jai Prakash, *J colloid Interface Sci.*, **229**, 230 (2000).
- A.I. Vogel, A Text book of Quantative Inorganic analysis Including Elementary Instrumental analysis (3rd ed.) Richard clay company, Ltd. Great Britain (1961).
- A.K. Saad, U. R. Riaz, M.A. Ali. *Waste Management.* **14**, 125 (1994).
- M. Corbin, In: The Handbook of Hazardous Waste Management, A. A. Metry (ed.). Technomic Publishing Co., Inc., Chicago. IL. pp158-215 (1980).