

Effect of Temperature on the Adsorption of Mg^{2+} on Kaolin from Aqueous Solutions and the stability Constants for Complex Formation

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Summary: Kaolin, an inexpensive clay mineral, available in abundance in our country has been employed as an adsorbent for the removal of Mg^{2+} from water at pH 7.0 within the temperature range (303-328 K). The linearity of the plots indicated langmuir type isotherms. The reaction was exothermic. At 303K the H^+_{rel}/Mg^{2+}_{ads} ratio n was fractional. At 318K at a time only one H^+ was released per metal ion adsorption and at 328 K two H^+ were released to the aqueous phase. Strong chemical bondings took place between oxygen atom of the surface and Mg^{2+} resulting in a surface complex species. In spite of the difference in structure between TiO_2 and kaolin, they show a similarity in their interaction with magnesium. Temperature had a significant effect on H^+_{rel} and the stability constants also increased with increasing temperature.

Introduction

Magnesium compounds are used extensively for refractories and insulating materials as well as in the manufacture of rubber, printing inks, pharmaceuticals and toiletry goods in the local industries. These industries emit magnesium in the liquid discharges which not only contribute to water hardness but also adversely affects the aquatic ecosystem. Magnesium is an important ion in maintaining the integrity of the human myocardium. However, its absorption above permissible limits can cause severe damage to the human health. Several classical methods exist for the removal of Magnesium from water. However, adsorption by clays and minerals seems economically viable and appears to be an important approach to controlling the hazard of environmental pollution. Very little has been reported about the adsorption of alkaline earth metals on kaolinite [1-3]. The purpose of this investigation was to study the effect of temperature on the extent of adsorption of Mg^{2+} on kaolin and to derive the stability constants for complex formation to gain the idea about the strength of bond between the adsorbent and adsorbate.

Results and Discussion

Characterization of Kaolin

The clay sample was supplied by Forte Ceramics Industries, Peshawar, Pakistan. The chemical analysis showed that silica and alumina were the major constituents of the sample. The IR spectra demonstrated [5-8] clear vibrational bands at 3700, 3610-60, 1120-15, 920, 800, 760, 690 cm^{-1}

(Table-1) which were similar to that of Kaolinite. The clay sample was further characterised by XRD and Differential Thermal Analysis. The XRD results of the adsorbent also revealed the dominance of kaolinite. The differential thermal analysis curve displayed exothermic and endothermic peaks at ca 590 and 960 °C [4] characteristics of Kaolinite.

Table-1: Mineralogical Analysis of Kaolin IR bands along with their possible assignments

Band Position (cm^{-1})	Assignment
3700	O-H Stretch
3610-60	O-H Stretch
1120-1015	Si-O Stretch
920	R-OH bend (R=A1,Fe)
800	Si-O Stretch
760	A1-O-H bend
690	Si-O Stretch

Adsorption study

The preliminary results showed that most of the adsorption of Mg^{2+} on the surface of kaolin took place in the first few minutes of the adsorption experiments. The adsorption of Mg^{2+} was accompanied by the release of H^+ to the aqueous phase of the suspension. At 303 K, the liberated H^+ re-adsorb on the surface of kaolin due to the amphoteric nature of kaolin resulting in a fractional H^+_{rel}/Mg^{2+}_{ads} ratio, n (Table-2). At 318 K only one H^+ were released to the aqueous suspension while at 328 K two H^+ were released per metal ion adsorption. The H^+_{rel}/Mg^{2+}_{ads} ratio, n changes from a fractional value to 2.0 at different temperatures and no specific stoichiometry could be evaluated for the

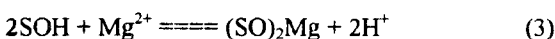
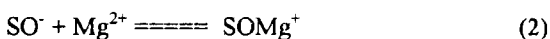
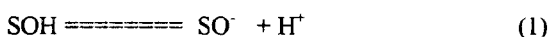
Table-2: H⁺/Mg²⁺ ratio, n for the adsorption of the Mg²⁺ on kaolin at different temperatures.

Temp. K	Initial Conc mg.L ⁻¹	Mg ²⁺ _{ads} mg.g ⁻¹	H ⁺ _{rel} mg.L ⁻¹	H ⁺ /Mg ²⁺ ratio,n
303	12.25	0.22	0.18	0.84
	24.50	0.35	0.06	0.17
318	12.25	0.10	0.18	1.73
	24.50	0.20	0.23	0.89
328	12.25	0.08	0.19	2.41
	24.50	0.14	0.29	2.17

Experimental conditions:

- * Kaolin, 0.6g; Electrolyte, NaClO₄, 0.01M
- * pH 7.0; Metal Ion Conc. 12.25, 24.5 mg L⁻¹
- * Suspension volume, 30. 32 ml,
- * Equilibrium Time 30 minutes

adsorption reaction. However, the possibility of the following equations can not be ruled out



The SOMg⁺ represents the adsorbed form of the Mg²⁺. While (SO)₂ Mg may be considered as the bidentate surface complex [9].

The positive charge developed in the surface plane, as a result of reaction (2) is balanced by the

counter ions (ClO₄⁻) in the β plane of the electrical double layer at the kaolin-solution interface.

Different values of n ranging from (0.73-1.95) have also been reported by Jang *et al* [9] during the adsorption of Mg²⁺ on TiO₂. Hence, inspite of the difference in structure between titanium dioxide and the clay minerals, they show similar behaviour in interaction with magnesium. Anatase, a form of TiO₂ and clay minerals like kaolin and mica have also shown similar behaviour by following a ring closure mechanism involving two adjacent adsorption sites increasing the entropy of the system compensating for the endothermic enthalpy change during the phosphate interaction with two reference clays and an anatase pigment [10].

The adsorption data followed the Langmuir type shapes (Figure 1) and was fitted to the linear form of the Langmuir adsorption equation expressed as,

$$\frac{C}{X} = \frac{1}{BX_m} + \frac{C}{X_m} \quad (4)$$

where C = Eq. Concentration mg L⁻¹

X = Amount Adsorbed mg g⁻¹

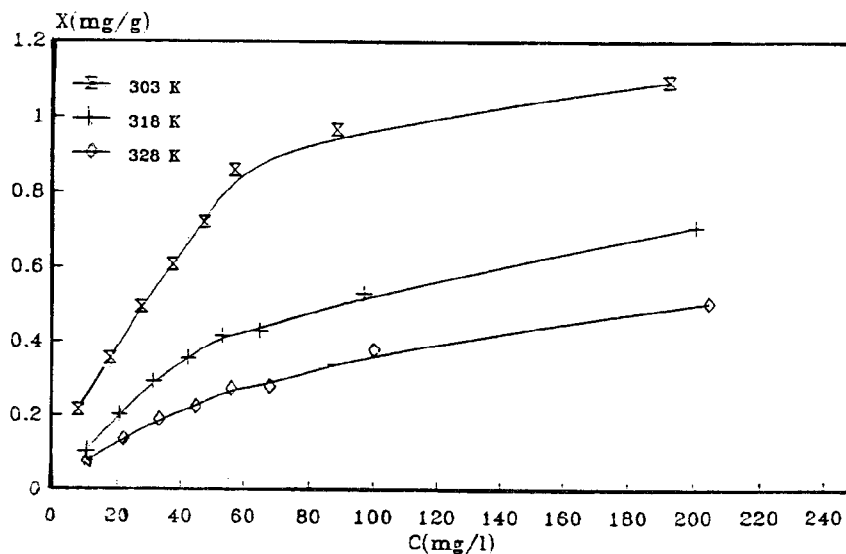


Fig. 1: Adsorption Isotherms of Mg²⁺ on Kaolin at pH 7.0

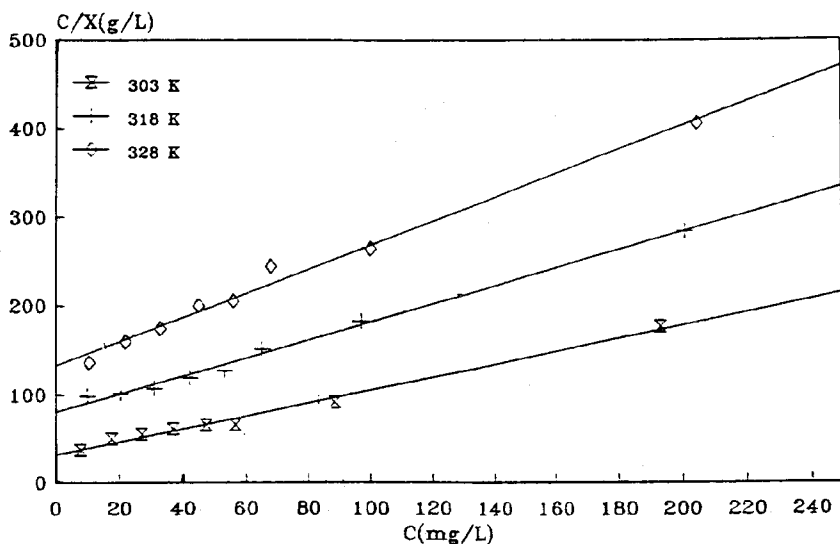


Fig. 2: Fig. 2: Adsorption isotherms of Mg^{2+} on kaolin at pH 7.0.

X_m = Maximum Adsorption Capacity $mg\ g^{-1}$

The parameter B is a constant related to the heat of adsorption, Q, [11-13] by the relation as

$$\ln B = \ln B' + \frac{Q}{RT} \quad (5)$$

where B' is a constant, R is the gas constant and T is absolute temperature (K).

The data were plotted in the form of C/X Vs C (Figure 2). The maximum adsorption capacity of the adsorbent at different temperatures and the value of B (X_m in moles g^{-1}) were calculated from the slopes and intercepts of the plots shown in Figure 2, and summarized in (Table-3). The value of X_m decreases with an increase in temperature. The decrease in adsorption with temperature may be attributed to the exothermic nature of the adsorption reaction. This behaviour of the system can be explained by assuming that at high temperature, the total energy of the adsorbate molecules is increased, on account of which their escaping tendency is also increased, hence the adsorption of Mg^{2+} species is decreased.

The heat of adsorption was calculated from the slopes of the plots of $\ln B$ Vs $1/T$, according to eq. (5) (Figure 3). The apparent value of 'Q' was

Table-3: Adsorption data for the Mg^{2+} on kaolin

Temp. K	pH	$X_m\ mg\ g^{-1}$	B	$pK_{(int)}$
303	7.0	1.37	560.10	9.93
318	7.0	0.98	307.46	9.08
328	7.0	0.74	247.67	9.06

found to be $27.6293\ kJ\ mol^{-1}$ and contrasts the value for a complex reaction. The heat of adsorption for a simple ion exchange reaction is usually equal to $8\ kJ\ mol^{-1}$ [14].

In addition to the exchange of H^+ of the adsorbent with the Mg^{2+} , strong chemical bonds may have formed between the oxygen atoms of the surface and the Mg^{2+} , and thus resulted in the surface complex species. The mean distance, δ between the surface of TiO_2 and the adsorption plane of the alkaline earth cation Mg^{2+} (range from 0.21 nm for magnesium) is in the range that can account for strong interaction or tight binding of alkaline earth cations to the surface of TiO_2 [9]. Titania and kaolin show a similarity in their interaction with Mg^{2+} , indicating that strong binding exist between the kaolin surface and Mg^{2+} .

Thermodynamic study

The free energy of adsorption (ΔG), enthalpy (ΔH) and entropy (ΔS), may be estimated using the following equations [15]:

$$\Delta G = -RT \ln B \tag{6}$$

$$\Delta H = R \frac{T_2 T_1}{T_2 - T_1} \ln \frac{B_2}{B_1} \tag{7}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{8}$$

Where "R" is the gas constant (8.32), B, B₁ and B₂ are constants (eq. 4) Table-3 related to the free energy of the system at temperature T, T₁ and T₂ respectively.

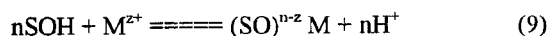
The negative values of ΔG (Table-4) indicate that the process involved is spontaneous. Also, at high temperature the low negative value of ΔG is an indication of low adsorption. Enthalpy changes at different temperatures (Table-4) were found to be negative which confirm the exothermic nature of the process. The negative values of ΔS (Table-4) suggest the possibility of favourable adsorption [16].

Table-4: Thermodynamics Parameters at various temperatures during the adsorption of Mg²⁺

Temp. K	pH	ΔG kJ mol ⁻¹	ΔH kJ mol ⁻¹	ΔS J mol ⁻¹
303	7.0	-15.95	-32.06	-53.15
318	7.0	-15.16	-18.77	-11.35
328	7.0	-15.04	-	-

Stability constants of the surface complex

The adsorption of the metal ions on Kaolin may be treated as surface complex formation between the surface sites and the adsorbate metal cations denoted as,



where SOH = surface adsorption sites

(SO)^{n-z} M = Surface complex of the metal ion

n = no of H⁺ released

The stability constant, K_(int), of surface complex, (SO)^{n-z} M may be written [17] as

$$K_{(int)} = \frac{[(\text{SO})^{n-z} \text{M}] [\text{H}^+] \exp(-nF \Psi_0/RT)}{[\text{SOH}] [\text{M}^{z+}] \exp(-zF \Psi_0/RT)} \tag{10}$$

Where Ψ₀ is the surface potential at the plan of adsorption, R and T are the gas constants and absolute temperature.

By assuming the Nerstian relationship [17] i.e.

$$\Psi_0 = \frac{2.303}{F} (\text{PZC-pH}) \tag{11}$$

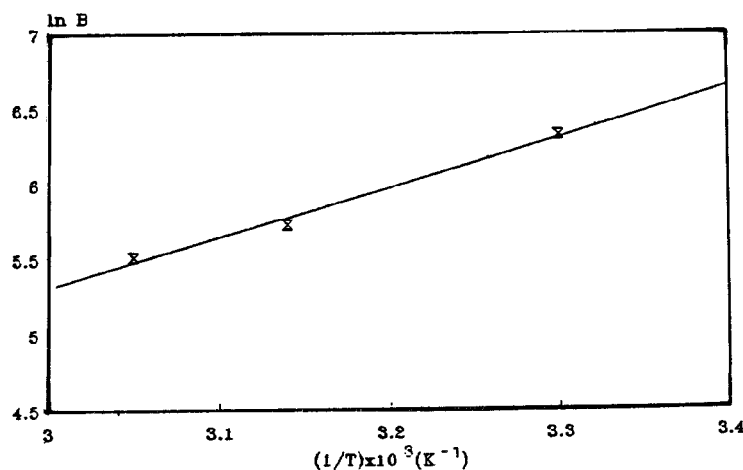


Fig. 3: Plot of lnB versus 1/T for the adsorption of Mg²⁺ on Kaolin at pH 7.0

Equation (10) may be written as,

$$K_{(int)} = K' \exp [(z-n) (PZC-pH)] \quad (12)$$

Where K' is the apparent stability constant of the surface complex and may be determined from the experimentally measured parameters. By substituting the values of PZC (5.4), pH, n, and K' in eq (12), known from the experimental data, the values of $pK_{(int)}$ were calculated for Mg^{2+} at different temperatures at pH 7.0 and presented in (Table-3).

Because temperature had a significant effect on the amount of H^+_{rel} already introduced (Table-2), the values of the stability constants also increased with the increase in temperature (Table-3).

Experimental

All the reagents used in this study were of analytical grade and were used without further purification. The clay sample was ground, passed through sieve No. 150 and then characterized by XRD, IR and Differential Thermal analysis prior to adsorption studies. A stock solution of Mg^{2+} was prepared by cleaning a magnesium strip in dilute HCl. The solution of Mg^{2+} in HCl was heated to dryness, and made to volume with 0.1M $HClO_4$.

In performing each adsorption experiment, 0.6 g of the adsorbent was thermostated and magnetically stirred for one hour with Mg^{2+} solutions of the desired concentrations at an adjusted pH value in a double walled cell connected to a water circulating bath with temperature variations of ± 0.5 . The pH of the suspension was maintained constant with either standardized 0.1, 0.01 M NaOH or $HClO_4$ during the adsorption experiments. The total volume of the suspension did not exceed 30.32 ml while maintaining a constant pH. The suspension was then filtered and the filtrates were analyzed for Mg^{2+} using an Atomic Absorption Spectrophotometer. No detectable adsorption was observed at the surface of filter paper. The amount of the metal ions adsorbed was computed from the difference between the initial and equilibrium metal ion concentration. Similarly, the number of mgL^{-1} of H^+ released to the aqueous phase as a result of the metal ions adsorption were estimated from the volume of NaOH solution used for maintaining constant pH during the adsorption experiments. The heat of adsorption was

calculated from the slopes of the plots of $\ln B$ Vs $1/T$, according to eq. (5) (Fig. 3).

All studies were carried out over the temperature range (303-328 K) and the ionic strength of the solutions was fixed at 0.01 M $NaClO_4$.

Conclusion

1. Because ΔG represents the free energy of interaction between the metal ion and the surface of kaoline, it must decrease with an increase in X_m .
2. As the adsorbent is available at a throw away price in our country and possess good potentiality for mg^{2+} removal from waste water. Its use as a substitute for activated carbon or other metal oxides seems commercially feasible and economically viable.
3. The data thus generated may prove useful for designing and fabricating a treatment plant for the removal of Mg^{2+} from wate water.

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