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Removal of Co(II) Ions from Water by Sorption on China Clay

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Summary: The adsorption of Co(II) by well characterized China clay in the pH range (3.0 - 6.5) at various temperatures followed the Langmuir isotherms. Co(II) removal is favoured by low concentration, low temperature, and low pH. The high adsorption capacity at low pH is attributed to the content of silica in China clay.

Introduction

Cobalt is an important metal and is frequently used in many industrial operations and as a catalyst in various industrial processes [1]. These industries emit untreated effluents into the dynamic water channels which deteriorate the quality of water and adversely affect the aquatic ecosystem.

Cobalt is an essential trace element for biological systems but toxic at high enough concentrations. Removal of toxic agents from water has been subject of continued research for the past few decades and several methods have been developed in this regard. Nevertheless, advanced technologies like the adsorption of heavy metals on activated carbon have an edge on the conventional processes because of easy handling and cost efficiency due to regeneration. However, due to their high costs the adoption of such technologies is becoming difficult for the developing countries like Pakistan.

China clay, a cheap clay mineral, has been employed by several investigators [2-8] as an adsorbent for the removal of heavy metal ions from water and waste water. Much has been reported about the factors affecting the adsorption processes [9-13]. In this work we will focus principally upon effect of temperature and pH on adsorption of Co(II) by China clay, not previously reported.

Results and Discussion

Characterization of China Clay

The analysis showed that China clay was mainly consisted of alumina and silica (Table-1). The XRD results of the adsorbent revealed the dominance of Kaolinite. Tourmaline, Quartz, Muscovite and Feldspar were present in minute amounts in addition to Kaolinite [14,15]. IR spectra demonstrated clear vibrational bands at 3,700, 3610-60, 1,120 - 1,015, 920, 800, 760, 690 cm^{-1} and were similar to that of kaolinite [16-20]. Furthermore, the differential thermal analysis curve (Fig. 1) displayed endothermic and exothermic peaks at ca. 590 and 960°C, characteristic of Kaolinite [14].

Table-1: Characterization of China clay

Constituent	Percentage by weight/unit
SiO_2	47.6
Al_2O_3	36.7
Fe_2O_3	0.9
CaO	0.1
MgO	0.3
Loss on Ignition	12.0
Surface area	10 m^2/g

Adsorption study

Preliminary kinetics experiments showed that most of the adsorption of Co(II) ions on the surface of China clay took place in the first few minutes of the adsorption experiments. The adsorption reaction was studied in the pH range (3.0-6.5).

Following the experimental evidence, at pH 6.5, the adsorption of Co(II) was accompanied by the release of H(I) ions to the aqueous phase of the suspension. As evident from the data in Table-2, after stoichiometric liberations of H(I) into the aqueous phase of suspension, some of the liberated H(I) re-adsorb on the surface of China clay, resulting in a fractional H^+_{rel}/Co^{2+}_{ads} ratio, n.

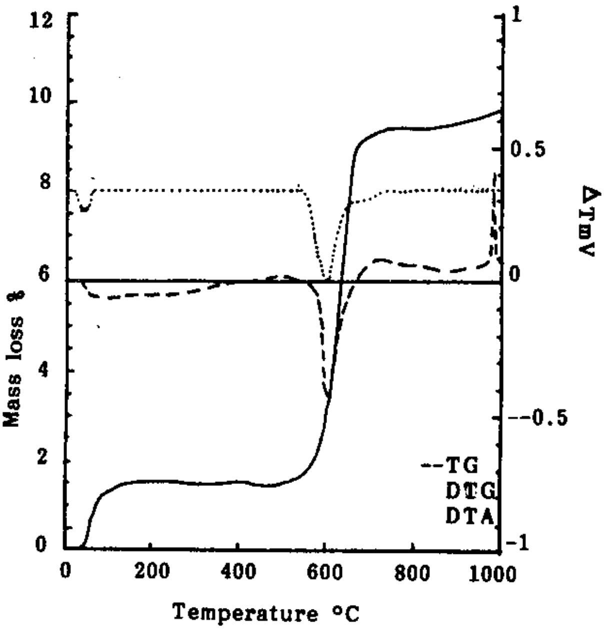

Fig. 1: Thermogram of clay sample

Table-2: H(I)/Co (II) ratio for the adsorption of the metal ions on China clay at different temperatures

Temperature K	Co(II), ads mg.g^{-1}	H(I)/Co(II)
298	0.642	0.4871
308	0.625	0.3018
318	0.616	0.2875
328	0.505	0.3762

Experimental Conditions:	China clay, 0.6 g. Electrolyte, $NaClO_4$, 0.01M, pH 6.5; Metal ion Conc. 22.6 mg/1, suspension volume, 30.32 mls Equilibrium Time 30 minutes.

Similar findings were reported by J.W. Murry and D.G. Kinniburgh [21,22] for the adsorption of heavy metals on MnO_2 and $Fe(OH)_3$. At pH 3.0 and 298K the total released H^+ ions are re-adsorbed on the surface and the value of n remained indeterminate. Therefore, no specific stiochiometry could be elucidated for the present investigation.

The data followed the Langmuir type shapes (Fig. 2). The amount adsorbed per gram of powder X, was calculated and C/X was plotted versus C. Linearity of the plots indicated a Langmuir type isotherm, expressed as

$$C/X = 1/Bx_m + C/X_m \qquad (1)$$

where C = Eq. Concentration (mg/1)

X = Amount Adsorbed (mg/g)

X_m = Maximum Adsorption Capacity (mg/g) and the parameter B is related to the heat of adsorption, Q by the relation [23-25] as mentioned below:

$$\ln B = \ln B' + Q/RT \qquad (2)$$

where B' is a constant, R is the ideal gas constant and T is the thermodynamic temperature.

(Fig. 3) depicts the linear form of the Langmuir isotherms for the adsorption of Co(II) by China clay at pH 6.5 at four different temperatures

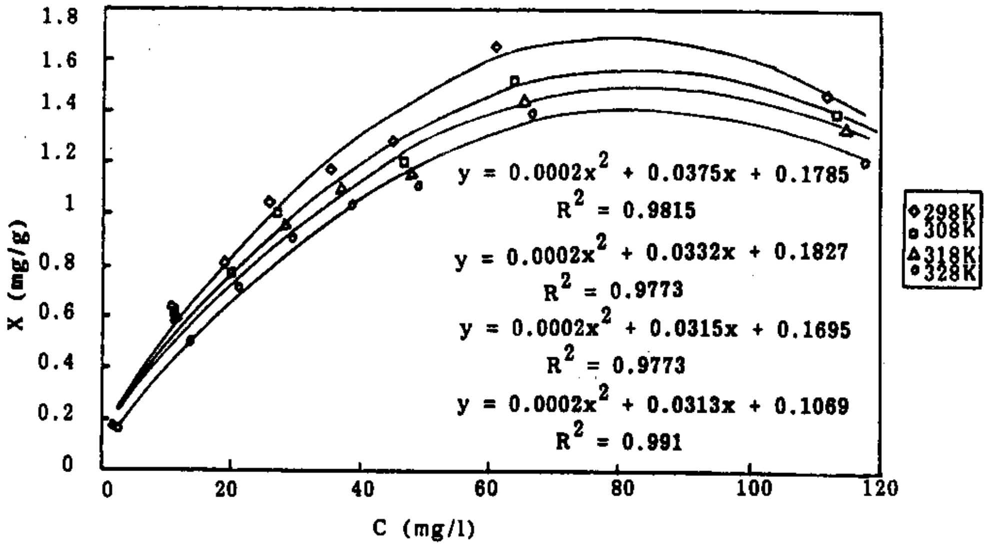

Fig. 2: Adsorption isotherms of Co(II) ions on China clay at pH 6.5

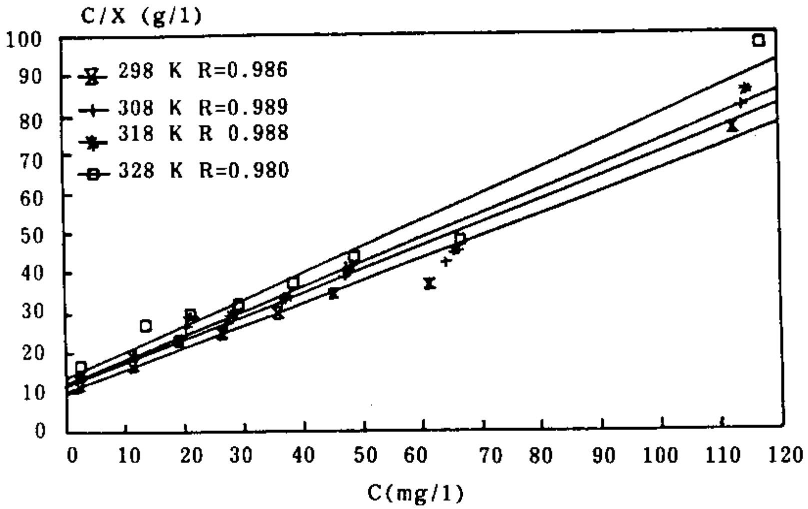

Fig. 3: Langmuir plots for the adsorption of Co(II) ions on China clay at pH 6.5.

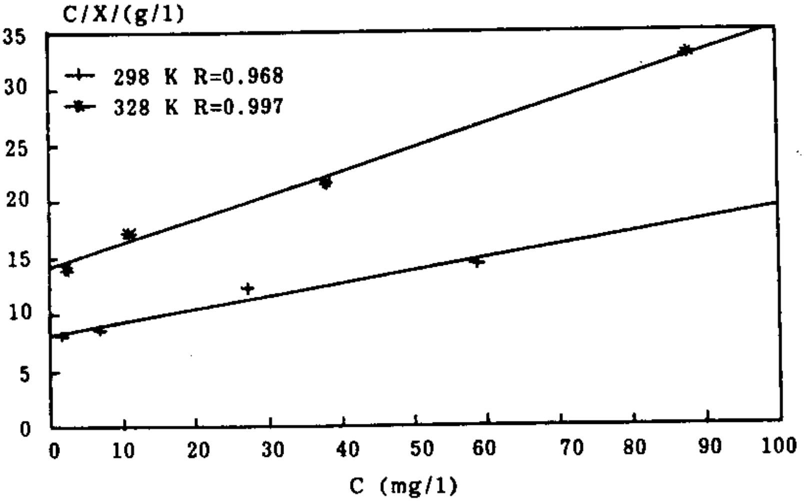

Fig. 4: Langmuir plots for the adsorption of Co(II) ions on China clay at pH 3.0.

while (Fig. 4) indicates such plots at pH 3.0 and at two reliable temperatures.

From the slopes and intercepts of these lines the value of X_m and B (X_m into mols.g^{-1}) were calculated and collected in Table-3.

The standard errors in the slope and intercept have also been reported in Table-3. Similarly, the heat of adsorption of Co(II) ions was calculated from the slopes of the plots of ln B versus 1/T (Table-4) according to eqn: 2. (Fig. 5)

Table-3: Adsorption data for the Co(II) ions on China clay

pH	Temp.	Xm mg g^{-1}	Std err of X Coeff. (S)	B	Std Err of Y Est (Const)
6.5	298	1.79	0.04	3304.14	3.52
	308	1.71	0.04	3044.09	3.39
	318	1.65	0.04	2887.50	3.60
	328	1.52	0.05	2875.45	5.21
3.0	298	8.93	0.02	819.59	0.92
	328	4.71	0.01	893.65	0.80

Table-4: Apparent heats of adsorption (Q) of Co(II) at different pH values.

pH	6.5	3.0
Q kJmol^{-1}	3.81	-2.22

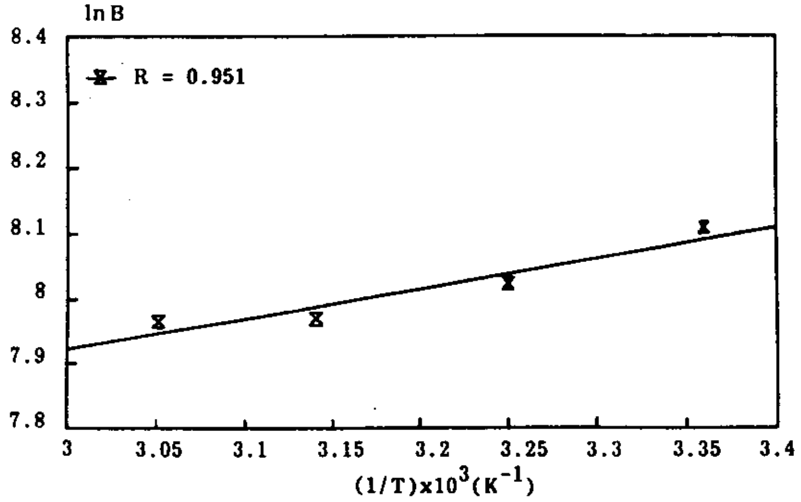

Fig. 5: Linear variation of lnB versus 1/T for the adsorption of Co(II) ions on China clay at pH 6.5

Table-5: Thermodynamics parameters at different pH during the adsorption of Co(II)

pH	Temperature K	ΔG kJmol^{-1}	ΔH kJmol^{-1}	ΔS Jmol^{-1}
3.0	298	-16.64	2.35	63.72
	328	-18.55		
6.5	298	-20.09	-6.26	46.42
	308	-20.56	-4.30	52.77
	318	-21.08	-0.36	65.16
	328	-21.74	–	–

sketches such plots at pH 6.5. As can be seen from Table-3, extent of adsorption increased with decrease in pH. The adsorption of Co(II) ions increased from 0.642 mg/g to 0.848 mg/g by decreasing the pH from 6.5 to 3.0 at 298K and 22.56 mg/1 metal concentration. The decrease in adsorption of Co(II) with increase in pH has been explained on the basis of decrease of negative charge on the surface of China clay with increase in pH. China clay contains metal oxides which are hydroxylated in aqueous solution. Such interface on acid-base dissociation, develops positive and negative charges on the surface [26]. The metal oxides of China clay acquire a negative charge at low pH and attract positively charged adsorbate ions by coulombic forces.

The negative charge density on the surface of the adsorbent decreases as pH increases. This behaviour of the system shows that the high adsorption capacity of the adsorbent is due to the content of silica in China clay.

The main constituent, silica, posses negative charge (pH_{pzc} = 2.5) in the experimental pH range [7] and is the main reason for attraction between the metal ions and the surface of China clay. The content of alumina in aluminosilicates [27] and fly ash [28] is important only in adsorption of anions due to its high [7] Zero Point Charge (pH_{zpc} = 8.3). The positive charge on alumina surface sites over the pH range of interest causes repulsion to the adsorption of metal cations on the surface of China clay.

The high adsorption capacity at low pH is thus assigned to the content of silica in China clay.

The change in the sign of the heat adsorption of Co(II) by China clay with the change in pH is indicative of a change in the mechanism of adsorption with a change in pH (Table-4). However, the `apparent' value of Q remained unaltered at different pH and contrasts the value of Q for a simple ion exchange. The value for a simple ion exchange is usually equal to 8 kJ mol^{-1} [29].

The change in the Free Energy of adsorption ΔG, Enthalpy ΔH and Entropy ΔS were determined using the following equations.

$$\Delta G = - RT \ln B \quad (3)$$

$$\Delta H = R (T_2 T_1/T_2 - T_1) \ln (B_2/B_1) \quad (4)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (5)$$

Where "R" is the gas constant. B, B_1 and B_2 are the constants (eq. 2) Table 3, related to the Free Energy of the system at temperatures T, T_1 and T_2 respectively.

The negative value of ΔG (Table-5) indicates the spontaneous nature of the process. The positive value of ΔH at pH 3.0 shows a change in mechanism while the negative value of ΔH at a pH 6.5 is a clear indication of exothermic nature of the reaction.

The increase in the positive value of ΔS at pH 6.5 gives thermodynamic support to the adsorption reaction of Co(II) ions on the surface of China clay. As mentioned earlier, the adsorption is a simple ion exchange. As such, due to the exothermic nature of the process, at higher temperature, the adsorbate molecules are relatively less mobile on the surface, the adsorption reaction is accompanied by an increase in the entropy.

Experimental

All the reagents used in this study were of highest purity available and were used without further purification.

The China clay was supplied by Forte Ceramics Industries, Peshawar, Pakistan. The clay sample was ground, passed through sieve No. 150 and then characterized by XRD, IR and Differential Thermal analysis before subjecting it to adsorption studies.

In performing each adsorption experiment, 0.6 g of the adsorbent viz. China clay, was thermostated and magnetically stirred for one hr. with ions of Co(II) solutions of the desired concentrations at an adjusted pH value in a 100 ml Pyrex glass beaker inside an incubator, type Memmert GTR 0214. A precision pH meter type Corning 120 was used for pH measurements. The pH of the suspension was maintained constant with either standardized 0.1, 0.01M NaOH or $HClO_4$ during the adsorption experiments. The total volume of the suspension did not exceed 30.32 mls while maintaining constant pH. The suspension was then filtered and the filtrates were analyzed for Co(II) ions using Zeeman 8000 Atomic Absorption Spectrophotometer.

A concentration of 1.68 ppm, adsorbed on the surface of filter paper, was added numerically to the equilibrium concentration before processing the data. The amount of the metal ions adsorbed was computed from the difference between the initial and equilibrium metal ion concentration. Similarly, the number of H^+ (mg/l) 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 ionic strength of the solutions was fixed at 0.01 M $NaClO_4$.

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