

**UTILIZATION OF BENTONITE AS A NATURAL ADSORBENT  
FOR THE SORPTION OF IRON FROM THE GROUND WATER  
EXPLOITED FROM ASWAN AREA, EGYPT.**

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**ABSTRACT:** Sorption of iron on bentonite was studied utilizing batch technique. Distribution coefficient " $K_d$ " was evaluated for bentonite – iron system as a function of contact time, pH, sorbent and sorbate concentration and temperature. Sorption results were interpreted in terms of Freundlich, Langmuir equations. Thermodynamic parameters for the sorption system were determined at three different temperatures. The values of  $\Delta H = -4.0 \text{ kJmol}^{-1}$  and  $\Delta G^\circ = -2.46 \text{ kJmol}^{-1}$  at  $25^\circ\text{C}$  ( $298^\circ\text{K}$ ) suggests that the sorption of iron on bentonite is an exothermic and a spontaneous process.  $\Delta G^\circ$  becomes less negative at higher temperatures and therefore less iron is sorbed at higher temperatures. The desorption studies with  $0.01 \text{ M CaCl}_2$  and deionised water at iron loading on bentonite show that more than 90wt.% of the iron is irreversibly sorbed probably due to the fixation of the iron by isomorphous replacement in the crystal lattice of the sorbent.

**Key Words:** Bentonite – desorption – distribution coefficient - enthalpy - Freundlich isotherm – groundwater – free energy – Iron – Langmuir isotherm – sorption.

## 1- INTRODUCTION :

Stratiform economic iron oxide ores have recently discovered around Bir Um Hubal area, south-east of Aswan city (Fig. 1, [1] ). The ore is hosted within Up Cretaceous Nubian sandstone formations. The depth of this iron ore ranges from few centimeters to five meters. It appears as bench like-form in a real photograph based on its resistance to weathering. A new project is currently establishing in the area of discovering in order to extract and manufacturing of iron and steel. The area of the proposed project lies within the very hot, extremely arid province of mountainous terrian. The ground water is the unique resource of water existing in this desert. Alternatively, the other nearest source of water is lake Nasser which is located at 30Km west to the concerned area. The ultimate need of the available ground water for domestic, irrigation and for industrial purposes is obvious for this sustainable development project. However, the using of ground water in such purposes is controlled by several factors, e.g, the magnitude of total dissolved solids (TDS)  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ , iron, alkalinity, hardness, pH value, conductivity, ...etc.

The main goal of the present work is to using of the concerned bentonite in reducing of Fe content in the exploited ground water in "Aswan – Iron and Steel Project" to be used in agricultural and industrial purposes. The idea is based on the high exchange capacity of bentonite and its ability to adsorb and/or exchange large quantities of dissolved salts.

**Geological Setting:** Inliers of Nubian sandstone (Up-Cretaceous) are underlying and bounded by mountainous terran of pre-cambrian basement rocks composed mainly of granitic and metamorphic siut. The area is dissected by many wadies extended in eastern-west direction and downstreamed into the Nile in the west. The floor of these wadies is occupied by quaternary sediments derived by physical weathering of the adjacent country rocks. Aswan project of exploitation and manufacturing of iron is currently establishing in the area. It is planned to cultivate 500 hictars with vegetables, fruits and other many types of crops. The soil in this area is mainly high permeable arenaceous desert soil and contain few amount of clays. It's thickness varies from several centimeters to 5 meters.

**Ground Water:** Three wells were drilled in the area east of Aswan up till now, their depth varies from 90 to 140 meter. The source of ground water is related to pluvial episods during Pleistocene (Said [2]) which is captured in lithologic and tectonic traps within subsurface basins.

**Bentonite:** Bentonite shale is discovered recently in Kurkur area south-west of Aswan (Abou Elmagd [3]). The bentonite component is made up of relatively large flakes which disperse readily in water into very thin units with remarkable swelling. It is composed mineralogically of montmorillonite (70-87%) and illite (13-29%)

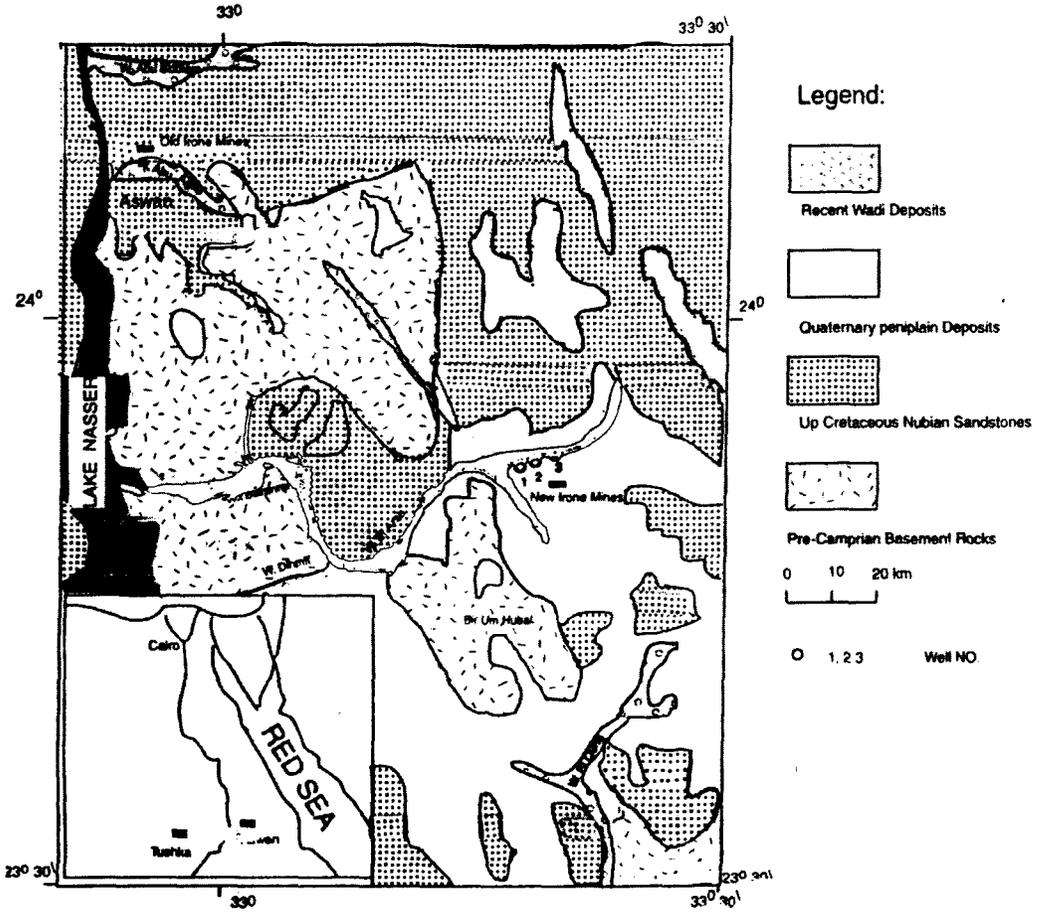


Fig. (1) A simplified Geological Map of Southeast Aswan Area, Egypt Showing Location of the Groundwater Wells (Modified After EGPC, 1987).

Nonclay fraction includes quartz and traces of calcite, gypsum and iron oxide. Chemically, XRF analysis reveals that the present bentonite is composed mainly of  $\text{SiO}_2$  (49–57 wt.%),  $\text{Al}_2\text{O}_3$  (23–30 wt.%),  $\text{CaO}$  (0.3–0.4 wt.%),  $\text{Fe}_2\text{O}_3$  (0.45–3.3 wt.%),  $\text{MgO}$  (0.01–0.10 wt.%),  $\text{Na}_2\text{O}$  (0.20–1.2 wt.%),  $\text{K}_2\text{O}$  (0.40–0.80 wt.%),  $\text{P}_2\text{O}_5$  (0.01–0.13 wt.%) and  $\text{TiO}_2$  (0.50–1.5 wt.%). Moreover, loss on ignition (LOI) is (15–16.5 wt.%).

Sorption of cesium on soils and clay minerals was studied (Jacop[4], Brouwer et al[5], Bunzyl et al., [6], Gulis et al. [7] and Sikalidis et al. [8]). Structural implications in cesium sorption on clay minerals were reported (Tamura and Jacob [9]). Bentonite, because of its physical and chemical properties, is considered as one of the most promising candidates for use as buffer materials in the geological disposal systems for high level radioactive wastes (Takahashi et al. [10], and Zhixiong [11]). Laboratory studies on bentonite samples from various deposits of many countries were performed (Hafez et al. [12], Miekeley et al. [13], Horyna et al. [14] and Konishi et al. [15]) to evaluate the suitability of this material as a backfill. The soil and clay minerals from different localities, because of the variations in their composition, may behave differently; therefore, each soil or clay deposit, if it is to be used as a backfill or for the disposal of low level radioactive waste into the ground, requires specific studies.

The present work aimed to make use of the discovered bentonite in reducing of  $\text{Fe}^{3+}$  ion which is present in, somewhat, high level in the well's water samples under study.

## 2- EXPERIMENTAL:

**Adsorbent:** Various bentonite samples were obtained through several visits to the field, Fig 1. The samples were picked up at random from individual lots of bentonite collected from different localities. The samples were individually processed. This was done by first crushing the bentonite sample in a thoroughly cleaned jaw crusher. A steel roller was then used to homogenize the sample. It was then subjected to sampling by coning and quartering. Finally it was pulverized in a ball mill and sieved through –250 mesh screen. Various physical, chemical and other structural properties of all the samples were determined. Bentonite was used without any heat or chemical treatment for the sorption studies reported in the present work.

**Ground Water Samples:** Ground water samples were obtained from three wells drilled in the working developed area; southern-east of Aswan city; Fig 1.

**Iron' Stock Solution:** The working standard iron' solutions were prepared from certified atomic absorption metal stock solutions,  $1000\mu\text{g ml}^{-1}$ , (Spectrosol BDH Chemicals Ltd., Pool, England by dilution.

**Instrumentation:** The pH of the solution was measured using microprocessor pH meter model 8519 by Hanna instruments, Italy. The shaking was performed in a thermostated shaker bath, USA. The centrifuge machine with a maximum 8000 rpm was used. Measurement were done using a Model 3110 Perkin-Elmer Atomic Absorption Spectrophotometer.

**Method:** The sorption of iron on bentonite was studied by batch method. A known weight of the bentonite was allowed to equilibrate with a graduated volume (keeping the bentonite : iron ratio at 1:20) of the spiked iron solution in a stoppered Pyrex glass flask at a fixed temperature in a thermostated shaker water bath for a known period of time. The flasks containing the weighed amounts of bentonite and iron solutions were separately kept in the thermostated bath before mixing for a sufficient period of time to attain the desired experimental temperature. After equilibration, the suspension was centrifuged in a stoppered tube for about 20 min at 5000 rpm. Iron content in the supernatant solution was then assayed by using AAS technique. Sorption of iron on the walls of glasses and centrifuge tubes, determined by running the blank experiments, was tested and was found to be regardless. Sorption of iron on bentonite was determined in terms of distribution coefficients,  $K_d$ , percentage extraction, P or amount sorbed per unit weight of the sorbent,  $x/m$  (g/g):

The distribution coefficient  $K_d$ , is defined as the concentration of a species sorbed per gram of the sorbent divided by its concentration per  $\text{cm}^3$  in the liquid phase:

$$K_d (\text{cm}^3/\text{g}) = \frac{m_s/M}{m_e/V} \quad (1)$$

where  $m_s$  and  $m_e$  are the masses of iron sorbed and remained in solution at the equilibrium, respectively, M is the mass of the bentonite in gram and V is the volume of the solution in  $\text{cm}^3$ . The percentage adsorption, P, was calculated from  $K_d$  by using

$$P (\%) = \frac{100XKd}{Kd + V/W} \quad (2)$$

Amount adsorbed per unit weight of the bentonite,  $x/m$ , was calculated from the initial and the final iron' solution concentration.

### 3- RESULTS AND DISCUSSION:

**Effect of Shaking Time:** The effect of shaking time on the sorption of iron on bentonite at three temperatures (i.e., 25, 35 and  $45 \pm 0.5^\circ\text{C}$ ) was tested. Graduated volume of iron solution, 50ml, was shaking with 2.50g of bentonite for different intervals of time extended from 5min upto 24h, Fig 2. The results show no regarded change in the sorption magnitude through the experimental time and temperatures. That is may be due to the rapid and spontaneous attainable of the equilibrium state. The instantaneous of uptaking of iron by bentonite shows that the ion-exchange mechanism is considered to be the noticeable mechanism (Saad et al. [16]).

**Effect of pH:** The effect of pH values (adjusted by using either NaOH or  $\text{HNO}_3$ ) on sorption of iron on bentonite was studied over a very wide scale of pH (e.i 1.5 – 11.0) and at  $35 \pm 0.5^\circ\text{C}$ . The results which are diagrammed in Fig 3 show an increasing in the sorption process (e.i increase of both  $K_d$  and P values) as the pH value increases. The greatest increase in  $K_d$  is observed in the range of 6 – 9 pH. That is may be due to the small number of the exchangeable sites present at low pH values as a result of the solubility of the constituents of bentonite at low pH, acidic medium.

**Effect of Sorbate' Concentration:** The study of the effect of iron' concentration on the sorption process indicates that the sorption of iron on bentonite is an iron' concentration' dependent process. The dependence of iron' sorption on its concentration was studied at  $35 \pm 0.5^\circ\text{C}$  by varying the metal concentration from  $10^{-7}$  to  $10^{-2}$  M. Fig 4 shows that both  $K_d$  and P values decrease with increasing iron concentration. The results suggest that both types of phenomena (i.e., adsorption as well as exchange) are taking place in the range of iron' concentrations studied. The removal of iron by exchange process may be due to isomorphous replacement or by ion-exchange mechanism. At low metal concentration, the value of  $K_d$  remains almost constant, while at high metal concentration the values decrease significantly. This suggests that energetically less favorable lattice positions or exchange sites become involved with increasing metal – concentration (Ertan et al. [17], and Alimdzhanova et al. [18]).

**Effect of Sorbent' Concentration:** The effect of bentonite' concentration on the sorption process was studied at  $35 \pm 0.5^\circ\text{C}$  by varying the amount of bentonite from 0.1 to 0.7g. The results are shown in Fig 5. The uptake of iron increases with the increasing of the amount of bentonite. This is due to the increasing of the available exchangeable sites.

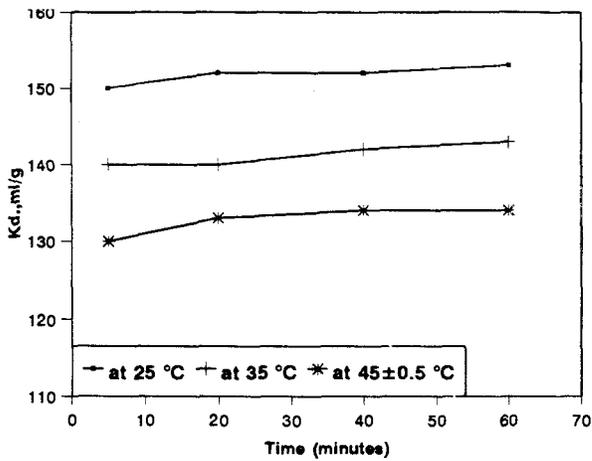


Fig. (2)

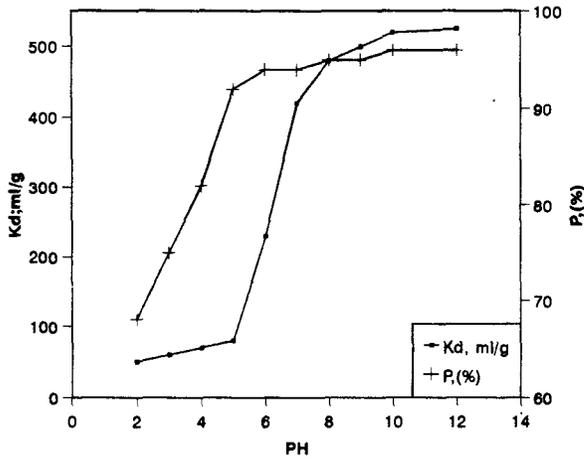


Fig. (3)

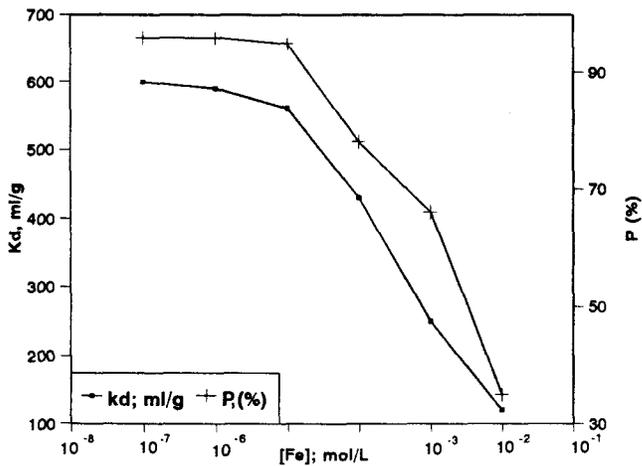


Fig.(4)

**Adsorption Isotherms:-** The adsorption isotherms at three different temperatures, 25, 35 and  $45 \pm 0.5^\circ\text{C}$ , were constructed, Fig 6. The range from 0.01 to 0.4M iron' concentrations were studied.

Freundlich adsorption isotherm was made use of for studying the sorption of iron on bentonite. The amount of the adsorbed iron per gram of the adsorbent;  $x/m$ , the equilibrium concentration,  $C$ , are correlate in the linear equation of :

$$\log x/m = \log K + n \log C \quad (3)$$

where  $K$  and  $1/n$  are constants.

The equilibrium concentration of iron studied was within the range  $1 \times 10^{-7}$  to  $1 \times 10^{-3} M$ . Plotting of  $\log x/m$  against  $\log C$  gives a straight line the slope of which is  $1/n$  value whereas its intercept corresponds to  $\log K$  value, Fig 7. The present work shows that the values of  $1/n$  and  $\log K$  are 0.80 and  $<1$ , respectively. Being the intercept,  $\log K$ , is less than 1, that is indicate (Aksoyoglu [19]) a concentration dependent in the range of iron concentration studied (non linear relationship).

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

$$\frac{C_e}{x/m} = 1/KV_m + C_e/V_m \quad (4)$$

where  $C_e$  is the equilibrium concentration of adsorbate in solution,  $x/m$  is the amount adsorbed per unite mass of adsorbent,  $V_m$  is the monolayer capacity, and  $K$  is the binding constant that is related to the heat of adsorption (Saad et al. [16]). Fig 8 shows the linear relationship between  $\frac{C_e}{x/m}$  (on the abscissa) and  $C_e$  the slope of which equal to  $1/V_m$ . The intercept equal to  $1/K.V_m$ .

**Thermodynamic Parameters:** Thermodynamic parameters, free energy and enthalpy of iron' sorption were calculated from the following relation:

$$\Delta G^\circ = -RT \ln K \quad (5)$$

where  $K$  is the binding constant obtained from Langmuir' equation, and

$$\ln K = \frac{-\Delta H^\circ}{RT} + \text{constant.} \quad (6)$$

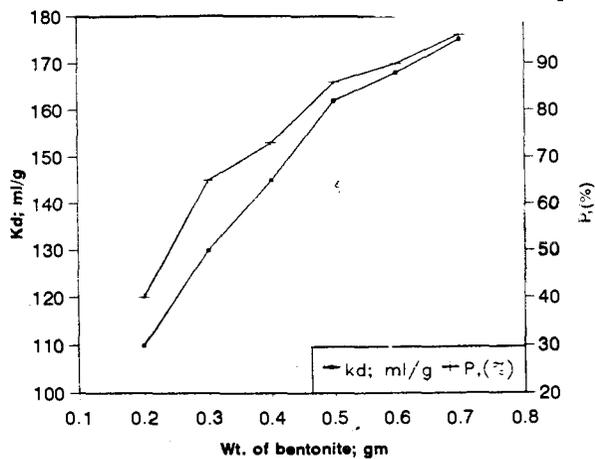


Fig. (5)

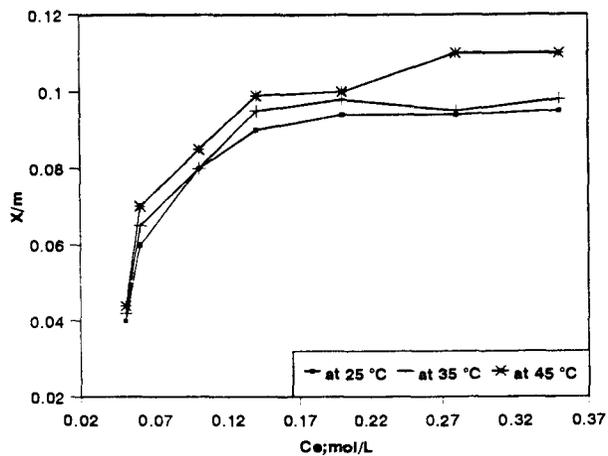
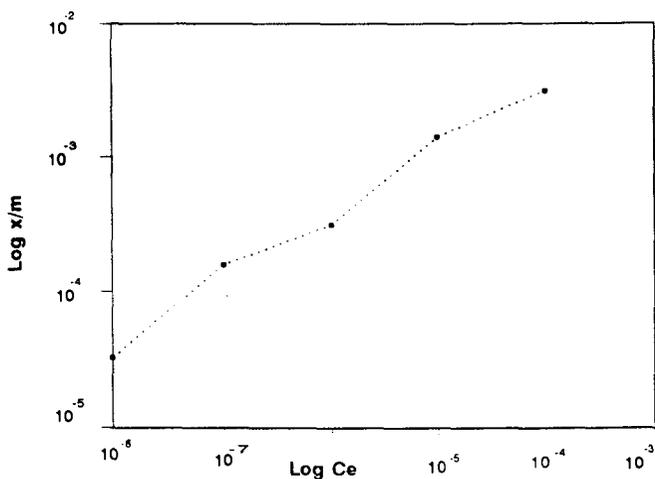


Fig. (6)



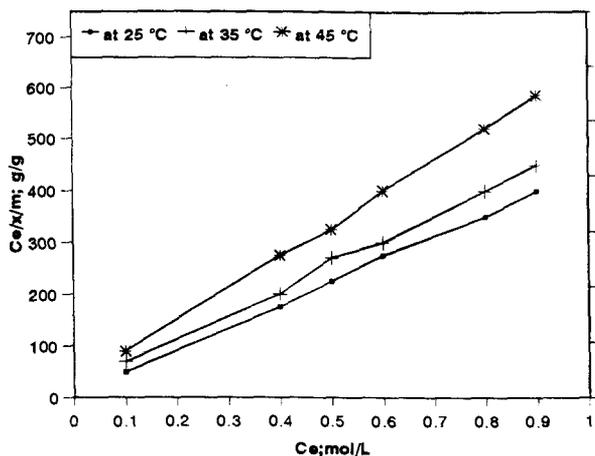


Fig. (8)

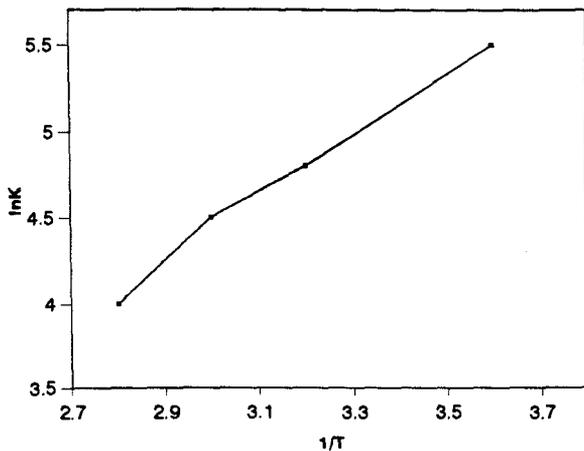


Fig. (9)

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (7)$$

was used to calculate the values of  $\Delta S^{\circ}$ . The data of thermodynamic parameters are given in Table [1]. The calculated values indicate that the iron sorption on bentonite is an exothermic and spontaneous process. The values of the monolayer capacity,  $V_m$  per 100g of the sorbent calculated from Langmuir's plot are 75.80, 70.90 and 60.93 m mol/100g at 298, 308 and 318K, respectively.

Table [1] Values of the Different Thermodynamic Parameters at Different Temperatures.

Temp.; K	$-\Delta H^{\circ}$ , (KJ mol <sup>-1</sup> )	$-\Delta G^{\circ}$ , (KJ mol <sup>-1</sup> )	$-\Delta S^{\circ}$ , (KJ mol <sup>-1</sup> )
298	4.00	2.46	0.0052
308	4.00	2.32	0.0054
318	4.00	2.23	0.0056

**Desorption of Iron:** Desorption studies were performed for various concentrations of iron and at three different temperatures. After decanting the remaining solution from the sorption process, the loaded bentonite was resuspended in 10ml of deionised water or  $1 \times 10^{-2} M$   $CaCl_2$  solution. Shaking for different periods of time and at fixed temperature was then done. The obtained results are tabulated in Tables [2 and 3]. The results in Table [2] show that the percentage sorption of iron on bentonite increases with the decrease in the bulk concentration of the metal whereas desorption with deionised water decreases with decreasing iron loading. The desorption decreases from 85 to 5.80 wt.% on decreasing in the loaded iron concentration from 0.830 to 0.460 m mole/g adsorbent. The results in Table [3] show that only 3.80 wt.% and 12.60 wt.% of iron is desorbed with deionised water and with 0.01M  $CaCl_2$  solutions, respectively. The extent of desorption does't change with time up to 48h. Being the values of desorption with deionised water at 308k are, to some extent, higher than the values at 298k. These results indicate (Saad et al. [16]) that at least two types of adsorption are involved depending upon the bulk concentration of iron and loading on bentonite. The first one is with high and the other is with low distribution coefficients. At higher loading, the percentage desorption is more, and as the loading of the metal decreases, the extent of desorption decreases. At low concentrations, iron is more held by the sorbent. The above mentioned results indicate that 'at low iron' loading, more than 90 wt.% irreversible sorption, that is may be due to the isomorphous replacement of iron in the crystal lattice of the sorbent (Saad et al. [16]).

Table [2] Effect of [Fe] on the Sorption / Desorption Processes.

[Fe] in solution, m mol/L	Wt.% sorption	Loading of Fe on clay m mol/g	Wt.% Desorption with deionised water
600	5.50 (1)	0.830	85.00 (55)
500	6.70 (2)	0.720	60.00 (52)
100	30.2 (3)	0.650	40.30 (46)
50	50.1 (5)	0.540	15.60 (30)
20	62.2 (6)	0.460	5.80 (20)

Table [3] Effect of Both Shaking Time and Temperature on the Desorption of  $Fe^{3+}$  Using Both Deionised Water and 0.12M  $CaCl_2$  Solution.

Time/Temp.	298°K		308°K	
	I <sup>(1)</sup>	II <sup>(2)</sup>	I <sup>(1)</sup>	II <sup>(2)</sup>
5 min	4.50 (1)	10.20 (5)	5.60 (4)	11.20 (5)
15 min	4.62 (1)	10.30 (5)	5.70 (4)	11.30 (5)
60 min	4.50 (1)	10.50 (5)	5.72 (4)	11.36 (5)
90 min	4.58 (1)	10.62 (5)	5.80 (4)	11.50 (5)
120 min	4.46 (1)	10.71 (5)	5.85 (4)	11.62 (5)
24 h	4.40 (1)	10.83 (5)	5.90 (4)	11.71 (5)
48 h	4.20 (1)	10.90 (5)	5.95 (4)	11.83 (5)

I<sup>(1)</sup> : Desorption with deionised water.II<sup>(2)</sup> : „ „ 0.012M  $CaCl_2$ .

## 4- CONCLUSION

Based on the above mentioned database, it could be concluded the following:

South valley bentonite is successively used for the sorption of iron incorporated with ground water extracted from the Nubian aquifer south-east of Aswan city.

- Sorption of iron on bentonite takes place instantaneously without appreciable effect of increasing of either time or temperature.
- The maximum uptake of iron by bentonite takes place at the pH range of 6 – 9 (at 35°C  $\pm$  0.5°C).
- Uptaking of iron by bentonite is directly proportional with the increasing of the amount of bentonite due to the increasing of the available exchangeable sites.
- At low iron loading, more than 90 wt.% irreversibly sorped due to the isomorphous replacement of iron in the crystal lattice of bentonite.
- Thermodynamic parameters indicate that iron sorption on bentonite is an exothermic and spontaneous process.
- Recycling of the exhausted (waste) bentonite via either known or developed methods is currently under consideration.

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