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EFFECT OF pH AND CONCENTRATION ON THE REMOVAL OF MAGNESIUM FROM MAGNESIUM CHLORIDE SOLUTION BY BENTONITE

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By virtue of their well-known cation exchange capacities of clays, particularly bentonites are important minerals to be used as adsorbent of various undesirable ions drained out as industrial waste. One of such pollutant is magnesium containing waste. The removal of magnesium from magnesium containing solutions is found to be dependent both on pH of the solution and the concentration of magnesium ions present in the solution. Using magnesium chloride solution of 50 mg/lit and 100 mg/lit concentration and bentonite (North West Frontier Province), it was found that adsorption equilibrium established within 6 h .

***Key word*: Bentonite, Adsorption, Freundlick equation**

Introduction

Industries such as medicine, toiletry, printing ink, refractories, rubber insulating material and some other chemical industries extensively use magnesium compounds in their manufacturing processes. In sewerages of these industries the concentration of the magnesium ions is generally above the permissible limit (50 ppm), which causes deleterious effects to human health. Clays have been used for the adsorption of organic molecules (Jhonston and Cardile 1987) inorganic metallic ions (Diez 1980) and dyestuff, in waste water. In the present study a Pakistani bentonite is used for the removal of magnesium ions from magnesium chloride solution.

Bentonites are essentially hydrous aluminium silicates, with magnesium or iron, alkalies or alkaline earth metals (Grim 1962). They are composed of small crystalline particles of one or more clay minerals. The structure of bentonite is composed of a single silica tetrahedron sheet and a single alumina octahedral sheet combined in a unit in such a way that the corners of silica tetrahedron and the layer of octahedral sheet form a common layer. All the corners of silica tetrahedrons point in the same direction and towards the centre of unit (Mitra *et al* 1979). Cleavage between sheets leads to plate-like particles and leave these layers unsaturated.

The ion exchange ability of bentonite is probably due to, *i)* Broken bonds due to sub-division of the giant crystal. *ii*) Disordered structure containing ions of incorrect valence. Where, there are unsaturated bonds or electrical charges, their counter ions can be adsorbed. This effect would be dependent on particle size (Worral *et al* 1958). The second cause of charged clay particles is the structural disorder due to isomorphism substitution of Al^{3+} for Si^{4+} and Mg^{2+} for Al^{3+}, giving rise to inherent negative charges. This is independent of particle size (Whittaker 1939). In addition, some anions may be adsorbed by the replacement of exposed hydroxyl ions and because of the structural arrangement of some of the anions with tetrahedral units (Foster 1951). This absorption behaviour of bentonite was observed to be influenced by various factors such as contact time, solution concentration (Miyazaki 1996), temperature (Shakila *et al* 1998) and pH (Compton *et al* 1994).

The present work has been undertaken with a view to investigate the adsorption characteristics of bentonite for the adsorption of magnesium from magnesium chloride solution and the effect of concentration of magnesium, pH of the salt solution on the extent of adsorption of magnesium.

Experimental

In present studies, bentonite from Peshawar area was used. Snow's method is used to determine the surface area (Iqbal 2001). The chemical analysis of the bentonite and other characteristics are given in Table 1. The method is described as below.

Determination of surface area of bentionite. Potassium iodide (KI) 71.3 g and 7.5 g of iodine (I_2) crystals were dissolved in a small quantity of distilled water and the volume made up to 125 ml. About 1 g of washed bentonite was taken in an iodine flask and 5 ml of iodine solution was added. It was allowed to stand for 2 h. Then 45 ml of distilled water was added and flask was gently spiralled for 1 min. It was kept for 1 h, 20 ml of the supernant solution was taken in titration flask and two drops of starch solution was added. A

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Table 1
Chemical and physical properties of bentonite

Representative chemical composition	
SiO_2	57.80%
Al_2O_3	20.80%
Fe_2O_3	3.00%
CaO	4.20%
MgO	3.00%
Na_2O	10.00%
K_2O	0.05%
Loss on ignition	10.00%
pH value (10% slurry)	7.00%
Brightness	57.00%
Specific surface area	200 m^2/g
Mean particle size (80%)	20microns

titration was made against standard sodium thiosulphate ($Na_2S_2O_3$) solution by noting the end point on the disappearance of colour. The surface area in m^2/g was calculated using the formula [12.5x (24-V)], where V is the volume of sodium thiosulphate used in titration.

ii. Determination of equilibrium time of adsorption of magnesium on bentonite clay. Finely ground bentonite 0.5 g was taken in different flasks, 50 ml of magnesium solution (50 mg / lit, and 100 mg / lit) was added and closed tightly by stopper. Then these flasks were placed on a water bath with magnetic stirrer, for various duration of time, i.e. 0.5, 1, 2, 3, 4, and 6 h. The solution was stirred at a constant temperature 25°C. The slurry was then filtered; 2 ml of filtrate was titrated against standard EDTA solution (0.01M) in the presence of 1 ml buffer solution (pH=10) and a few drops of Eriochrome black T (EBT) indicator. The end point was noted when colour changed from wine-red to blue. The quantity of magnesium ions adsorbed was calculated by the difference in concentration of blank solution and sample solution for different time periods and equilibrium time was determined by plotting the time (hours) versus extent of adsorption of magnesium μg/g.

iii. Determination of adsorption isotherm of magnesium on bentonite. Magnesium chloride solution of different concentration, i.e., 20, 40, 60, 80 and 100 mg/ lit were prepared. Then 50 ml solution of each concentration was transferred to conical flasks containing 0.5 g bentonite. The flasks were tightly closed by means of cork and stirred for 6 h at a constant temperature. The slurry was then filtered and 20 ml from the clear filtrate were titirated against standard EDTA (0.01 M) solution in the presence of 2 ml buffer solution (pH=10) and a few drops of EBT indicator. The end point was noted when the colour changed from wine-red to blue. The quantity of magnesium adsorbed was calculated by taking the difference between the blank concentration and sample concentration using the following formula.

$$\text{Apparent adsorption } (\mu g/g) = \frac{(V_1+V_2)\times M\times \text{At.Wt. of Mg}\times 100}{\text{Wt. of clay (g)}}$$

Where,

Wt. = Weight of clay (g)
M = Molarity of EDTA solution
V_1 = Volume of EDTA solution used for 50 ml blank magnesium salt solution.
V_2 = Volume of EDTA solution for 50 ml magnesium salt solution containing clay sample.

Determination of the effect of pH on adsorption isotherm on clay. The pH of magnesium solution (20, 40, 60, 80 and 100 mg/lit) was adjusted (7-8) by the addition of 0.1 N NaOH in the pH range of 7-8. The determination of adsorption isotherm at pH range 7-8 was also performed for each concentration, pH of magnesium chloride solution was also adjusted in the range of 3-4 by gradual addition of 0.1 N HCl. The same procedure was adopted for the determination of adsorption isotherm at intermediate pH. Blank determination was also performed for each concentration to study the effect of pH on the adsorption of magnesium on bentonite.

Results and Discussion

The surface area of bentonite determines by using Snow's iodine adsorption method comes out to be 200 m^2/g at pH7 under ambient conditions. The surface area is much higher (about twice) than ordinary China clays (90 m^2/g), which is an indication of its effectiveness for adsorption of metal ions.

Effect of time on adsorption of magnesium from two different concetrations (50 mg/lit, 100 mg/lit) of magnesium chlorides of bentonite is shown in Fig 1. It is evident that equilibrium is established within 6 h in both cases. Apparently, concentration of the solution seemed to have no effect on the equilibrium time. However, the amount of magnesium ions adsorbed from the concentrated solution is higher as compared to dilute solution.

Fig 2 depicts the effect of pH of adsorbent solution on the quantity of magnesium ion adsorption. In strong acidic solution (pH 2-3) almost a straight line is obtained. However, the amount adsorbed is small. It appeared at low pH, the magne-

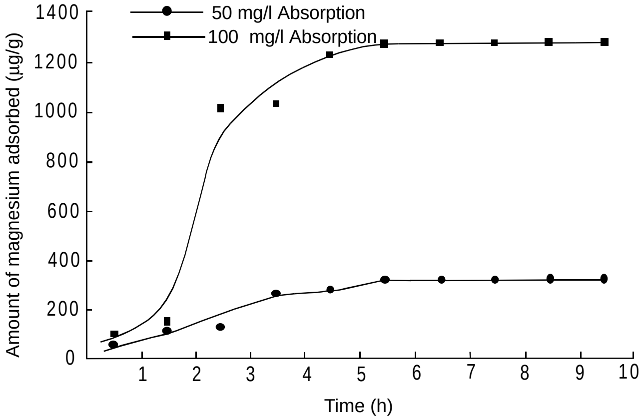

Fig 1. Adsorption of magnesium from magnesium chloride solution at different interval clay dosage = 0.5 g.

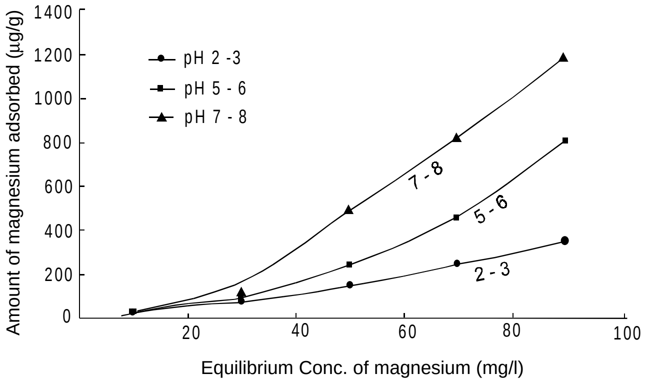

Fig 2. Adsorption of magnesium from magnesium chloride solution at different pH ranges clay dosage = 0.5 g.

sium ions have less opportunity to come in contact with the negatively charged surface, which preferred H^+ ions that are easily available from the medium and consequently reduce the number of active sites. Similar behaviour has been reported (Iqbal *et al* 2001) while studying the adsorption of Mg^{2+} on China clay. However, the quantity of the adsorption on bentonite is 3-4 times higher than China clay, which can be explained by taking into account the much larger surface area of the bentonite used in the present study. It is observed that as the pH of the solution changes to higher values, there is a marked increase in the adsorption of magnesium ions. The highest adsorption of magnesium ions was obtained at 7-8 pH. One of the contributory factors for the higher adsorption at 7-8 pH can be solubility of $MgCl_{2,}$ which is less soluble at this pH range.

Generally adsorption phenomenon of solute from a solution is explained by using Freundlick equation (Barrow 1966), which in logarithmic from as:

$$\mathrm{Ln}(x/m) = \ln k + 1/n \ln c$$

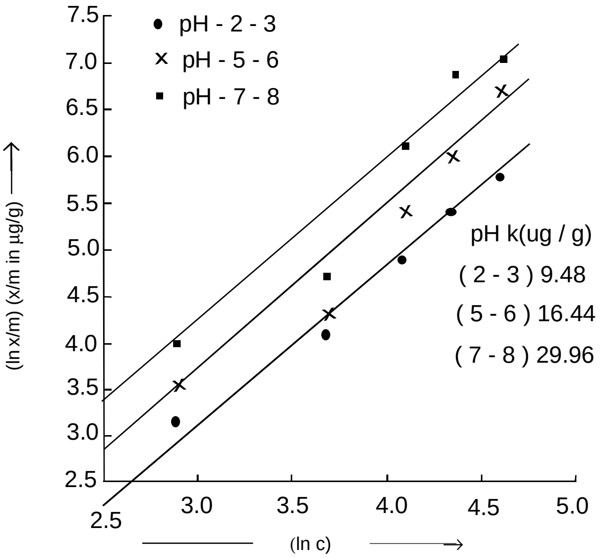

Fig 3. Freundlich isotherm of magnesium from magnesium chloride solution at different pH ranges clay dosage 0.5 gm

Where "x" is the amount of solute adsorbed and "n" is the amount of adsorbent. "c" is the equilibrium concentration and "k" is the adsorption capacity.

Adsorption data obtained in the present work are plotted in Fig 3. Three adsorption isotherms with almost same values of slope were obtained, which indicates that mode of adsorption is similar throughout the pH range investigated. It is evident from the plot that the value of adsorption capacity constant (k) increases with the increase in pH value of the solution. Adsorption capacity constant has minimum value of 9.48 at pH range (2-3), which increases to 16.44 for pH range (5-6) while the maximum value 29.96 was obtained for the pH range (7- 8). These values are in accordance with earlier observation that there is an enhanced adsorption of magnesium ion at higher pH value.

Conclusion

Pakistan has huge deposits of bentonite, which can be used for the removal of magnesium ions to minimize the pollution level. Present investigation indicates that bentonites have the advantage of higher surface area and better adsorption capacities than China clay. Removal of magnesium ion was found to be pH dependent. pH range seemed to be the best for efficient removal of magnesium ions.

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