Thermodynamic Effect on Boron Removal from Aqueous Solutions by MgAl Layered Double Hydrotalcite

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Thermodynamic Effect on Boron Removal from Aqueous Solutions by MgAl-Layered Double Hydrotalcite

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Abstract: *Boron is an element of requirement for the growth of plants, animals and humans. Though environmental issues and health hazards are related to its applications in various industries; such as plants' growth retardation and the effect on humans' nerve system. In this research adsorption capabilities of Mg-Al Layered Double Hydrotalcite (LDH) on boron were tested to remove it from aqueous solutions. Experiments were conducted with variety of temperatures, and initial boron concentration; thus finding the most optimum factors and conditions. Results showed that with high temperatures faster removing rate of the contaminant from aqueous solutions was achieved. Moreover, thermodynamic analysis depicted that the adsorption process of boron on Mg-Al LDH is endothermic and involves both physisorption and chemisorption.*

Keywords: Boron; Mg-Al; Layered-Double-Hydrotalcite; Adsorption.

1. INTRODUCTION

Being used in many industries, boron is in demand for the production of various fertilizers, insecticides, corrosion inhibitors in anti-freeze formulations for motor vehicles and other cooling systems, buffers in pharmaceutical and dyestuff production, bleaching solutions in paper industries and in detergents. As well as glass, ceramics, electronics and detergents [1, 2]. Although boron is an element needed for plants but only in controlled amounts, otherwise it could result in growth retardation [3]; which was observed in arid and semi-arid areas in South Australia, Turkey [4]. Humans' nerve system is also affected by consumption of large amounts of boron. Regulations have recently been set by the World Health Organization (W.H.O.) to determine the maximum concentration limits for boron in drinking water to be less than 2.4 mg/L [5]. Many methods were tested for the removal of boron [6] and one of the common practices is adsorption process using hydrotalcite or hydrotalcite-like materials; in this paper Mg-Al LDH adsorption properties are investigated with boron. A range of different temperatures is applied to investigate the thermal effect on the removal process. Furthermore, thermodynamics analysis is conducted to study the nature of the adsorption process of the Mg-AL LDH.

2. MATERIALS AND METHODS:

2.1 Preparation of Mg-Al bimetallic:

The hydrotalcite-like material was synthesized for Mg-Al bimetallic Oxide. The materials used for the synthesis are $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH [7, 8]. Synthesis was carried out in the duration of three days [9]; 700 mL aqueous solution containing 0.1 mmol (25.6406 g) of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.05 mmol (18.7565 g) of $Al(NO_3)_3 \cdot 9H_2O$. Then, it was added drop wise to 1500 mL of 2 M NaOH solution stirred vigorously with a mechanical mixer at 400 rpm. The temperature was kept at 45± 3 °C during the process. Slurry obtained was then heated for 2 hours (T=85± 3 °C) under slow mixing 200 rpm. The solution was kept in room temperature for 12 h. Next day; The solid product was separated by centrifugation and washed with deionized water several times until pH reached 10-11 and conductivity was constant. The solids were drying at 60℃ for 48. Part of the product was calcined at 550℃ for 4 h. The solids were dry enough to be crushed into powder-like form and measured. Then it was kept in a concealed container.

2.2 Batch preparation:

Boron stock solution was prepared using H_3BO_3, 500mg/L. For every experiment 100 mL of solutions were used with boron concentration of 5, 10, 20 mg/L, Initial pH at 9 and Mg-Al LDH dosage of 2 g/L was found to be the optimum pH condition for boron removal according to our previous study [9]. The separation of samples is conducted with syringe filters 2 µm. UV-vis spectrophotometer was used for boron concentration measurement in samples; BoroVer 3 Boron Reagent Powder Pillow, Sulfuric Acid, concentrated, ACS and Deionized water were used.

2.3 Removal effect:

In this test a dosage of 2g/L of Mg-Al LDH were used on boron contaminated stocks with initial concentrations of (5, 10, 20) mg/L; to study the removal efficiency of Mg-Al LDH on boron. Removal efficiency was calculated using the following formula [10-12]:

$$Removal\ efficiency\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

Where; C_o and C_e are initial and equilibrium boron concentrations respectively.

2.4 Temperature effect:

Temperature experiment was conducted to study the effects of different temperatures (T= 25, 40, 55, 70 °C) in the removal of boron with initial concentration of 20 mg/L. Mg-Al LDH were added to the flasks with boron solution. Stirring with 25 °C for 24 hours. Samples were taken in (10min, 3hrs, 6hrs, 12hrs, 18hrs, 24hrs).

3. RESULTS AND DISCUSSION:

3.1 Removal efficiency:

Although the dosage remained similar in all the batches (2g/L) successful removal of boron was achieved with all. The higher the initial concentration was the longer it took for Mg-Al LDH to adsorb the contaminant Fig. 1. Where the 5 and 10 mg/L of initial B concentration reached maximum at less than 10 hours the 20mg/L sample took over 24 to reach maximum.

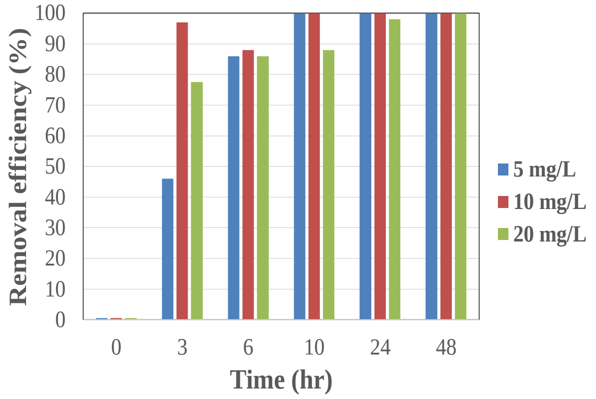

Fig. 1 removal efficiency with different initial boron conc. samples over time.

3.2 Temperature effect:

This test showed the removal rate of the Mg-Al LDH is effected with temperature. The higher the temperature got the faster the removal of the contaminant; as shown in the Fig. 2 at temperature 70 ℃ removal rate reached equilibrium at about 6 hours whereas the other temperatures have not reached the maximum rate even at 24 hours.

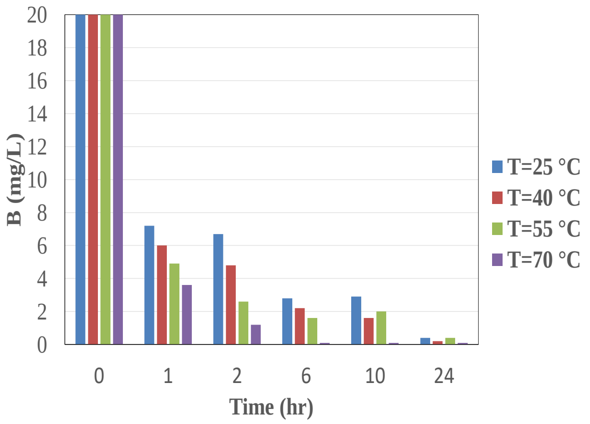

Fig. 2 effect of different temperatures on boron adsorption process.

3.3 Thermodynamic analysis:

Thermodynamic analysis was conducted on the adsorption data using the following equations:

$$\Delta G° = -RT \ln K \qquad (2)$$

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \qquad (3)$$

Whereas R is the Universal Gas constant (8.314 J/mol K), K is Adsorption equilibrium constant, $\Delta G°$ is change in Gibbs free energy (KJ/mol), T is temperature (Kalvin), $\Delta S°$ is change in entropy (J/mol K) and $\Delta H°$ is change in enthalpy (KJ/mol).

The values of these thermodynamics parameters were evaluated by plotting lnK vs 1/T, and knowing the slope and the interception values.

Temp.°C	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol K)
25	-26.77019421	104.0469778	432.0369254
40	-29.94807013		
55	-33.28740924		
70	-47.96147746		

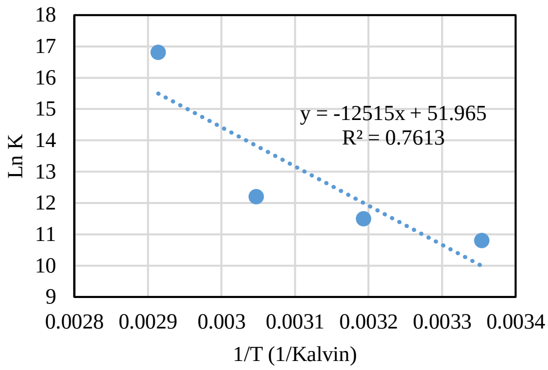

Fig. 3 Linear plot of thermodynamic analysis.

The negative value of $\Delta G°$ indicates the endothermic nature of the removal of boron by MgAl-LDH indicating the enhancement in boron removal by raising the operating temperature. Moreover, the positive value of entropy change indicates that the randomness of the solid/liquid interaction increases within the adsorption process of Boron. The magnitude of enthalpy change (104.04 KJ/mol) and The magnitudes of the change of the free energy indicate that boron removal by MgAl-LDH involves both physisorption and chemisorption processes.

4. CONCLUSION:

Mg-Al LDH showed promising results in removing boron contamination from aqueous solutions. Temperature has high effectivity on the removal rate; at 70 ℃ equilibrium was achieved at about six hours of mixing with a nearly full removal of the 20 mg/L boron concentration, whereas it took longer time to reach equilibrium with the other temperatures. Even with high initial boron concentration (20 mg/L), Mg-Al LDH had removed almost 99.9 % of the contaminant. Thermodynamic analysis showed that the adsorption mechanism of boron by Mg-Al LDH was endothermic in nature and involves both of physisorption and chemisorption.

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