

Sorption Mechanism and Capacity Evaluation of Palygorskite from Iraq to Remove Pb from Aqueous Solution

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Abstract

The use of the palygorskite of Iraq as an adsorbent for the removal of Pb from aqueous solution was investigated by the mean of batch technique. Iraqi palygorskite was collected from Digma and Akashat Formations (Masstrachian and Danianage) from the western Iraqi Desert. Palygorskite exists within the clay-rich sediments; therefore it was concentrated by separation from clay fraction. A series of adsorption tests were conducted to analyze the sorption mechanism and capacity of palygorskite. Standard solutions of Pb were prepared with known concentrations (10, 25, 50, 75, 100, 125, 150, 175, 200, 225, and 250 ppm). Each solution was mixed with 1gm of palygorskite, and treated with total volume up to 100 ml for 1hr with stirring at temperature of 25°C. The treated palygorskite was then separated by filter paper. Each filtrate solution was subjected to physical and chemical measurements. Solid to liquid ratio, Adsorption equilibrium reaction time, pH and Pb ion concentration are determined. The results of this study revealed that there is negative relationship between pH and each of electrical conductivity (EC), total dissolved solids (TDS) and salinity. The pH of the treated solution decreased from 7.2 to 2.37. Electrical conductivity, TDS and salinity in the initial solutions increased and ranged between 960-14000 $\mu\text{s/cm}$, 482-11900 ppm and 0.2-8.2‰ respectively. The sorption capacity was recorded as 99.5% of 10 ppm solution, whereas it was 22.22% of 250 ppm solution.

Keywords: Palygorskite; Adsorption; Sorption; Capacity; Equilibrium time.

Introduction

Palygorskite characterizes by many characters; some of them, it cannot swell because the structure consists of three dimensional chains and it has an unusual needle-like shape is formed by cleavage parallel to the 110 plane along the Si-O-Si bonds holding the strips together [1]. Palygorskite is a crystalline hydrated magnesium aluminium silicate with a unique chain structure that gives it unusual colloidal and sorptive properties. It consists of a double chain of tetrahedrons of silicon and oxygen (Si₄O₁₁) running parallel to the long axis. Palygorskite is clay can adsorb metal cations from solution [2]. The palygorskite was found to be rather receptive to the adsorption of heavy metal ions, and fairly high amounts of calcium, potassium and magnesium ions were sorbed from the Palygorskite into the solution [1]. Palygorskite is very sorptive clay due to the extremely large surface area which is 167m²/g approximately. Both external and internal structures contribute to this surface area. The internal bundles, or haystacks, aid the external surface area in achieving great amounts of adsorption. Palygorskite can take up water to 200% of its own weight [1]. The presence of heavy metals in aquatic environments because of their toxic nature and other adverse effects on receiving ecosystems has been of great concern for scientific community [3,4]. The treatment of rich heavy metal aqueous solutions is realizable by mean of many methods including: ion exchange, chemical precipitation, ultra filtration, electrochemical deposition, among which, adsorption on appropriate adsorbent (low cost and abundance of the latter) is one of the most efficient in terms of simplicity and feasibility of operation and low consumption of energy [5].

The purpose of this research is to provide the adsorption capacity of a palygorskite collected from palygorskite-rich sediments from Iraq to remove Pb from aqueous in a single batch system under and to determine the solid to liquid ratio, adsorption equilibrium time, pH and metal concentration.

Materials and Methods

Adsorption experiments were conducted using palygorskite clay mineral which was collected from Digma Formation from the Western Desert of Iraq to assess the ability of palygorskite on adsorbing Pb

from solution. The collected samples were palygorskite-rich sediments, therefore, and for preparing a pure palygorskite, one sample of the palygorskite-rich sediment was chosen for separating palygorskite. It was prepared in the Laboratory of Geochemistry, Department of Geology, College of Science, and University of Baghdad. A sample of pure palygorskite must be prepared. To meet this issue, two major processes were performed. First is that, clay minerals are separated from the whole samples of palygorskite-rich sediments. Second, palygorskite is separated from clay mineral suits to obtain a sample of as pure palygorskite as possible as. The detailed procedures of Paul et al. [6] and Robert and Dennis [7] were done on whole sample (crude sample). A preparation processes done on pure palygorskite include drying and gentle grinding. Palygorskite was dried in an electric oven at 80°C for several hours before use. The stock solution was prepared by using Pb(NO₃)₂. Ten Pb initial solutions of concentration (10, 25, 50, 75, 100, 125, 150, 175, 200 and 225 ppm) were prepared. All experiments were conducted at room temperature to determine the solid to liquid ratio, conditioning time, effect of solution pH, and the effect of Cd concentration on sorption efficiency.

Results and Discussion

A patch style of set of laboratory experiment was conducted to determine the appropriate conditions. The effect of solid to liquid ratio, Adsorption equilibrium reaction time, pH and Pb ion concentration are studied as follows:

Sorbant mass (solid to liquid ratio)

The sorption (% (of Pb on palygorskite was studied at different

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Received July 11, 2013; Accepted August 07, 2013; Published August 12, 2013

Citation: Awadh SM, Towfik SM (2013) Sorption Mechanism and Capacity Evaluation of Palygorskite from Iraq to Remove Pb from Aqueous Solution. J Geol Geosci 2: 126. doi: 10.4172/2329-6755.1000126

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palygorskite masses (0.25, 0.5, 1.0, 1.5, 2.0, 2.5, and 3 g/100 ml) keeping initial Pb concentration (100 and 200 ppm), temperature (25°C) and contact time (1 h) constant. The results of the lab experiments are listed in Table 1. Such approximate conditions have been used by Hefne et al. [8]. The results showed that the adsorption (%) of Pb was increased with increase the palygorskite mass, and the maximum removal of Pb was observed with 1 gm dose (Figure 1). With increasing palygorskite mass, the corresponding increase in adsorption (%) is less, because the cations find difficult to approach the adsorption sites due to overcrowding of clay mineral particles (Palygorskite) termed as a kind of solid concentration effect [9]. Accordingly, the solid to liquid ratio was determined to be 1gm palygorskite to 100 ml metal solution.

Equilibrium reaction time

A set of the laboratory experiments was performed in order to quantify the time required for completing the adsorption and absorption of Pb onto palygorskite. In order to perform accurate sorption (%) experiments, the effect of time on sorption (%) of metals onto palygorskite must be determined. The results of time versus 100 ppm Pb sorption (%) are listed in Table 2. The sorption increases proportionally with increasing time. The maximum sorption (89.9%) achieved after a time of 1h (Figure 2). Whilst, the sorption efficiency

decreased when the time reaction continued to 70 and 80 min (Table 2) and (Figure 2). On this basis, the equilibrium reaction time is determined to be 1h.

Sorption experiments

The experimental results of Pb treated with 1 gm of palygorskite for ten concentrations are listed in Table 3. The Pb concentrations in the initial solutions were reduced after the end of the experiment. The adsorption (%) at the initial concentration (10 ppm) was 99.5% (Table 3). It began to decrease with increasing the Pb concentration. Pb adsorption (%) for the initial solutions (25, 50, 75, 100, 125, 150, 175, 200, 225 ppm) was 99.8, 96.72, 91.1, 81.9, 76.48, 67.2, 31.43, 23.5, 22.2 (%) respectively (Table 3). Figure 3a clearly shows the status of decrease adsorption efficiency with increase concentration.

A considerable amount of Pb adsorbed onto palygorskite with increasing concentration of the initial solution has been detected. In case of the initial solution (10 ppm), the amount of Pb tends to be almost totally adsorbed (9.95 ppm); but in case of the initial solution of 150 ppm, the amount of pb adsorbed on palygorskite is 100.8 ppm (Figure 3b); this is the maximal sorption (%) of Pb on palygorskite. Amount of adsorption decreased sharply for solutions of high concentrations (175, 200 and 225 ppm) (Figure 3b). Basically, as of our knowledge, the Total Dissolved Solid (TDS) is directly proportional with increasing concentration; this means a positive relationship between TDS and concentration (Figure 3c). The decrease of TDS value was an evidence for the happening adsorption process (Figure 3c). TDS of initial solutions ranges between 850 ppm and 19120 ppm (Table 3) due to the Pb concentration in each solution. After the end of the experiment, the decrease of TDS from 482 ppm to 11900 ppm indicates for adsorption. For this set of experiments, pH (2.9-1.36) of the initial solutions increased with increasing of adsorption until it reached between 7.0 and 2.37 (Table 3 and Figure 3d). A significant amount of Pb adsorption in the pH 2.97 was found.

Mass (gm)	Sorption (%)	
	100 ppm	200 ppm
0.25	20.0	12.0
0.5	35.0	20.0
1.0	83.0	82.9
1.5	83.0	83.0
2.0	82.6	83.1
2.5	82.9	82.6
3.0	83.0	82.8

Table 1: Results of Pb sorption (%) on different masses of palygorskite.

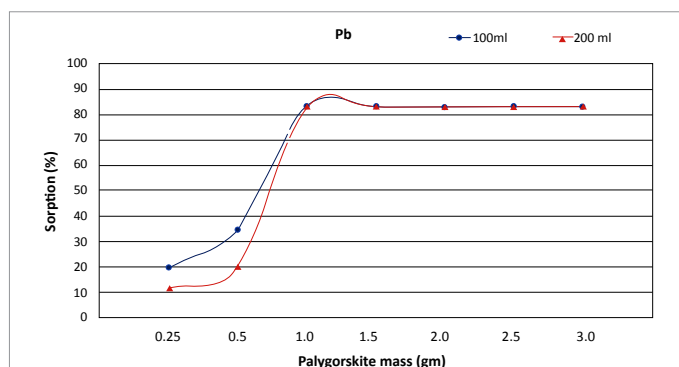


Figure 1: Effect of palygorskite mass on adsorption % of Pb at different concentration (100 and 200 ppm) and at 25°C.

Time (Min.)	Sorption (%)
10	25
20	47
30	60
40	70
50	79
60	89.9
70	89.7
80	89.8

Table 2: Results of sorption (%) of 100 ppm Pb (100 ml) onto 1 gm palygorskite with time.

Conclusions

The following conclusions are drawn from the present study:

- A strong competition between cations (Heavy metals) on the negative sites on palygorskite occurs at a high concentrated solution causing decrease in sorption efficiency.
- The decrease of TDS and EC values in the final solution is a function of the sorption efficiency of palygorskite. TDS and EC decrease with the trend of alkaline pH due to adsorb the positive charged metal ion (Pb) from the solution onto the negative palygorskite surface.

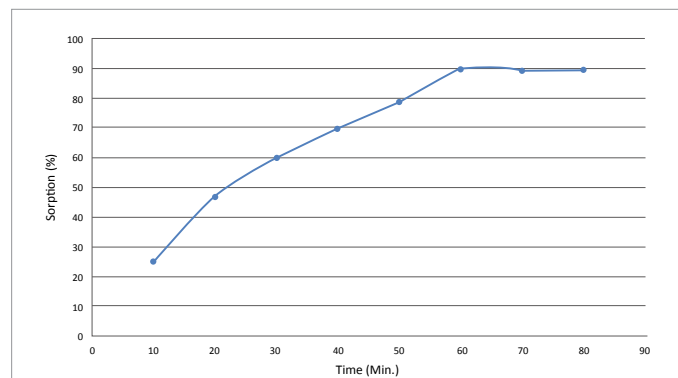


Figure 2: Equilibrium time of sorption (%) of 100 ppm Pb onto palygorskite.

Sample number	Before experiment						After experiment							
	Initial conc. (ppm)	Total Vol (ml)	PH	TDS (mg/l)	EC ($\mu\text{s}/\text{cm}$)	T $^{\circ}\text{C}$	PH	TDS (mg/l)	EC ($\mu\text{s}/\text{cm}$)	T $^{\circ}\text{C}$	Final conc. (ppm)	Sorption (ppm)	Sorption (%)	Salinity (‰)
1Pb	10	100	2.9	850	1691	24.5	7.0	482	960	24.6	0.05	9.95	99.5	0.2
2Pb	25	100	2.33	2125	3610	24.4	5.01	880	1760	24.2	0.06	24.94	99.8	0.7
3Pb	50	100	2.02	4250	7020	24.4	4.4	2060	3130	23.9	1.64	48.36	96.72	1.5
4Pb	75	100	1.86	6370	10820	24.4	4.1	3160	4510	24	6.67	68.33	91.1	2.3
5Pb	100	100	1.73	8510	15300	24.3	3.45	4012	5900	24.0	18.1	81.9	81.9	3.2
6Pb	125	100	1.62	10600	18020	24.3	3.22	5400	7500	24.0	29.4	95.6	76.48	4.1
7Pb	150	100	1.54	12700	22225	24.3	2.97	6710	8600	23.9	49.2	100.8	67.2	4.8
8Pb	175	100	1.46	14870	25279	24.2	2.48	8720	10900	24.0	120	55	31.43	6.2
9Pb	200	100	1.41	17000	30600	24.2	2.32	9920	12400	24.1	153	47	23.5	7.1
10Pb	225	100	1.36	19120	33840	24.1	2.37	11900	14000	23.9	175	50	22.2	8.2

Table 3: Results of laboratory experiments of lead (Pb) sorption on palygorskite in ten solutions of various concentrations.

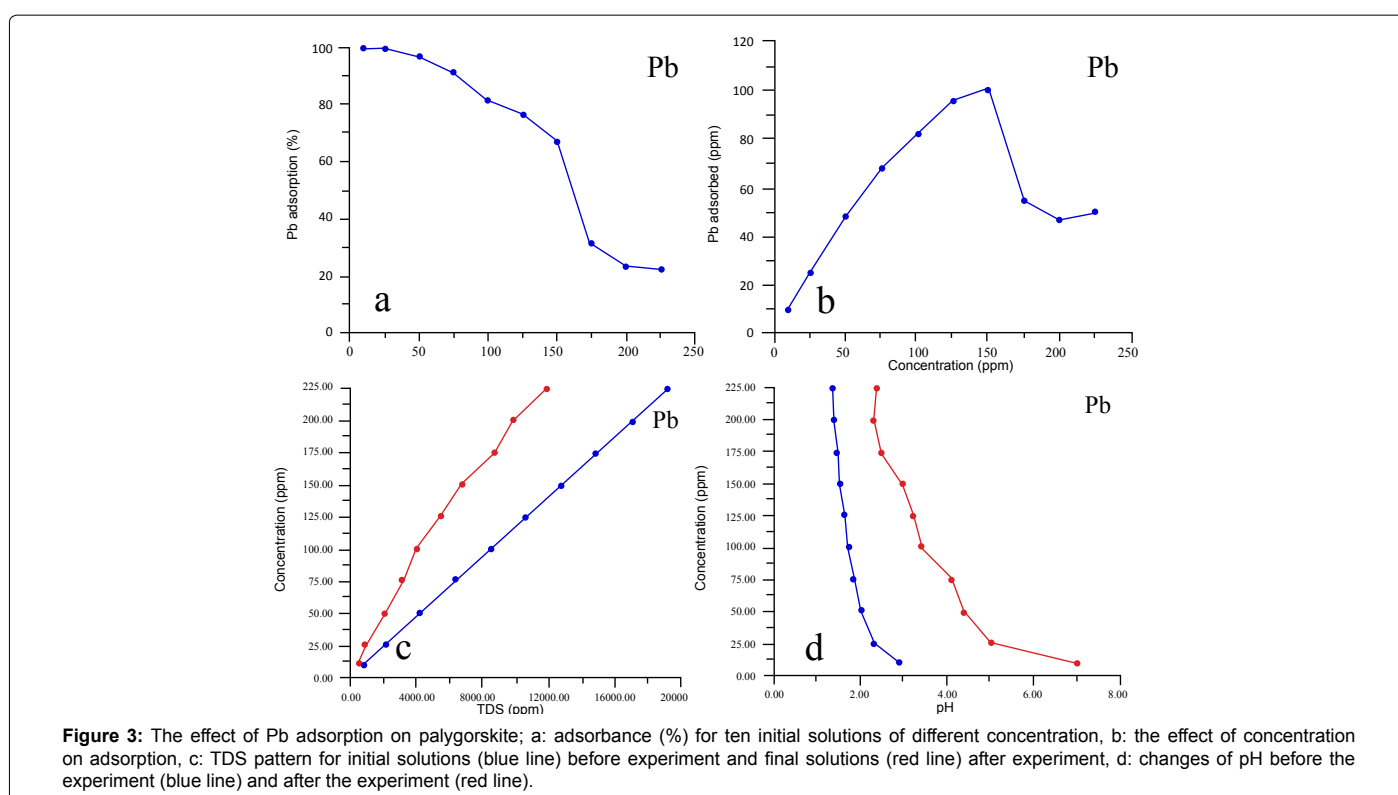


Figure 3: The effect of Pb adsorption on palygorskite; a: adsorbance (%) for ten initial solutions of different concentration, b: the effect of concentration on adsorption, c: TDS pattern for initial solutions (blue line) before experiment and final solutions (red line) after experiment, d: changes of pH before the experiment (blue line) and after the experiment (red line).

- The mass of adsorbents and reaction equilibrium time are controlling factors for sorping metals onto the palygorskite. The mass of adsorbent (palygorskite) affects on the sorption (%). The sorption (%) of Pb increased and the maximum removal was observed with 1 gm dose. With the increasing of palygorskite mass, the adsorption efficiency least, because difficulty of the Pb to approach the adsorption sites due to overcrowding of clay mineral particles (palygorskite) termed as a kind of solid concentration effect. Accordingly, the solid-liquid ratio was determined to be 1 gm to 100 ml. The sorption (%) increases proportionally with the equilibrium reaction time where the maximum sorption (%) is determined at 60 minutes.

- The basic mechanism governs the heavy metals adsorption characteristics of palygorskite at different pH is adsorption and ionic exchange. The hydrogen number (pH) changes in the initial solutions toward alkaline referring to the occupation some negative sites in palygorskite structure by protons (H⁺). Hydrogen also competes with heavy metals (Pb) on the negative sites in palygorskite.

- The tendency of solution toward the alkaline occurs with the solutions of low concentration rather than the solutions of high concentration because no further cations competes with the H⁺ on the negative site of palygorskite [10].

Recommendations

This study has found that the palygorskite is good absorbent material promising for liquid purification of pollutants, in particular heavy metals. Study of the reaction using palygorskite for the removal of heavy metals in waste-water is a fruitful scope of the present investigation. These investigations could be extended to try the removal of organic compounds from liquids. In addition, the adding of catalytic organic matter will be beneficial.

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