2013 2nd International Conference on Geological and Environmental Sciences
IPCBEE vol.52 (2013) © (2013) IACSIT Press, Singapore
DOI: 10.7763/IPCBEE. 2013. V52. 12

Experimental Research on the Adsorption Equilibrium Time of Tipical Sedimentary Rock Adsorbing Heavy-metal–Take Molybdenum for Example

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Abstract. The paper systematically studies the adsorption equilibrium time on three kinds of typical sedimentary rocks under different adsorption equilibrium temperatures, rock particle diameters and initial solution concentrations taking ammonium molybdate for example. The test shows that the adsorption equilibrium time on three kinds of typical sedimentary rocks under general temperature is short and usually less than two hours. If any other three factors among the four factors such as rock type, temperature, rock particle diameter and initial solution concentration are same, the bigger the rock particle diameter is, the shorter the adsorption equilibrium time is; the higher the temperature is, the shorter the adsorption equilibrium time is and the lower the initial solution concentration is, the shorter the adsorption equilibrium time is. Conversely, these adsorption equilibrium times will become long. Adsorption equilibrium time of mudstone is the shortest and that of sandstone is the longest.

Keywords: Sedimentary Rocks, Adsorption Equilibrium Time, Ammonium Molybdate, Adsorption Equilibrium Temperature, Rock Particle Diameter, Solution Concentration

1. Introduction

In order to understand the migration and transformation law of heavy metal ions in rock and soil, people are usually concerned for adsorption capacity of heavy metal ions in rock and soil, affecting factors of adsorption and isothermal adsorption model, etc. There are some researches on adsorption equilibrium time just under considering one factor and no systematically researches on the adsorption equilibrium time[1-3]. For perfectly understanding the adsorption equilibrium law of the heavy metal ions in rock and soil, this paper systematically studies the adsorption equilibrium time taking ammonium molybdate for example on three kinds of typical sedimentary rocks such as limestone, mudstone and sandstone under different temperatures, rock particle diameters and initial solution concentrations by a large number of adsorption equilibrium tests.

2. The Factors Affecting the Adsorption Equilibrium Time

Heavy metal ions adsorption equilibrium time of rock depends not only on rock composition and structure, the chemical performance of heavy metal ions, but also on the water environment. The factors that affecting the adsorption equilibrium time are rock type, the rock particle diameter, physicochemical properties of heavy metal ions, the initial solution concentration, water temperature, pH and total dissolved solids and so on.

Different rock particle diameters affect not only adsorption capacity but also adsorption equilibrium time. It is found that with the zeolite particle specific surface area increases, the heavy metal adsorption capacity also increases and the adsorption equilibrium time is shortened[4]. The molecular weight, molecular diameter, valence and polarity of heavy metal ions also affect the adsorption. Generally the higher molecular weight is, the stronger adsorption (with family) is, but with higher molecular weight, diffusion rate of adsorbed ions within the pore of the particle surface will slow down and the adsorption equilibrium time is extended. The same kind of metal ion under the same experiment condition, with the increase of the initial solution concentration, heavy metal adsorption volume of per absorbent increase, and the adsorption equilibrium time extends[5]. Temperature-effected mechanism of adsorption equilibrium time is as follows: ① increasing temperature makes the adsorption rate of heavy metal ions in rock particles increases, the adsorption capacity increases and the adsorption equilibrium time is shortened; ② physical adsorption is accompanied by the release of energy, so increasing temperature will make the reduction of physical adsorption and make absorption prolonged. Influence of pH value on heavy metal ions adsorption is mainly for controlling the solubility of heavy metal ions, affecting the adsorption characteristics of natural colloids in the rock particles and controlling various adsorption reaction on the surface of the rock particles [6-7].The presence of other ions in solution also affects the adsorption of heavy metal ions, generally with ionic strength increases, the adsorption capacity of heavy metal ions reduces and the adsorption equilibrium time extends.

In this paper, based on oscillation experiment method, distilled water is used in adsorption of molybdate ion complex anion of ammonium molybdate in limestone, sandstone and mudstone, so the influence of pH value and other ions in solution on adsorption can be ignored.

3. Experimental Method

3.1. Experimental preparation

Collecting some fresh limestone, sandstone and mudstone in field, then crushing, sifting and pretreating them. Firstly, in order to remove pollutants and organic matter on the rock surface, rinse rocks with distilled water after cracking them into pieces about 1cm, dry and then soak with 1% to 2% hydrochloric acid about 10min, wash rocks 3 to 4 times with distilled water and dry again. Then further cracking, sifting, place rocks in clean beaker respectively according to rock particle diameter, such as less than 0.5mm, 0.5 ~ 1.0mm, 1.0 ~ 2.0mm and larger than 2.0mm , seal and reserve.

Solution is prepared into different concentrations of ammonium molybdate by the pure $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. DKB1906 low temperature thermostat is used for constant temperature sink.

3.2. Concentration analysis method

JP-303 polarographic analyzer and catalytic polarography are used to analyze solution concentration. When the concentration of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ is less than 20μg/l, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ concentration and catalytic wave could be a linear relationship. Prepare standard solution with different concentrations (C0), which are as follows: 0μg/l, 0.2μg/l, 0.4μg/l, 0.8μg/l, 1.6μg/l, 2.0μg/l, 4.0μg/l, 6.0μg/l, 8.0μg/l, 10.0μg/l, 12.0μg/l, 14.0μg/l, 16.0μg/l, 18.0μg/l and 20.0μg/l. Then measure wave height (e2) of standard solution respectively, the standard relative curve between $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ concentration and catalytic wave height is shown in figure 1.

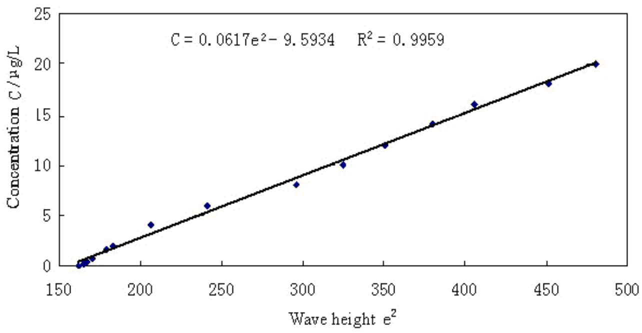


Fig. 1: The standard relative curve between $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ concentration and catalytic wave height

3.3. The adsorption equilibrium time

Weigh the rock powder reserve of a sample size 20g, put it into a 250ml beaker, measure 250ml standard solution which is prepared by the analytically pure ammonium concentration and put into the beaker containing rock powder sample, then place the beaker into a constant temperature sink to maintain oscillation.

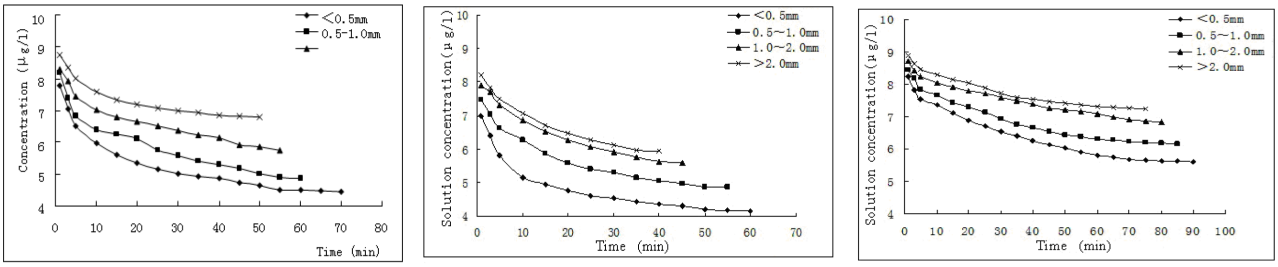
Take appropriate solution into the centrifuge tube to centrifuge and clarify according to a certain time interval, take the upper clear liquid of the tube to the concentration analysis. when the concentration remained unchanged, the adsorption equilibrium time is gotten.

4. The Adsorption Equilibrium Time of Three Kinds of Rocks under Different Rock Particle Diameters, Temperatures and Initial Solution Concentrations

4.1. Adsorption equilibrium time at different rock particle diameters

Experimental conditions: three kinds of rock particle diameters are as follows: <0.5mm, 0.5 ~ 1.0mm, 1.0 ~ 2.0mm, > 2.0mm. Ammonium molybdate solution volume is 250ml, the initial solution concentration is 10μg/l, weight of rock adsorbent dosage is 20g, adsorption equilibrium temperature is 10 ℃.

The time-dependent curves of solution concentration at different rock particle diameters are shown in Figure 2. As the diameters decreases, the adsorption equilibrium time of three kinds of rocks have different degrees of growth, adsorption equilibrium time of limestone at four different diameters is 70, 60, 55, 50minutes, which of mudstone is 60, 55, 50 , 45minutes, and which of sandstone is 90, 85, 80, 75minutes. The relationship between diameters and adsorption equilibrium time is shown in Figure 3, as the diameters increase, the adsorption equilibrium time is shortened. Under the same condition, adsorption equilibrium time of sandstone is the longest, limestone takes the second place and mudstone is the shortest. The fitting curve of the adsorption equilibrium time of three types of rocks changes with the diameters can be seen that the slope of the limestone is the largest, indicating that diameter has the greatest impact on the limestone adsorption equilibrium time.



(1)limestone (2)mudstone (3)sandstone

Fig. 2: The time-dependent curves of solution concentration at different rock particle diameters

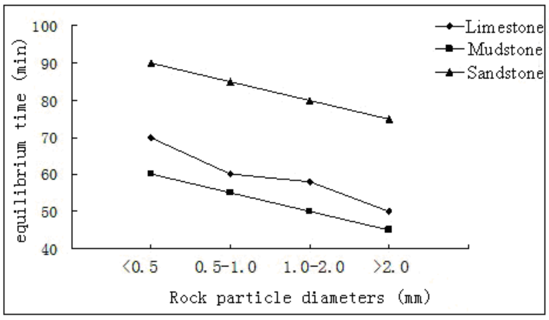
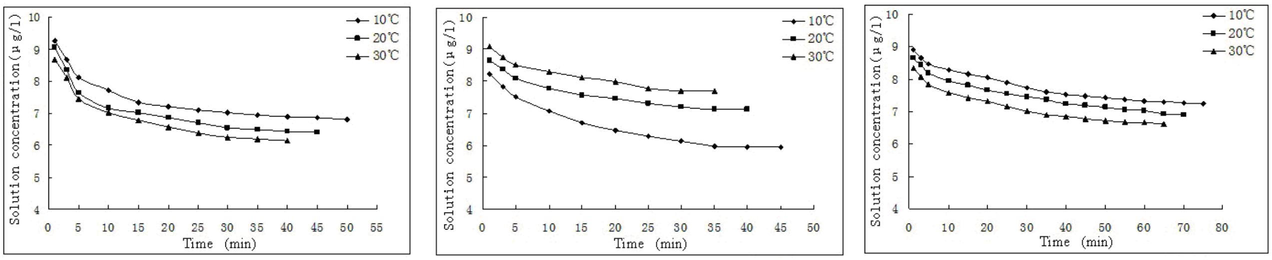


Fig. 3: The relationship between rock particle diameters and adsorption equilibrium time

4.2. Adsorption equilibrium time at different temperatures

Experimental conditions: the rock particle diameters of three kinds of rocks are > 2.0mm, ammonium molybdate solution volume is 250ml, the initial solution concentration is 10μg / L, weight of rock adsorbent dosage is 20g, adsorption equilibrium temperature is 10 ℃, 20 ℃ and 30 ℃.

The time-dependent curves of solution concentration at different temperature are shown in Figure 4. As the adsorption equilibrium temperature increases, the adsorption equilibrium time of three kinds of rocks gets shorter, adsorption equilibrium time of limestone at three different temperature is 50, 45, 40minutes, which of mudstone is 45, 40, 35 minutes, and which of sandstone is 75, 70, 65 minutes. The relationship between adsorption equilibrium temperature and adsorption equilibrium time is shown in Figure 5. Adsorption equilibrium time of sandstone is the longest, limestone takes the second place and the mudstone is the shortest. Curve slopes of these rocks are the same, indicating that adsorption equilibrium temperature has the same impact on adsorption equilibrium time of these rocks .



(1) Limestone (2) Mudstone (3) Sandstone

Fig. 4: The time-dependent curves of solution concentration at different temperature

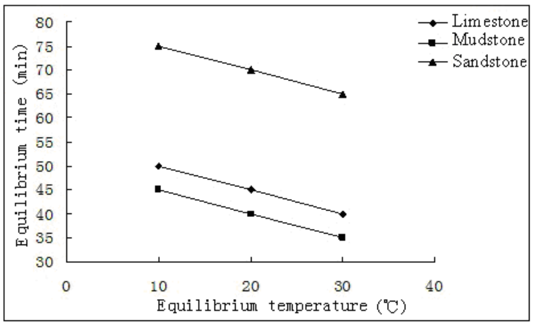
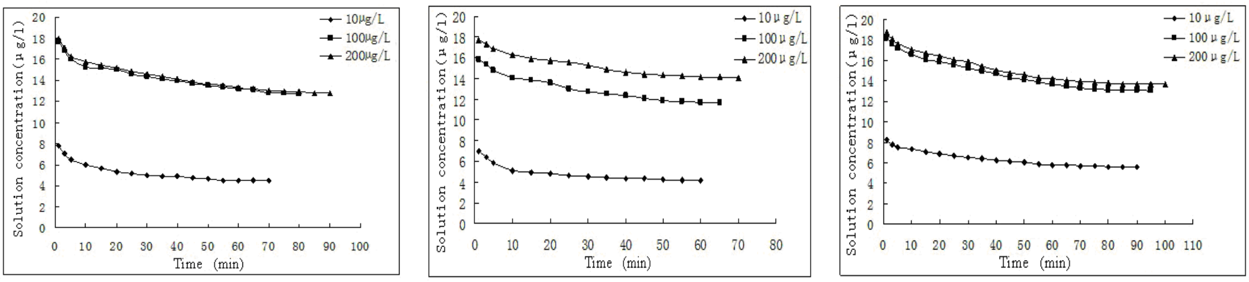


Fig. 5: The relationship between adsorption equilibrium temperature and equilibrium time

4.3. Adsorption equilibrium time at different initial solution concentration

Experimental conditions: the rock particle diameters of three kinds of rocks are <0.5mm, ammonium molybdate solution volume is 250ml, initial solution concentration is 10μg/l, 100μg/l and 200μg/l, weight of rock adsorbent dosage is 20g, the adsorption equilibrium temperature is 10 ℃ .

The time-dependent curves of solution concentration at different initial solution concentrations are shown in Figure 6. With the initial solution concentration increases, molybdenum adsorption rate of limestone gets slow, the time required to reach adsorption equilibrium extended. Adsorption equilibrium time of limestone at three initial solution concentrations is 70, 80, 90 minutes, which of mudstone is 60, 65, 70 minutes, and which of sandstone is 90, 95, 100 minutes. The relationship between initial solution concentration and adsorption equilibrium time is shown in Figure 7, adsorption equilibrium time of sandstone is the longest, limestone takes the second place and mudstone is the shortest. Curve slope of limestone is the largest, indicating that initial concentration has the greatest impact on adsorption equilibrium time of limestone.



(1) Limestone (2) Mudstone (3) Sandstone

Fig. 6: The time-dependent curve of solution concentration at different initial concentrations

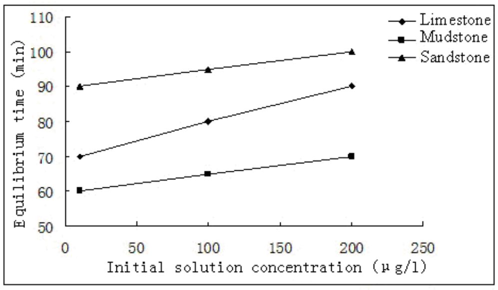


Fig. 7: The relationship between initial solution concentration and adsorption equilibrium time

5. Conclusions

Following rules are gotten through the above adsorption equilibrium experiments under different adsorption equilibrium temperatures, rock particle diameters and initial solution concentrations:

Ammonium adsorption equilibrium time of three kinds of typical sedimentary rocks at general temperature is very short, usually no more than 2 hours;

Under the same adsorption equilibrium temperature, same initial solution concentration and same rock type condition, the bigger the rock particle diameter is, the shorter the adsorption equilibrium time is, otherwise the longer the time is;

Under the same initial solution concentration, same rock type and same rock particle diameter condition, the higher the adsorption equilibrium temperature is, the shorter adsorption equilibrium time is, otherwise the longer the time is;

Under the same adsorption equilibrium temperature, same rock type and same rock particle diameter condition, the smaller the initial solution concentration is, the shorter adsorption equilibrium time is, otherwise the longer the time is;

Under the same adsorption equilibrium temperature, same initial solution concentration and same rock particle diameter condition, the adsorption equilibrium time of sandstone is the longest, limestone takes the second place and mudstone is the shortest.

6. References

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