Experiments on Microalgae Mud Adsorbing Heavy Metal Pb(II) Ions and Study on its Thermodynamics

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Abstract. By using microalgae mud (MAM) taken from a high-efficiency algae pond as raw material to treat domestic sewage, this paper investigated the effects of such factors as the amount of microalgae added, shaking time, pH, temperature, the concentration of Pb ions and the rotating speed of the shaking table on the performance of MAM in the adsorption of the heavy metal Pb (II) by use of the single factor control variable method. Research results show that when the initial concentration of Pb(II) is 30mg/L, the amount of MAM added is 30g/L, the pH is 4, and the rotating speed of the shaking table is 180rpm, the maximum adsorption rate of Pb(II) may reach 85.51% after the solution is shaken and reacts at 25 °C in a thermo shaker for 30min. By further studying the adsorption rate of Pb(II) and fitting the adsorption isothermal equations, we found that the best effect can be achieved when the pH was 4 and the adsorption time was kept for 30min or above, with a maximum adsorption capability of 22.52mg/g in theory, and that the adsorption process was in line with the Langmuir and Freundlich adsorption isothermal models, and the correlation coefficients R2 of these two models were both greater than 95%, which demonstrates MAM was easy to adsorb Pb(II) ions, and the adsorption process was of monomolecular physical adsorption.

1. Introduction
With the development of industry in recent years, emissions of industrial waste water containing heavy metals, particularly those from such industries as chemical engineering, electroplating, mining, smelting, electronics and leader tanning, are increasing year by year[1], causing serious water body pollution. While among these types of pollution, industrial waste water containing heavy metals brings the most serious environmental pollution. Industrial waste water contains a large amount of metal ions, such as Cd(II), Cu(II), Zn(II) Cr(II), Hg(II), Ni(II) and Pb(II), and these metal ions have a high stability in water bodies, so they may do harm to aquatic plants and animals when accumulated to a certain level, and further have a direct or indirect effect on the health of human beings themselves through food chains, therefore, heavy metal pollution has become one of the most serious environmental issues across the world[2]. It is reported that among the 21 cities along China's Yangtse River, Chongqing, Yichang, Panzhihua, Wuhan, Nanjing and Shanghai are facing a severe situation, with over 65% of their water bodies having been polluted by heavy metals[3]. Furthermore, some of other major water systems, such as the Pearl River, the Tai Lake, the Huai River, the Yellow River, the Hai River, the Songhua River and the Liao River, also face quite serious challenge from heavy metal pollution[4]. In such a circumstance, it has become crucial to control and treat heavy metal pollution in water bodies.

The treatment of heavy metals in water by physical or chemical method tends to have its limitation and bring secondary pollution, while bio-adsorption technology[5] is to adsorb, degrade and enrich...
pollutants in the environment by use of plants, animals and/or micro-organism co-existing with them so as to lower the concentrations of pollutants in water bodies. Compared with the chemical precipitation method, physical remediation method and membrane separation method commonly used by physical or chemical method, the bio-adsorption method features its low cost, wide resources, small secondary pollution, simple operation and reusability of raw materials, and is expected to materialize the resource utilization of solid waste[6]-[8]. In recent years, bacteria, microzyme, mold, algae and macromolecular organisms such as chitosan, starch, plant fiber and cellulose were commonly studied to treat heavy metals as bio-adsorbents. Compared with the traditional physical and chemical adsorption methods, the bio-adsorption method is an innovation, which will have a broad prospect in the treatment of heavy metal waste water due to its high efficiency, energy saving, easy operation and desirable environmental protection. This paper studied the adsorption process of MAM on Pb(II) ions in water, as well as its mechanism and affecting factors, so as to lay a foundation for the development of high-efficient and low-cost heavy metal adsorbents, the exploration of new approaches and the industrial application of the treatment of waste water containing heavy metals.

2. Materials and Methods

2.1. Experimental Materials and Instruments
MAM: taken from Liaozhong District Biological Sewage Treatment Plant in the city of Shenyang as MAM precipitation collected from a high-efficiency algae pond used for treating domestic sewage through filtration and drying and stored in 4 refrigerators for future use. The MAM contains green microalgae, diatoms, cyanobacteria and other microorganism cells. Main experimental reagents: ethanol, phosphate buffer, glutaraldehyde, isoamyl acetate, NaOH, Pb(NO₃)₂, HCl, etc., which are all analytical pure reagents and purchased from Sinopharm Group Chemical Reagent Co., Ltd.; water used in the experiments is deionized water.

2.2. Experimental Method
The main affecting factors for MAM to adsorb Pb(II) were investigated by the single factor experimental method. In the experiments, the amount of MAM added, shaking time, pH, temperature, the concentration of Pb(II), the rotating speed of the shaking table were selected as the factors that have remarkable effects on the adsorption rate of the heavy metal Pb(II) in the water. Three parallel samples and a control group (with no MAM added) were set in the experiments.

2.3. Determination Method
Determination of the concentration of Pb(II): Pb ions were tested using a full-spectrum direct-reading plasma emission spectrometer (PES), with the analytical spectral lines of Pb(II) being 220.353r and 217.000r respectively. The concentrations of heavy metal ions were calculated by the standard curve method as below: under the given analytical conditions, the standard series solutions of not less than three different concentrations of to-be-determined elements were determined (the medium used in the standard solutions and their acidities should be consistent with those of the test solutions), so as to plot standard curves and calculate regression equations by taking the response value of the analysis line as ordinate and concentration as abscissa, with relevant regression coefficients higher than 0.99. Determine the response values of the test solutions, and then calculate the contents of all to-be-determined elements in the samples after consulting relevant concentrations from the standard curves or regression equations. Blank experiments were conducted under the same analytical conditions, with blank interference deducted as required in the manual for instrument operation.

2.4. Selection of the Adsorption Model
Isothermal adsorption, isobaric adsorption and constant-volume adsorption are three types of adsorption, of which isothermal adsorption is the most widely used. When the temperature is constant, an isothermal adsorption balance will be obtained, at this moment, the curve of relationship between equilibrium adsorption quantity (qₑ) and equilibrium concentration (Cₑ) is called the isothermal isotherm. The isothermal isotherms used in this paper are as below:
(a) Langmuir isothermal equation
Expressed linearly as:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}
\]  

Expressed non-linearly as:

\[
q_e = \frac{q_m b C_e}{1 + b C_e}
\]  

Langmuir equation, as one of commonly used adsorption isotherm equations, was put forward by physicochemist Langmuir Itying in 1916 based on the molecular movement theory and some hypotheses, and now is widely applied to studies on adsorption, generally, to the single layer adsorption.

(b) Freundlich isothermal equation
Expressed linearly as:

\[
\ln q_e = \frac{1}{n} \ln C_e + \ln K
\]  

Expressed non-linearly as:

\[
q_e = K C_e^{1/n}
\]  

The Freundlich equation, as one of commonly used adsorption isotherm equations, is suitable for multiple molecular layer adsorption. In this equation, the magnitude of \(n\) reflects how difficult the adsorption would be. Where \(q_e\) (mg/g) is the equilibrium adsorption quantity; \(C_e\) (mg/L) is the concentration of the solute while an adsorption balance is reached; \(q_m\) (mg/g) is the saturated adsorption quantity; \(b\) is Langmuir constant; \(K\) and \(1/n\) are empirical constants.

3. Results and Discussion

3.1. Optimization of the Removal Rate of Pb (II)
The effect of MAM on the rate of removal of Pb (II) by changing the initial conditions is as shown in Figs.1-5.

![Figure 1](image1.png) Effect of the amount of MAM added

![Figure 2](image2.png) Effect of initial pH

![Figure 3](image3.png) Effect of shaking time

![Figure 4](image4.png) Effect of temperature
The effects of the amount of MAM added, shaking time, pH, temperature, the concentration of Pb ions and the rotating speed of the shaking table on the performance of MAM to remove Pb(II) were determined by changing initial conditions, as shown in Figs. 1-5. As can be seen from Fig.1, with the increase in the amount of MAM added, the removal rate of Pb(II) rises gradually, till the amount of MAM added reaches 30g/L, at this moment, the removal rate reaches its maximum of 78%, after that, with the increase in the amount of MAM added, the removal rate no longer rises and tends to be steady. As can be seen from Fig.2, when raising the pH from 3 to 5, the removal rate of Pb(II) keeps at a high level, above 80%. As can be seen from Figs. 2-5, temperature, shaking time and rotating speed all have a certain effect on the removal rate of Pb(II), and with the increase in the temperature, shaking time and rotation speed, the removal rate presents an up-and-down trend. Before attaining the optimal conditions, the rise in temperature can improve the adsorbing rate, the increase in shaking time can make adsorption more even and complete, the increase in rotating speed can make sewage better contact with the porous structure of MAM and enlarge the surface area for adsorption, thus improve the removal rate. However, a drop in removal rate may appear when the temperature, shaking time and rotating speed attain the optical conditions, which may be the result of the desorption of Pb (II). In summary, the maximum adsorption rate of Pb(II) can reach 85.51% at the optimal experimental conditions, that is, when the initial concentration of Pb(II) is 30mg/L, the amount of MAM used is 30g/L, the rotating speed of the shaking table is 180rpm, and the adsorption reaction proceeds in a thermo shaker at 25℃ for 30min.

### 3.2. Adsorption Isothermal Parameters of Pb (II)

Aqueous solutions were formulated with a Pb(II) concentration of 5, 10, 20, 30 and 50mg/L respectively, and adjusted with 0.1mol/L HCl and NaOH to keep their pH at 4. Add MAM to the solutions with an amount of 30g/L, sample after shaking the solutions at 25℃ for 30min under the condition that the rotating speed of the shaking table is kept at 108r/min, and then centrifuge the solutions for 10min under the condition that the rotating speed is kept at 180 r/min. Determine the concentrations of Pb(II) in the supernatants and calculate the removal rate (see Table 1). Experimental data was fitted using Langmuir and Freundlich isothermal equations[9] (see Table 2).

| Initial concentration(mg/L) | Equilibrium concentration(mg/L) | Removal rate (%) |
|----------------------------|---------------------------------|-----------------|
| 4.29                       | 1.36                            | 68.28           |
| 9.38                       | 2.21                            | 76.41           |
| 18.46                      | 4.58                            | 75.17           |
| 26.90                      | 4.77                            | 82.26           |
| 45.20                      | 9.79                            | 78.35           |

Experimental data was fitted using Langmuir and Freundlich equations, and the results are as shown in Table 2. From the correlation efficient R² obtained by fitting the two model equations, it can be judged that the adsorption rate of Pb(II) has a quite high degree of fitting with both the Langmuir and Freundlich equations. In general, the Langmuir model is intended to study single molecular layer adsorption, a type of physical adsorption; the Freundlich model is used to describe multiple molecular layer adsorption, but...
when $n<1$, this model describes a situation of single molecular layer physical adsorption, and adsorption is easy to happen when the value of $n$ varies between 0.1 and 0.5 means, while $n>2$ means adsorption is difficult to happen. In this experiment, the value of $n$ is 0.7970, which means adsorption is easy to happen, and the adsorption is of single molecular layer physical adsorption.

| Model     | Parameter          | Correlation Coefficient | Fitting Equation          |
|-----------|--------------------|-------------------------|---------------------------|
| Langmuir  | $q=22.52\text{mg/g,}$ $b=11.12/\text{mg}$ | $R^2=0.9567$ | $Y=0.4937x-0.0444$ |
| Freundlich| $K=2.3287\text{mg/g,}$ $n=0.7970$ | $R^2=0.9578$ | $Y=1.2547x+0.8453$ |

4. Summary

Through single factor experiments, this paper concludes that MAM can remove the heavy metal Pb(II) out of water desirably, and the maximum adsorption rate of Pb(II) is 85.51% under the optical removal conditions, that is, when the amount of MAM is 30g/L, pH=4, the rotating speed of the shaking table is 180rpm, and the reaction time is 30min or above.

When MAM is used to adsorb Pb(II) in water, the maximum adsorption quantity in theory is 22.52mg/g, which means MAM is easy to adsorb Pb(II) in water, following a single molecular layer physical adsorption process. Therefore, it is advisable to use MAM to treat industrial waste water containing heavy metals.

5. References

[1] G.F.Shen.: Think about urban sewage treatment policy, China Environmental Protection Industry, (2004), No2, p. 16
[2] W.C.Gao: Optimization and Mechanism Study of Biosorption of Cu (II)Pb (II) from Aqueous Solutions by Microbial Flocculants of MBFGAI(MS, Hunan University, China 2011)
[3] W.F.Sun and D.Xiao: Current situation and management technology of heavy metal pollution in water body, Energy and Energy Conservation,(2012),No2,p.49
[4] X.Yue,K.Liu and X.L.Xia: Preventive Medicine Tribune,Vol.20(2014),No 3,p.209
[5] L.Li: Study on Heavy Metal Resistance and Biosoption of Lead (II ) Ions from Aqueous Solution by WT6-5(MS, Northeastern University, China 2013)
[6] M.G.Geoffrey: Journal of Chemical Technology & Biotechnology,Vol.84(2009),No 1,p.13
[7] X.L.Hou,A.Q,Liu and L.P.Cai: Subtropical Agriculture Research,Vol.8(2009),No 2,p.106
[8] M.A.Ashraf,K.Mahmood and A.Wajid: Proceedings of International Conference on Food Engineering and Biotechnology(ICFEB 2011)[C](Bangkok, Thailand, May 7-9,2011),Vol,9,p.60
[9] I.Qureshi,S.Memon and M.Yilmaz: Comptes Rendus – Chimie,Vol.13(2010),No 11,p.1416

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