Adsorption Properties of Microwave Modified Diatomite on Heavy Metals in Landfill Leachate

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Abstract: Adsorption properties of diatomite modified by microwave on lead, chromium and cadmium in landfill leachate under different conditions were studied with diatomite as adsorbent, and the best microwave modification conditions were determined in this study. Meanwhile, the adsorption and removal effects of diatomite on Pb, Cr and Cd in landfill leachate under different adsorption conditions were investigated which including adsorbent dosage, adsorption time, temperature, pH and the ion strength. The results showed that the best adsorption removal efficient of heavy metal ion in landfill leachate can be obtained under the adsorption conditions of low ionic strength, alkaline leachate, with adsorption temperature of 25℃, the adsorption time of 40 min, and the modified diatomite dosing quantity of 5~10g/L.

1. Introduction
Landfill leachate is generated at landfill sites as a result of precipitation, infiltration, compaction and waste degradation. The concentration of organic and inorganic components is higher in landfill leachate, and it contains more than ten kinds of heavy metal ions[1,2]. Thus, it should be treated before discharge in the environment or to a sewage system for treatment[3,4]. The diatomite is a natural nano-materials with a light weight, large specific surface area, super strong adsorption, noise resistance, wear resistance, thermal properties, corrosion resistance and other outstanding performance[5]. A large number of silicon hydroxyl groups (Si-OH) are distributed on the surface and the inner surface of the micropores. Generally, the hydrogen ions H⁺ of silicon hydroxyl in aqueous solution will be dissociated. When combined with the adsorbed water, the particles will have a certain surface negative electricity to adsorb positive charges[6]. Therefore, the application of diatomite is widespread increasingly in the treatment of heavy metal pollution.

After sulfated modification or alkalized modification of diatomite, the maximum adsorption capacity of primary diatomite for Pb²⁺ and Cd²⁺ increased compared with that without modification[7-9]. While modified the diatomite with sixteen alkyl trimethylamine bromide solution, manganese dioxide and calcium carbonate, the effects of diatomite dosage, adsorption time and initial pH value on the adsorption properties of modified diatomite were studied[10-12].

Although diatomite and modified diatomite have been used to adsorb heavy metal pollutants in waste water, little research has been done on the adsorption of heavy metals in landfill leachate by microwave modification of diatomite. In this study, the adsorption effect of modified diatomite on heavy metals in landfill leachate under different conditions was investigated by determining the
optimum conditions for microwave modification of diatomite. The application of this repair technology has a certain guiding significance for the application of modified diatomite in the treatment of landfill leachate.

2. Materials and Methods

2.1 Reagents and instruments
Hydrochloric acid, sodium hydroxide, sodium chloride, analysis pure. Experimental diatomite is purchased from Linjiang Yiruishi diatomite Co. Ltd. The landfill leachate is taken from East solid waste disposal center in Xiamen city. The deionized water is made by the laboratory of the Department of Environment Engineering.

Galanz microwave oven (P70D20TJ-D3), electric thermostat blast dryer (DHG-9146A), constant temperature oscillator (TH2-320), low speed large capacity centrifuge (TDL-40C), ICP (OPT/MQ 700DV), electronic balance(TE 124S), pH meter(PB-10).

2.2 Preparation of microwave modified diatomite
Diatomite was immersed in hydrochloric acid and deionized water according to a certain ratio of solid to liquid about (1:5~20), and was modified by microwave under microwave irradiation. The power was set to 490 W and the time was in the range of (0~10min). Precipitated the mixture, poured out the supernatant and being filtered, the microwave modified diatomite was prepared. The filtered solid was dried in the oven with the temperature range from 65°C to 85°C, and the dried solid was activated for 0.5-2 h at constant temperature of 100°C. Put the soil sample into mortar and stirred evenly, then sieved with 100 mesh, the microwave modified diatomite is obtained.

2.3 Adsorption experiment
The microwave modified diatomite was added into landfill leachate from which heavy metal will be removed. Then put it in a incubator, set a certain reaction temperature (25~45°C), rotate speed (200rpm) and time (20~120min) to fully contact reaction. Made Centrifugal separation and the supernatant is a landfill leachate after removing heavy metals.

2.4 Analysis method
The standard curves of Pb, Cr and Cd are obtained by using OPT/MQ 700DV inductively coupled plasma emission spectrometer at 220.353 nm, 267.716nm and 228.802nm respectively. Landfill leachate and landfill leachate treated by modified diatomite were also measured at the same wavelength. The concentrations of Pb, Cr and Cd were determined from the standard curve by Optima 7000 DV ICP emission spectrometer.

3. Results and Discussion

3.1 Effect of microwave irradiation time on the modified diatomite
The microwave power was controlled at 490 W and the microwave irradiation time was set in 0min, 5min, 8min and 10min respectively. A certain amount of microwave modified diatomite was prepared by mixing diatomite, 1 mol/L hydrochloric acid and deionized water. 0.1g modified diatomite was added to 10mL landfill leachate of, placed in the incubator at 25°C, and the reaction time was 40min at about 200rpm. After that, centrifuged the supernatant and the concentration of heavy metals was measured by ICP.
Figure 1. The changes of adsorption of modified diatomite under different microwave irradiation time.

As shown in figure 1, in the range of 0~5 min, increase the time of microwave irradiation can improve the adsorption properties of modified diatomite. When the irradiation time is 5 min, the adsorption property of modified diatomite to heavy metals is the best. While the irradiation time is longer than 5 min, the adsorption capacity decreased with increasing of irradiation time and even less than the diatomite without microwave irradiation. This is mainly because the part of impurities and moisture in diatomite can be removed with appropriate microwave irradiation, promote the formation of the pore and improve the adsorption performance of diatomite. Further prolonging the time of microwave irradiation will increase the temperature of diatomite, destroy the structure and even cause the pulverization of diatomite, thus reducing the adsorption ability of diatomite to heavy metal ions.

3.2 Effect of solid-liquid ratio on the modified diatomite

The mixture of diatomite, hydrochloric acid and deionized water in the mass ratio of 1/5, 1/7, 1/10, 1/20 are prepared. The microwave modification conditions was set for microwave power 490 W and irradiation time 5 min. 0.1 g modification diatomite was added into the 10mL landfill leachate. The mixture was placed in a incubator at 25°C and rotated for 40 min at 200 rpm. The supernatant was separated by centrifugation and the concentration of heavy metals was measured by ICP. The result is shown in figure 2.

Figure 2. The changes of adsorption of modified diatomite under different solid-liquid ratios.

It can be seen from figure 2 that the best solid-liquid ratio of diatomite in 3 heavy metal ions is also different. For Pb and Cd, the best solid-liquid ratios of modified diatomite are both 1/7, as for Cr, it is 1/10. The hydrochloric acid will increase the surface roughness of diatomite particles, form more micropores and grooves. The greater the specific surface area, the stronger the adsorption capacity of diatomite.

3.3 Effect of adding amount on adsorption of heavy metals
0.05 g, 0.07 g, 0.1 g, 0.15 g and 0.2g modified diatomites were added to 10 mL landfill leachate respectively. The mixture was placed in an incubator at 25°C and rotated for 40 min at 200 rpm. The supernatant was separated by centrifugation and the concentration of heavy metals was measured by ICP. The result was shown in figure 3.

![Figure 3](image)

**Figure 3.** The changes of adsorption of modified diatomite under different dosages.

As shown in figure 3 we can see, the adsorption capacity of Cd would decreased with the modified diatomite dosage increased. The best dosage of modified diatomite was 0.05 g, i.e. 5 g/L. As for Pb and Cr, the adsorption performance was the best with the modified diatomite dosage of 0.1 g, i.e., the modified diatomite dosage was 10 g/L.

3.4 Effect of adsorption time on adsorption of heavy metals

0.1 g modified diatomite was added to the landfill leachate and put in 25 °C incubator. A series of reaction time, i.e., 20 min, 40 min, 60 min, 90 min, 120 min, were set with the 200 rpm respectively. The supernatant was separated by centrifugation and the concentration of heavy metals was measured by ICP. The result was shown in figure 4.

![Figure 4](image)

**Figure 4.** The changes of adsorption of modified diatomite under different adsorption time.

It was shown from figure 4, when the adsorption time was less than 40 min, the modified diatomite adsorption curve of heavy metals increased with the extension of adsorption time. When the adsorption time reached 40min, the modified diatomite adsorption properties for heavy metal ions was best. While the adsorption time was prolonged, the adsorption properties of modified diatomite for heavy metal ions decreased. Therefore, the best adsorption time of the modified diatomite to heavy metal ions was 40min.

3.5 Effect of adsorption temperature on adsorption of heavy metals

0.1 g modified diatomite was added to the landfill leachate and put the mixture in an incubator. A series of reaction temperature, i.e., 25°C, 35°C, 45°C, were set and rotated for 40 min at 200 rpm. The
supernatant was separated by centrifugation and the concentration of heavy metals was measured by ICP. The result was shown in figure 5.

![Figure 5](image.png)

**Figure 5.** The changes of adsorption of modified diatomite under different adsorption temperature.

The adsorption temperature is one of the important factors affecting the adsorption properties of Modified Diatomite on heavy metal ions. The adsorption of heavy metal ions by diatomite will increase with the increase of temperature, but overheated is not conducive to the adsorption. According to figure 5, the best adsorption temperature of modified diatomite on heavy metal ions is 25°C.

3.6 Effect of pH on adsorption of heavy metals

The pH of landfill leachate was regulated by adding some hydrochloric acid and sodium hydroxide. Added 0.1g modified diatomite to the 10ml landfill leachate with different pH respectively, put the mixture in an incubator and rotated for 40 min at 200rpm. The supernatant was separated by centrifugation and the concentration of heavy metals was measured by ICP. The result was shown in figure 6.

![Figure 6](image.png)

**Figure 6.** The changes of adsorption of modified diatomite under different pH.

As shown in figure 6, for Cr, the landfill leachate was acidic when the pH was low and H\(^+\) will produce competitive adsorption, which was not conducive to the adsorption. With the increase of pH, the competitiveness of H\(^+\) was reduced, and the removal efficiency and adsorption performance of modified diatomite on Cr were obviously improved. The main reason lies in that heavy metal ions are removed mainly by binding to the OH\(^-\) in the solution under alkaline conditions. As for Pb and Cd, the removal efficiency of the modified diatomite can reach the highest because the pH value of the landfill leachate was weak alkaline (pH 8.77) in the natural environment.

3.7 Effect of ionic strength on adsorption of heavy metals
A different amount of sodium chloride solid was added to the leachate to change its ionic strength, 0.01 mol/L, 0.1 mol/L, 1 mol/L, respectively. Added 0.1g modified diatomite to the 10ml landfill leachate with different pH respectively, put the mixture in an incubator and rotated for 40 min at 200rpm. The supernatant was separated by centrifugation and the concentration of heavy metals was measured by ICP. The result was shown in figure 7.

Figure 7. The changes of adsorption of modified diatomite under different ion concentrations.

As shown in figure 7, compared with landfill leachate, adding sodium chloride solid to change the ionic strength of landfill leachate improved the adsorption performance of modified diatomite to Cr, while it don't have much influence on Pb and Cd. So a certain amount of sodium chloride solid can be added to improve the removal efficiency of modified diatomite on Cr.

4. Conclusion
The adsorption properties of microwave modified diatomite on heavy metal ions such as lead, chromium and cadmium in landfill leachate under different conditions were studied, and the best microwave modification conditions were determined.

The removal efficiency of heavy metal ions such as lead, chromium and cadmium in landfill leachate under different adsorption conditions was also investigated, including the dosage of adsorbent, adsorption time and temperature, pH and ionic strength of landfill leachate. Some conclusions can be drawn as follows:

1) The best microwave modification conditions for diatomite are diatomite and 1mol/L hydrochloric acid and deionized water, among which the solid-liquid ratio is 1:(7~10), the microwave power is 490W, and the microwave irradiation time is 5min.

2) The best adsorption conditions for removing heavy metal ions such as lead, chromium and cadmium in landfill leachate by modified diatomite were low ionic strength and alkaline landfill leachate. The adsorption temperature was 25℃, the adsorption time was 40min, and the dosage of modified diatomite was 5~10g/L.

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References
[1] Renou S, Givaudan JG, Poulain S, Dirassouyan F, Moulin P. Landfill leachate treatment: Review and opportunity. J Hazard Mater 2008, 150(3):468–493.
[2] Aktas O, Cecen F. Addition of activated carbon to batch activated sludge reactors in the treatment of landfill leachate and domestic wastewater. J Chem Technol Biotechnol 2001, 76:793–802.
[3] Zazouli MA, Yousefi Z. Removal of heavy metals from solid wastes leachate by Coagulation-Flocculation process. J Appl Sci 2008, 8:2142–2147.
[4] Zazouli MA, Maleki A, Izanloo H. Assessment of raw leachate characteristics and its
pretreatment by Lime. Asian Journal of Chemistry 2010, 22:6155–6163.

[5] G. Gustavo, C. Edgar, C. Saúl, H. Jonas, M. Johanne, Synthesis of zeolite Y from diatomaceous earth as silica source, Microporous Mesoporous. Mater. 2016, 219:29–37.

[6] Wu JL, Yang YS, Lin JH. Advanced tertiary treatment of municipal wastewater using raw and modified diatomite. Journal of Hazardous Materials B. 2005, 127(1-3):196-203.

[7] Su YW, Yang ZJ, Zhou YZ. A review of the adsorption of heavy metal ions by diatomite and its application to the remediation of environmental heavy metal pollution. Non-metallic mineral industry in China. 2007, 28(1): 94-101.

[8] Liu P, Zhao QR, Yuan LB. Adsorption of Pb (II) by Modified Diatomite. Yunnan Chemical Technology. 2003, 30(5):11-13.

[9] Patricia M, Carolina M, Enrique CU. Cd$^{2+}$ adsorption on alkaline-pretreated diatomaceous earth: equilibrium and thermodynamic studies. Environmental Chemistry Letters. 2011, 9(1):55-63.

[10] Luo DC, Liu JF. Study on the adsorption properties of modified datomite on Pb$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$ in Wastewater. China Mining. 2005, 14(7): 69-71.

[11] Cai HL, Wang ZJ. Study on the preparation of calcium carbonate modified diatomite and its adsorption properties. Guangzhou Chemical Industry. 2011, 39(17): 43-46.

[12] Aldegs Y, Khraisheh MA, Tutunji MF. Sorption of lead ions on diatomite and manganese oxides modified diatomite. Water Research. 2001, 35(15):3724-3728.