Stabilization effect on heavy metal contaminated soil of Pb, Zn, Cd using bentonite and attapulgite

Hong-Jiang Guo[1, 2], Chun-Ping Li[1, †], Yong Ye[3] and Ai-Qin Wang[2]

[1]*Beijing Building Materials Academy of Science Research / State Key Laboratory of Solid Waste Reuse for Building Materials, Beijing, China;*
[2]*Zhongyuan University of Technology, Zhengzhou, Henan Province, China;*
[3]*Beijing Eco-island Science and Technology Co., Ltd, Beijing China.*
[†]*E-mail: lichp-xj@163.com*

The experiment was carried out on the stability of heavy metals with the high concentration of heavy metal solution, which was prepared by absorbing bentonite and bentonite. The results show that after adding a certain amount of adsorption material in heavy metal solution, bentonite, concavo convex rod soil and heavy metal ion solution after reaction, on Pb and Cd adsorption rate can reach more than 80%; scanning electron microscope results show that a large amount of metal ions adsorbed on the surface of the adsorption material. Further with the aid of X ray diffraction analysis, Bentonite, attapulgite and heavy metal ions to generate $CdCO_3$, $PbCO_3$ and $PbSiO_3$ and other new materials. The experimental results show that bentonite and attapulgite can be used in the treatment of heavy metal pollution.

Keywords: Heavy Metal; Configuration Solution; Scanning Electron Microscopy (SEM); XRD Spectrum.

1. Introduction

Along with our country's comprehensive national strength and social development, the development of the past do not attach importance to the environment, bring a lot of environmental pollution problems, the soil heavy metal pollution problem has attracted much attention[1], the main cause of soil pollution is the unscientific industrial and agricultural production[2]. Pb, Zn, Cd and as in the soil can be found in the soil for a long time because of the adsorption of soil colloids and particles. Heavy metals are difficult to be absorbed by other plants, it is also very difficult to be degraded by microorganism, other heavy metals in the soil will be bio-accumulated through the food chain [3], eventually to the human life safety hazard therefore, soil heavy metal pollution control has been urgent [4].

Soil pollution remediation involves a variety of physical, chemical and biological remediation techniques, such as: adsorption, microbial remediation, electrokinetic remediation, phytoremediation, cement solidification/stabilization treatment, etc [5-9].adsorption materials mainly include physical adsorption and chemical adsorption. When the surface of the adsorbed molecules and the adsorption materials are mainly dominated by van Edward force and hydrogen bond, the adsorption is physical adsorption. In the presence of electron exchange and transfer between the adsorbed molecules and the adsorption materials, the formation of chemical adsorption. In the presence of electron exchange and transfer between the adsorbed molecules and the adsorption materials, the formation of chemical adsorption. The existing commonly used in heavy metal Pb, Zn, Cd on the adsorbent adsorption mainly including activated carbon, graphite[10-11], clay[12-13], chitosan, fly ash. Seaweed [14], humic acid, agricultural waste, resin, bentonite [15] and microbial [16].

In this experiment, we adopt the bentonite, and attapulgite to stabilize the high concentration of heavy metal solution [17], we use precipitation rate, morphology of scanning electron microscopy (SEM) and X-ray diffraction (XRD) as the index analysis agent of heavy metals Pb, Zn, Cd stabilizing effect and analysis the stability mechanism, with a view to lay the foundation for Pb, Zn and Cd contaminated site remediation.

2. Materials and Methods

2.1 *Adsorption material*

Reagent for preparation of heavy metal solution, Pb $(NO_3)_2$, Zn $(NO_3)_2 \cdot 6H_2O$, Cd $(NO_3)_2 \cdot 4H_2O$, Manufacturer is the National Pharmaceutical Group Chemical Reagent Co., Ltd, standard for analysis of pure. Bentonite and attapulgite are used for commercial purposes.

2.2 *Heavy metal solution*

Reference to the national standard of soil quality three, use $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and respectively by leaching concentration of 2 times, 10 times, 20 times and 100 times to configure high risk of heavy metals solution, the solution concentration respectively:Pb:1032mg/L,4998 mg/L,10097 mg/L,49000 mg/L;Zn:1021 mg/L,5110 mg/L,10188 mg/L,25400 mg/L;Cd:26 mg/L,62 mg/L,146 mg/L,1143 mg/L.

The bentonite and attapulgite of 1g were dissolved in the water in the water according to the ratio of solid to liquid of 1:15. with a glass rod stirring constantly become turbid liquid, turbid liquid is added to the heavy metal solution, then with deionized water Constant volume 50mL,static set 24 hours,

from the upper clear liquid,0.45um membrane, and the filtrate was used to determination of heavy metal leaching, concentration and pH value. collection the agent of heavy metal precipitates formed by the reaction, the precipitate with deionized water to clean the 3 to 5 times, the sediment into the culture dishes, in a freezer freeze drying, determination of sediment mineral composition and microscopic characteristics etc..

2.3 *Determination index and method*

The pH value in the solution and supernatant was determined by electric potential method [18]. The total amount of heavy metals in the solution and supernatant was determined by ICP-AES (ICP 6300, Thermo) [19]. The phase composition and microstructure of precipitates were analyzed by XRD diffraction (Japan D/max-2200) and electron microscopy (DXS-1P) [20].

3. Results and Discussion

3.1 *Results and analysis of pH in supernatant fluid*

The bentonite and attapulgite were added to the prepared heavy metal solution, the adsorption of heavy metal ions on Pb, Zn, Cd adsorption effect and pH value changes were found in the following table.

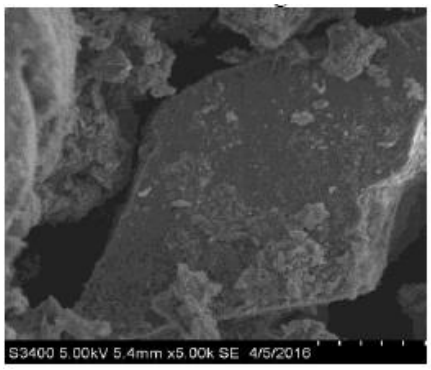
From the Table 1: Different concentration of heavy metal ion solution after adding adsorption bentonite and attapulgite, the supernatant of Pb, Zn, Cd concentration decreased significantly, with increasing the adsorption capacity of heavy metal material particle concentration increases. The bentonite on Zn and Cd, the adsorption rate reached more than 90% and 80%, at the same time has a good adsorption capacity for Pb, attapulgite on Pb, Cd ions also has good adsorption effect, especially on the Cd ion adsorption, the adsorption rate reached 80%,but a poor adsorption of Zn. With bentonite, attapulgite supernatant pH increased to varying degrees, from acid to weak acid or weak alkaline.

Table 1. Test results of heavy metal supernatant after adding adsorption material

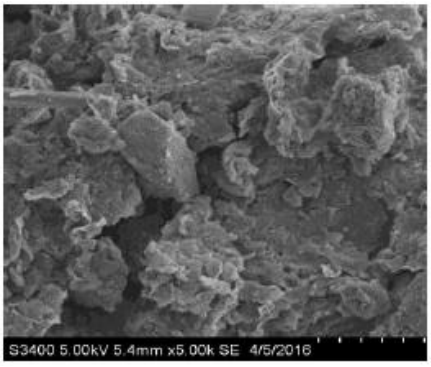
			The concentration of the original solution(mg/L)	Concentration of supernatant after adding reagents(mg/L)	Adsorption rate (%)	PH of the original solution	The PH of supernatant after adding the reagent	The Change of pH value
Bentonite	Pb	Pb(1)	1032	19.57	98.10	5.69	8.50	+2.81
		Pb(2)	4998	478.26	90.43	5.65	6.39	+0.74
		Pb(3)	10097	2274.43	77.47	5.55	5.98	+0.43
		Pb(4)	49000	18613.72	62.01	5.41	5.56	+0.15
	Zn	Zn(1)	1021	5.02	99.51	5.32	6.97	+1.65
		Zn(2)	5110	128.07	97.49	4.76	6.28	+1.52
		Zn(3)	10188	284.91	97.20	4.58	6.14	+1.56
		Zn(4)	25400	714.80	97.19	4.19	6.90	+2.71
	Cd	Cd(1)	26	3.14	87.92	6.99	9.41	+2.42
		Cd(2)	62	11.50	81.46	6.64	9.36	+2.72
		Cd(3)	146	16.08	88.99	6.43	9.27	+2.84
		Cd(4)	1143	11.98	98.95	6.09	7.28	+1.19
Attapulgite	Pb	Pb(1)	1032	1.09	99.89	5.69	7.52	+1.83
		Pb(2)	4998	23.13	99.54	5.65	6.24	+0.59
		Pb(3)	10097	387.28	96.16	5.55	5.73	+0.18
		Pb(4)	49000	14662.88	70.08	5.41	5.56	+0.15
	Zn	Zn(1)	1021	123.89	87.87	5.32	6.77	+1.45
		Zn(2)	5110	1301.95	74.52	4.76	6.23	+1.47
		Zn(3)	10188	2895.19	71.58	4.58	6.11	+1.53
		Zn(4)	25400	8304.10	67.31	4.19	5.87	+1.68
	Cd	Cd(1)	26	0.67	97.43	6.99	7.60	+0.61
		Cd(2)	62	1.84	97.03	6.64	7.56	+0.92
		Cd(3)	146	8.84	93.94	6.43	7.32	+0.89
		Cd(4)	1143	191.70	83.23	6.09	6.59	+0.50

3.2 *The SEM of sediment*

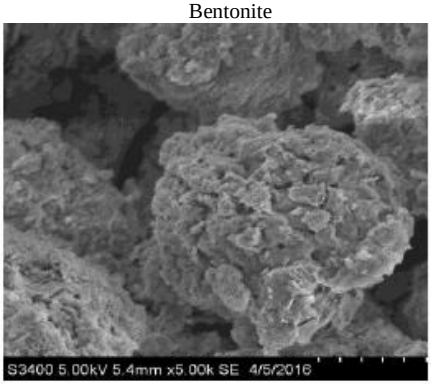
The results of SEM analysis of bentonite and attapulgite and heavy metal reaction were shown in Figure 1.



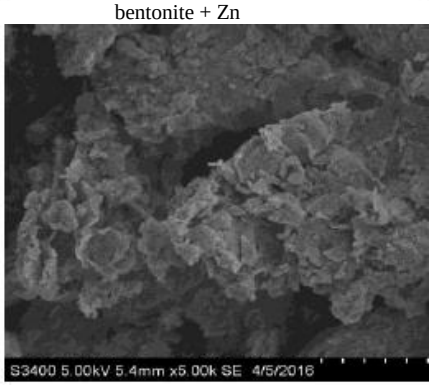
Bentonite



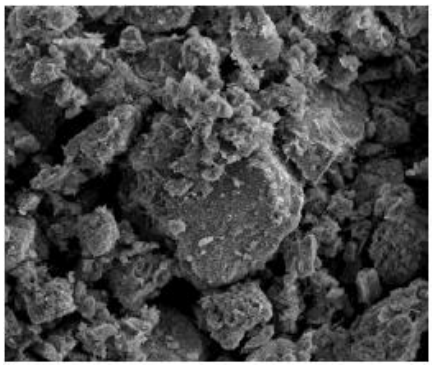
bentonite + Zn



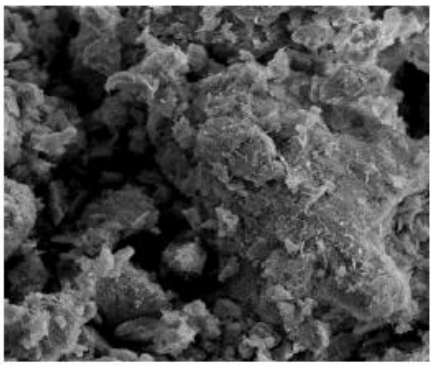
bentonite +Cd



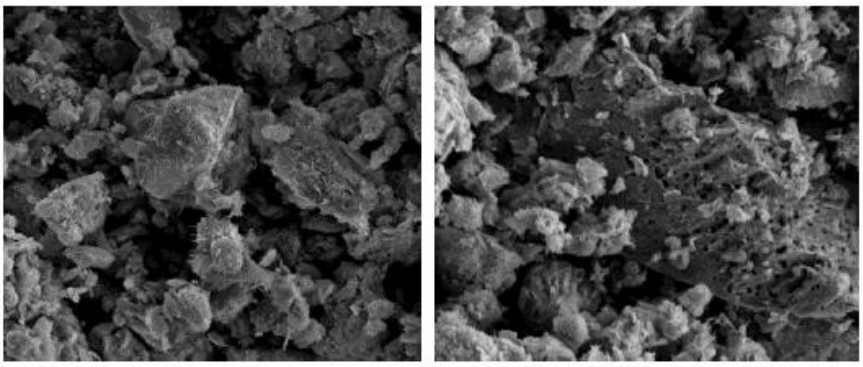
bentonite +Pb



attapulgite



attapulgite + Zn



attapulgite + Cd attapulgite + Pb

Fig. 1. SEM before and after the addition of adsorption materials.

From Figure 1 shows that the surface of bentonite by the plane structure of the original, after the soil particle surface adsorption in solution of Pb, Zn, Cd, the surface of the soil particles into a layered structure, while soil particles become small, increases the soil particle surface, increase the specific surface area of the soil particles. There by increasing the adsorption capacity of bentonite. After dissolving in deionized water, attapulgite surface covered with acicular and flocculent materia, with no added heavy metal ion solution the surface structure of soil particles is distinct. Attapulgite particles have large dense pores to increase the adsorption capacity of metal ions. That is to say bentonite and attapulgite have better adsorption performance on Pb, Zn and Cd.

3.3 *XRD analysis of mixture*

The results of XRD analysis of the mixture of adsorption materials and heavy metal adsorption are shown in Figure 2.

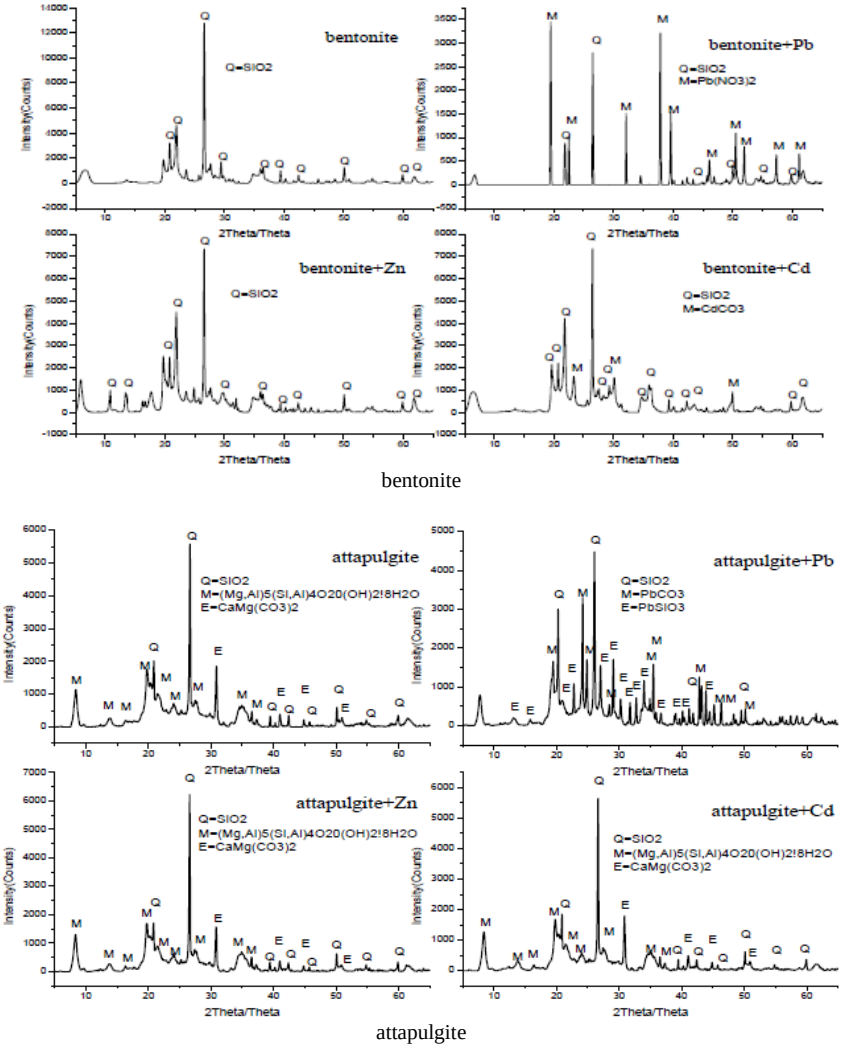


Fig. 2. X diffraction analysis before and after adsorbing material

From Figure 2 shows, bentonite and attapulgite adsorption solution of heavy metal ions and generate $CdCO_3$, $PbCO_3$ and $PbSiO_3$.

3.4 *Effect mechanism of attapulgite and diatomite on heavy metal*

Effects of bentonite and attapulgite on Pb, Zn and Cd, in addition to the physical adsorption of metal ions also accompanied by the new material $CdCO_3$, $PbCO_3$ and $PbSiO_3$ generation. This is due to small soil particle surface functional

groups, in aqueous solution and electrolyte ions in solution occurred ion exchange reaction generated due to the stability of the new compounds.

4. Conclusion

(1)Add a certain amount of bentonite and attapulgite in different heavy metal solution, the reaction of 24h at room temperature, which bentonite, attapulgite of Pb, Zn, Cd adsorption effect were better. In the supernatant pH increase, but changes were smaller. Therefore, in the follow-up on the curing of heavy metal pollution for reusing in should be considered cured pH change and adsorption material surface modification.

(2)In SEM images could be seen bentonite and attapulgite of Pb, Zn, Cd ions were strong adsorption capacity, and with heavy metal ions in aqueous solution mutual effect with new compounds of $CdCO_3$, $PbCO_3$ and $PbSiO_3$ generation.

(3)Effect of bentonite and attapulgite and heavy metal ions, reduction of heavy metal ions in solution by physical adsorption, and thus play a role in the solidification/stabilization of heavy metal ions. At the same time, the water soluble state of bentonite and attapulgite clay and heavy metal ions also by ion exchange generated new compounds solidified heavy metal.

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