CHEMICAL ENGINEERING TRANSACTIONS
VOL. 59, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Zhuo Yang, Junjie Ba, Jing Pan

ISBN 978-88-95608- 49-5; **ISSN** 2283-9216
DOI: 10.3303/CET1759156

Study on Environmental Chemical Behavior and Dust Control of Lead and Cadmium in Atmosphere

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With the development of modern science and technology, environmental problems have gradually become the basic problem of survival and development, especially the arrival of the industrial era, the urban environment has been paid more attention to. After the environment is polluted, the harmful substances in the atmosphere are increased, and the toxic heavy metals made damages to the environment by a series of reactions, and even did harm to human body. In this paper, a southern city of China is taken as the research base to carry out the research on the morphology and polluting characteristics of Lead and Cadmium in the atmospheric pollution and dust. Such work provides basic environmental survey data for the pollution status, air quality, environmental pollution degree and so on, and provides scientific basis for the regional environmental pollution prevention and control policies, which has a positive effect on the environment protection.

1. Introduction

Environment is the basis for the survival and development of human beings and all other lives. Since 1950s, with the development of industry, the urban environment has been widely affected by human activities, and the environmental problems caused by nature and human activities have been paid more and more attention to. As a part of the atmospheric environment system, the air has a very big impact on the environment and the ecological system, and the trace heavy metal elements in the atmosphere have direct and indirect effects on humans and animals and plants. Atmospheric dust particles contained toxic heavy metals, and because of its small size, it can enter the lower respiratory tract of the human body, deposited into the lungs, and even through the alveoli and enter the blood, doing great harm to the human body (Abhishek, et al., 2016). Atmospheric dust will enter the soil by precipitation and dry deposition, which is absorbed by the plants, and enters the food chain, to cause harm to human. Since 70s, environmental scientists have recognized that the biological toxicity of heavy metals is not only related to its total amount, but also determined by its distribution to a larger extent. As a result, the research on atmospheric dust is a hot topic in the field of environment, geology, chemistry and so on multidisciplinary field in recent years.

2. Research status

At present, the methods of determination of trace Cadmium and Lead are as follows: atomic absorption spectrometry, spectrophotometry, atomic fluorescence spectrometry, ICP and so on. In the determination of trace amounts of Cadmium and Lead, atomic absorption spectrometry (AAS) is the main analytical method, including flame atomic absorption spectrometry and graphite furnace atomic absorption spectrometry (Yan, et al., 2014). Some scholars studied the sulfhydryl cotton enrichment and separation method for determination of Cadmium by flame atomic absorption spectrometry. The method determines that the sensitivity of Cadmium is 3.95 μg/L, which is ten times as it is without enrichment and separation with sulfhydryl cotton, simple in method and good in selectivity. Some scholars used sulfhydryl cotton for preconcentration, and determined the trace Cadmium in sodium metaborate, anhydrous sodium acetate, anhydrous sodium carbonate, disodium hydrogen phosphate and so on reagents by Flame Atomic Absorption Spectrometry. The method is simple and rapid, and the standard deviations determined were less than 4.61%.

Please cite this article as: Ziying Sun, 2017, Study on environmental chemical behavior and dust control of lead and cadmium in atmosphere, Chemical Engineering Transactions, 59, 931-936 DOI:10.3303/CET1759156

Photometric method is mainly divided into the following categories: porphyrin reagent spectrophotometry, triphenylmethane reagent spectrophotometric analysis, azo reagent spectrophotometry, nitrogenous reagent spectrophotometry, fluorescence spectrophotometry, kinetic spectrophotometry, dual wavelength spectrophotometry, centrifugal photometric, and Kalman filtering phase separation spectrophotometry analysis method. Hydride generation atomic fluorescence spectrometry in recent years is also quite perfect and commonly used test method. Wu Cheng determined Cadmium in soil under acidic condition. It can reduce the influence of the coexisting elements in soil on the determination of Cadmium after adding suitable reagents. The analysis results basically coincide with the guaranteed value, and the relative deviation is less than 10% (Liu, et al., 2015). This method has high sensitivity, precision and accuracy. To sum up, in these several kinds of analytical methods, the cost of photometric method is the lowest, the sensitivity is high, but the determination is easy to be interfered by the coexisting ions, and the detection limit is higher. The interference of Cadmium and Lead determination by atomic absorption spectrometry is small, the operation is simple, and the detection speed is fast. However, the flame atomic absorption spectrometry detection limit is high, which can only reach μg/mL level (Hassan et al., 2015). As a result, when the Cadmium and Lead content contained in the samples is low, it is necessary to determine it with sulfhydryl cotton or other method for pre enrichment and separation.

3. Research methods

3.1 Experimental instruments and reagents

Table 1: Experimental instrument

Equipment name, type, and precision	Manufacturer
Water bath thermostat (SHA-C)	Jintan Huafeng Instrument Co., Ltd.
KR adjustable electric heating plate	Yancheng Scientific Instrument Factory
Electric centrifuge (80-2)	Shanghai Yuefeng Instrument Co., Ltd.
Electronic balance (AL104, 0.0001g)	Mettler - Toledo Instruments Co., Ltd.
Dual channel atomic fluorescence Spectrometer (AFS-2202, 1%)	Beijing Haiguang Instrument Co., Ltd.
Flame atomic absorption spectrophotometer (GGX-6, 1%)	Beijing Geological Instrument Factory
Electrothermal constant temperature drying box (DG-250E)	Chengdu Hongxing Electric Oven Factory
Digital acidity meter (PHS-3C, 1%)	Jiangsu Electronic Analysis Instrument Factory
Visible spectrophotometer (721, 1%)	Shanghai Analytical Instrument General Factory
Magnetic stirrer	Shanghai Kangyi Instrument Co., Ltd.
Agate mortar	
40, 80, and 200 mesh nylon screen	
A variety of specifications, such as tubes, bottles, beaker and other glassware	

Table 1 shows the Experimental instrument. Main reagents: hydrochloric acid, hydrofluoric acid, nitric acid, perchloric acid, sulfuric acid, magnesium chloride, sodium acetate, hydroxylamine hydrochloride, hydrogen peroxide, potassium borohydride, potassium hydroxide, cobalt sulfate, thiourea, sodium hydroxide, sodium pyrophosphate, anhydrous sodium sulfate, potassium dichromate, sulfite iron, phenanthroline, silver sulfate, dioctyl phthalate pH standard reagent, phosphate mixture pH reagent, Borax pH standard reagent, sulfosalicylic acid, and ammonia (the forefront drug reagents were analytically pure). Among them, the metal Cadmium (spectral purity) is provided by Tianjin Fine Chemical Research Institute, and nitrate, guaranteed reagent (GR) is supplied by Shenyang Chemical Reagent Factory (Rivelino et al., 2012).

3.2 Preparation and storage of Cadmium standard solution

Electronic balance is used to accurately weigh 0.5000 grams of Cadmium (pure spectrum), dissolved in 25 mL (1+5) HNO_3 (GR), micro dissolved, and after cooling, moved into a 50 mL volumetric flask and diluted with deionized water and set the volume. This solution is the standard stock solution with Cd concentration of 1.000mg/mL. When in use, dilute it to the required concentration as needed.

3.3 Sampling and preparation of atmospheric dust samples

Atmospheric dust samples are taken from the natural atmospheric dust in the urban and rural areas. In order to be able to reflect the direct impact of atmospheric dust on the human body, we choose the sampling height of 1.5 to 2 meters (the general human breathing height) (Tang, et al., 2016). In order to eliminate the metal pollution that maybe caused in the sampling process, we use brush sweeping the falling dust on the wooden doors and windows, glass surface and other wooden objects with no paint falling, and the samples will be placed in polyethylene plastic sampling bag, and we tie the bag to prevent contamination. The collected samples were naturally dried and it removed rare matter, and then grinded by agate mortar in 200 mesh sieve, and the sample were stored in plastic flasks after being fully mixed.

3.4 Analysis and test method

Determination of the total Cadmium content in the dust fall samples: the samples were digested with HCl-HNO3-HF-HCl mixed acid system and made into a solution. Cadmium standard solution with 1.000mg/mL concentration was diluted to the standard solution of Cadmium of 100.0ng/mL, and Cadmium standard solution was used. The content of Cadmium in the standard solutions is determined by atomic absorption spectrometry, drawing standard curve. At the same time, we determined the absorbance of dust fall samples, and obtained the Cadmium content in soil samples by using the standard curve method. Table 2 shows the working conditions of atomic absorption spectrophotometer

Table 2: Working conditions of atomic absorption spectrophotometer

Determination wavelength (nm)	Lamp current (mA)	Slit width (mm)	Fuel assist ratio	Burner height (mm)
228.8	3.5	0.4	1:7	10

Determination of total Lead content in atmospheric dust fall samples: the atmospheric dust samples were digested with HCl-HNO_3-HF-$HClO_4$ mixed acid system and made into a solution. Standard Lead solution was configured with Lead standard kinds solution. We determined the content of Lead in the standard solutions by atomic absorption spectroscopy, drawing the standard curve. In the meanwhile, we determined the absorbance of dust fall samples, and obtained the Lead content in atmosphere samples by using the standard curve method. Table 3 shows the working conditions of atomic absorption spectrophotometer

Table 3: Working conditions of atomic absorption spectrophotometer

Determination wavelength (nm)	Lamp current (mA)	Slit width (mm)	Fuel assist ratio	Burner height (mm)
283.3	4.0	0.4	1:7	8

Determination of dust fall samples pH value: weigh the atmospheric dust sample 1g, add distilled water 5mL, namely soil water mixing ratio of 1:5, stir the atmospheric dust suspension with a magnetic stirrer for 1min, place it for 30min to make it clarify, and use a pH meter to determine the pH value.
Determination of humic substances in dust samples: the method of potassium dichromate volumetric method was used to determine the content of humus in the dust fall samples. The principle for using potassium dichromate method (external heating) for the determination of humus content in samples of atmospheric dust is: at the temperature of 170-180 DEG C, dust organic carbon has redox reaction with overdose $K_2Cr_2O_7$-H_2SO_4 oxidation solution. The reaction is as follows:

$$3C + 2K_2Cr_2O_7 + 8H_2SO_4 = 2Cr_2(SO_4)_3 + 2K_2SO_4 + 8H_2O + 3CO_2 \uparrow \quad (1)$$

The residual quantity of $K_2Cr_2O_7$ is conducted with titration with ferrous sulfate standard solution. And through the actual consumption of $K_2Cr_2O_7$, the content of organic carbon is obtained. The reaction formula of $FeSO_4$ solution titration is shown as follows:

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O \quad (2)$$

The steps for using potassium dichromate method (external heating) to determine the humus content in samples of atmospheric dust are: weigh the mixed dust sample 0.1000g over 200 in 100mL flask, add a little powdered silver sulfate, absorb 10.00mL (0.068mol/l) $K_2Cr_2O_7$-H_2SO_4 solution and add into the three angle bottle, mount on the condenser tube, heat it on the heating board to boiling, and keep boiling 5±0.5min (Susana et al., 2017). After the cooking is finished, the triangular bottle is taken off for cooling for a short time, and the inner wall of the condensing pipe and the outer wall of the bottom end are rinsed with water, and the

washing liquid needs to flow into the original triangle bottle. Add 2 to 3 drops of Phenanthroline and titrate the remaining $K_2Cr_2O_7$ with 0.1mol/$FeSO_4$ standard solution. The process of color change is orange-yellow to blue-green, and to brown-red.

The content of Cadmium in the dust fall samples was measured, and the five kinds of atmospheric dust were extracted by Tessier extraction method:

Exchangeable state: take 1.0000g dust samples accurately, add 10mL1.00mol/l$MgCl_2$ solution, place in 25 degrees' constant temperature water bath, and continuously oscillate for 2h, and conduct centrifugation for supernatant.

Carbonate binding state: the 10mL1.00mol/lNaAc solution in the residue was transferred to HAc to pH=5.0, place for 8h, and then continuously oscillate for 2h at a constant temperature of 25 DEG C in the bath, and conduct centrifugation for supernatant.

Fe and Mn oxide binding state: take 10mL0.25mol/l$NH_2OH{\cdot}HCl$ in the residue, place at a constant temperature of 95 DEG C in the water bath, intermittently oscillate for 3h, and after the cooling, conduct centrifugation for supernatant.

The extracted solution was transferred into a 50mL volumetric flask, and then the content of the solution in the solution was determined by atomic fluorescence spectrometry. Table 4 shows the Working conditions of atomic fluorescence photometer

Table 4: Working conditions of atomic fluorescence photometer

Photomultiplier tube negative pressure (V)	Atomization temperature (DEG C)	Height of atomization (mm)	Light flow (mA)	Carrier gas flow rate (mL/min)	Shielding gas flow (mL/min)
280	200	8	60	400	1000

3.5 Leaching experiment

A glass tube with a diameter of 5.0cm and a length of 20.0cm was used as the leaching column, and it was added with the atmospheric dust column 0.5g. There is a hole at the bottom of the leaching column, which can be used to filtrate the leachate. The leachate is contained by acid burette, placed above the column leaching, controlling the leaching liquid flow. The leaching solution was prepared and the pH value of the leachate was adjusted, and the leachate was leached with different pH value of the leaching solution and distilled water, respectively. The total amount of leachate was liquid to solid ratio of 30:1, each sample collected the leaching solution after the leaching for 2, 5, 10, and 30 hours, and the Cadmium in the leaching solution was determined by atomic fluorescence spectrometry.

4. Results

The nitrogen oxides and sulfur dioxide produced by human activities are discharged into the environment, which combine with the water vapor in the atmosphere to form nitric acid and sulfuric acid. When these pollutants fall down with the precipitation, they will form acid rain with low pH value, and when the pH value is below 5.6, it will cause acid rain pollution. China's acid rain pollution showed an accelerating trend in development from 80s, and the range of acid rain pollution gradually developed from south to north and from the city to the rural areas. With the deposition of acid rain, the dust in the atmosphere will be brought into the soil, and the speciation of some metal elements in the dust can be changed after entering the soil, and thus having impact on the environmental chemical behavior of these elements.

The experimental data of Cadmium leaching out of the polluted air samples after different acid rain and acid rain leaching are shown in the figure 1 and figure 2.

Lead leaching quantity also reached the same data and trend graph. As a result, comprehensively considering the above leaching experiment data, experimental conditions and characters of dust, in the experiment using the leaching solution for the leaching, the trend of leaching quantity of Cadmium and Lead with time can be explained as follows: during the first 2 hours in the experiment conducted, the leaching liquid continues to penetrate in the dust samples, and it has chemical changes with parts of dust fall in the dust samples, so a certain number of the Cadmium and Lead are leached out. But at this time, the leachate did not penetrate all the dust samples, so the Cadmium and Lead leaching rate has not reached the maximum value. With the continuing of leaching, leaching liquid continuously penetrating into the soil has sufficient quantity that it can fully react with dust samples. That is to say, in 2~5 hours, the leaching of Cadmium and Lead has a sharp increase and reaches the maximum of the Cadmium leaching amount in a single time period. Since then, due to the full reaction after 2~5 hours, the content of Cadmium and Lead in the dust samples that can fully react with leaching solution and being leached out is lower and lower (Pedro, et al., 2016). In 5~10 hours, 10~20

hours, 20~30 hours three periods, Cadmium and Lead leaching quantity decreased in turn, and the leaching quantity value greatly reduced compared to that in 2~5 hours. The changing trend of Cadmium and Lead leaching quantitywith time is the performance of reaction of leaching solution with Cadmium and Lead in the dust samples. Accordingly, in this experiment, the reaction between the leachate and Cadmium and Lead in dust samples can be divided into three stages, and the time intervals of the three stages are 0~2 hours, 2~5, and 5~30 hours. Cadmium and Lead leaching amount was mainly distributed in 0~2 hours and 2~5 hours, namely the first and second stage of the reaction.

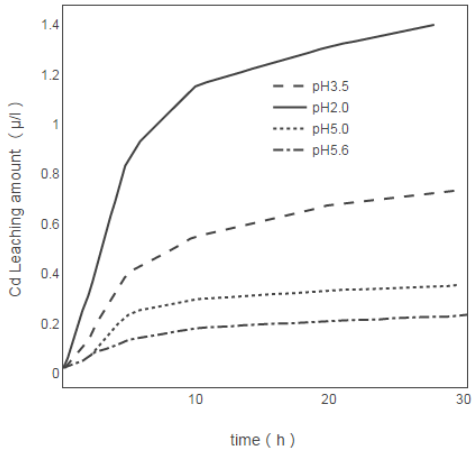

Figure 1: The time of a different pH value of the same atmospheric dust fall samples not contaminated-Cd leaching amount

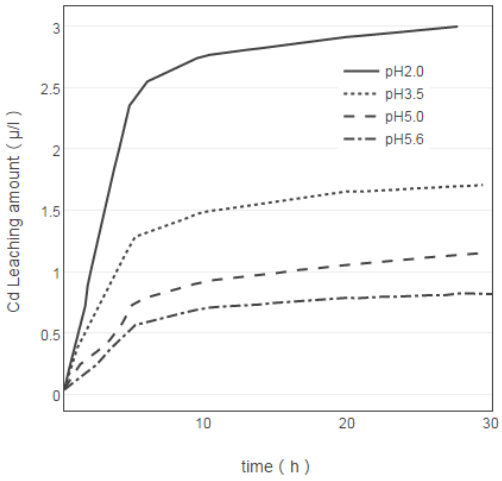

Figure 2: The time of a different pH value of the same atmospheric dust fall samples contaminated-Cd leaching amount

5. Conclusion

This paper collects the dustfall samples in an area in the south, makes use of arithmetic average value method of samples proposed by Hu Hanming to calculate the background value of Lead in the region, and takes the background value as the basis for judging whether the atmosphere in the region is polluted by Cadmium and Lead. Finally, we draw a conclusion that, the content of Cadmium and Lead in the atmospheric dust samples collected from the Industrial Development Zone, mining factory or heavy traffic highway main road is greater than the background value. And the atmospheric dust is greatly affected by industrial production, transportation and other activities. The pollution of Cadmium and Lead in the atmospheric dust is

closely related to the surrounding environment of the sampling points. That is to say, the more serious the environmental pollution around the sampling points, the more serious the Cadmium and Lead pollution of the collected dust fall samples. It also shows that the pollutants emitted by human activities such as industrial production are the source of atmospheric dust pollution. At the same time, through the leaching experiment, it can be concluded that Cadmium and Lead in dust fall easily migrate under the action of acid rain, then enter the ecosystem, and do harm to the environment and body health.

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