Asian Journal of Chemistry; Vol. 26, No. 1 (2014), 21-24

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.15206

Effects of Municipal Sludge and Wheat Straw Pyrolysis on Changes of Shapes of Heavy Metals

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Received: 25 January 2013; *Accepted*: 29 April 2013; *Published online*: 26 December 2013; AJC-14464

Conditions of municipal sludge and wheat straw pyrolysis, that was the temperature and proportioning, were changed by experiment. The five-step continuous extraction put forward by tessier was adopted to extract numbers of heavy metals including Cu, Zn, Pb, Cd, Cr, Ni and different kinds of shapes in the carbon powder by pyrolysis. Perkin elmer analyst 700 atomic absorption spectrometer was adopted to detect the content of extraction and the change regulation of different kinds of shapes under sludge and wheat straw pyrolysis was examined. The experimental results shown that the formation of carbon powdered by pyrolysis was compared with sludge before pyrolysis.

Keywords: Sludge, Wheat straw, Pyrolysis, Heavy metals, Shapes.

INTRODUCTION

Besides the traditional use of land, the compost[1] and the green farming, the resource utilization of sludge could also be prepared for building materials including ceramic site, ceramic tile, cement, biochemical fiber board and active carbon[2-3]. Municipal sludge always contains large quantities of heavy metals which is easy to pollute the soil, ground water, animals and plants. Thus to prevent and control the problem is high on the agenda. The method of certain proportion of maize straw was added to the watery sludge and the active carbon was prepared by pyrolysis was adopted by Zhang *et al.*[4,5] to reduce the problems of secondary pollution and the high cost which occurred to the environment led by the traditional method of preparing the sludge activated carbon[6]. At the same time, it could make full use of the heat of wheat straw and improve the utilization. The problem concerning the distribution and morphology of heavy metals in the sludge[7], the stability of heavy metals[8] the deposition and bioavailability of heavy metals in the soil has attracted great attention.

The five-step continuous extraction[9] put forward by Tessier was adopted to offer the analyses of the morphology of heavy metals to the carbon powder from sludge and wheat straw pyrolysis. The heavy metals were classified as five kinds, such as exchangeable form, bound to carbonates, Fe-Mn oxide form,sulfides and bound to organic matter and residual form. The previous three kinds were of bad morphological stability and they were easy to be absorbed and utilized by plants. The bioavailability of sulfides and bound to organic matter was very complex. Part of organic molecules degraded to dissolve out part of heavy metals and may do harm to the environment, but this was often considered as biologically inactive part. The residual form which was hard to release under the normal conditions in the environment and was stable in the residues in the long term existed in silicates and the primary and secondary mineral lattices biologically inactive part. The pollution of heavy metals mainly came from the previous three kinds of forms.

EXPERIMENTAL

Experiments with carbon powder formed by the pyrolysis under the predetermined temperature after the mixture of certain proportion as the raw sludge and crushing stalk, Then the carbon powder was grinded by agate mortar and dried, preserved and backed up after mixing with 200 mesh nylon sieve.

The chemicals used as analytical reagent, mainly including concentrated nitric acid, perchloric acid, chlorine hydride, magnesium chloride, hydroxylamine hydrochloride, sodium acetate, acetic acid, ammonium acetate and 30 % H_2O_2, *etc.*

A constant temperature bath oscillator, vacuum suction pump, table top centrifuge, Perkin Elmer analyst 700 atomic absorption spectrometer and glass wares include beakers, reagent bottles, cylinders, volumetric flasks, pipets, glass rods, funnels of various types. Experiments with glass and plastic wares were soaked in 14 % HNO_3 overnight and they were washed by deionized water.

Experiment of municipal sludge and wheat straw pyrolysis: Corn straw to dry weight ratio of 0, 10, 30, 50 % respectively was added to the raw sludge, the 40 g was added to a custom-made quartz glass tube after mixed evenly and were installed in the tubular furnace of the temperature less than 100 °C, finally, the carbon powder was achieved after being heated under the preset temperature (600, 700, 800 °C) for 0.5 h.

Extraction of different morphology of heavy metals: The five-step continuous extraction[9] put forward by tessier was adopted to extract various kinds of the morphology of heavy metals from samples. Sequential extraction procedure of heavy metals was as follows:

(1) Exchangable form (M1): 1 g of dry sludge were measured and placed in the 20 mL centrifuge tube and the solution of 8 mL $MgCl_2$ were added. The manual concussion for 1 h under the conditions of 25 °C, was centrifugated for 20 min (2500 rpm), the supernatant was removed, placed in a conical flask to nitrification, the lower solid was washed, centrifugated, the liquid water was discarded and the lower solid was separated.

(2) Bound to carbonates (M2): The lower solid was added to the 1 mol/L sodium acetate (8 mL) solution. The manual oscillation for 6 h at room temperature, was centrifugated for 20 min (2500 rpm). The supernatant was removed, placed in a conical flask for nitrification, the lower solid was washed, centrifugated. The liquid water was discarded and the lower solid was kept.

(3) Fe-Mn oxide form (M3): The lower solid was added to the 1 mol/L 8 mL $NH_2{\cdot}OH$ HCl solution and was kept under the conditions of 96 °C, at the same time was shook manually for several times and centrifugated for 20 min (2500 rpm). The supernatant was removed, placed in a conical flask for nitrification. The lower solid was washed, centrifugated, the liquid water was discarded and the lower solid was separated.

(4) Sulfides and bound to organic matter (M4): The lower solid was added to the 8 mL 0.02 mol/L HNO_3 solution and 5 mL 30 % H_2O_2 (pH = 2) solution, the manual intermittent concussion for 4 h under the conditions of water bath of 85 °C, 2 mL ammonium acetate were added by manual intermittent concussion, was shook for 0.5 h under the conditions of water bath of below 85 °C, was centrifugated for 20 min (2500 rpm). The supernatant was removed, placed in a conical flask for nitrification, the lower solid was washed, centrifugated, the liquid water was discarded and the lower solid was separated.

(5) The residual form (M5): The lower solid and 1 mL concentrated HNO_3 were added to the beaker, were heated to nearly dry. The operation was repeated many times until the solid was white. 2 % small amounts of dilute HNO_3 were added to thermal dissolution, had constant volumes in a 50 mL volumetric flask.

One mL HNO_3 was added to the extract after each step of the experiment of centrifugal filtration under the volumetric determination. Ten mL ultrapure water was added to residues obtained from every steps, the oscillation for 10 min at room temperature, centrifugated for 10 min and 3000 rpm, then the solution was removed, could enter the next step after repeating 2 times. Glass and plastic containers used for measuring the heavy metal content were soaked in 20 % HNO_3 solution for 24 h, then were used after being washed by the deionized water and ultra-pure water for many times.

RESULTS AND DISCUSSION

The content of Cd, Zn, Pb, Cu, Ni and Cr in sludge, wheat straw and various kinds of carbon powders, the results were listed in the Table-1. The content of six heavy metals was arranged from high to low was Cu > Zn > Cr > Pb > Ni > Cd. Because the sewage treatment plant mainly dealt with the wastewater of surrounding residential areas, schools and some small processing plants, the content of Cu and Zn was high in the sludge while the content of other kinds of heavy metals is less.

The residual rate of heavy metals in pyrolytic carbon powders varies on the element and the pyrolysis temperature. For pure sludge, after the heavy metal elements were pyrolyzed at 600 °C, the content of six heavy metals was arranged from high to low was Cu > Zn > Cr > Pb > Ni > Cd. The residual rate of heavy metals was Cr 98.47, Pb 95.11, Zn 94.79, Ni 92.77, Cu 86.22 and Cd 33.69 % respectively. For Zn, Pb, Cr, Ni, Cu, although there were slightly losses after pyrolysis of 600 °C, but a lot of the residual still existed in carbon powders.

Cadmium was greatly influenced by the temperature because the Cd is a volatile metal, but the absolute content was low. A small amount of volatility will lead to a sharp drop in the residual rate.

Distribution of the morphology of heavy metals: Experimental blank solution was as a base fluid, standard solution containing different concentrations of heavy metals was made. Various forms of the content of Cd, Zn, Pb, Cu, Ni and Cr in the extract was measured by using a standard curve. Heavy metal speciation in dried sludge and residues are shown in Figs. 1 and 2.

Effects of the adding numbers of straws on heavy metal speciation: Fig. 1 showed the various kinds of tables from the distribution of heavy metals in the carbon powders under the same pyrolysis temperature varies with changes of the adding numbers of straws. Cd, Zn, Cu, Ni and Cr had the same change

TABLE-1
CONTENT OF HEAVY METALS IN SAMPLES (MG/KG DRY MATERIAL)

Addition of straw %	Pyrolysis temperature (°C)	Cd	Zn	Pb	Cu	Ni	Cr
Pure sludge	Not pyrolysis	8.04	1315.85	37.11	43309.90	25.84	97.00
Pure straw	Not pyrolysis	0.09	1.84	0.83	25.16	2.19	0.16
0	600	2.70	1247.29	35.30	37341.8	23.97	95.52
10	600	2.21	1124.46	32.94	33607.62	20.22	89.34
30	600	2.03	826.7	30.49	30169.86	19.21	77.03
50	600	1.84	585.4	25.95	26468.43	14.75	59.01
30	700	1.13	949.34	37.52	29452.21	24.41	103.8
30	800	0.46	763.77.	39.68	21199.63	20.79	80.75

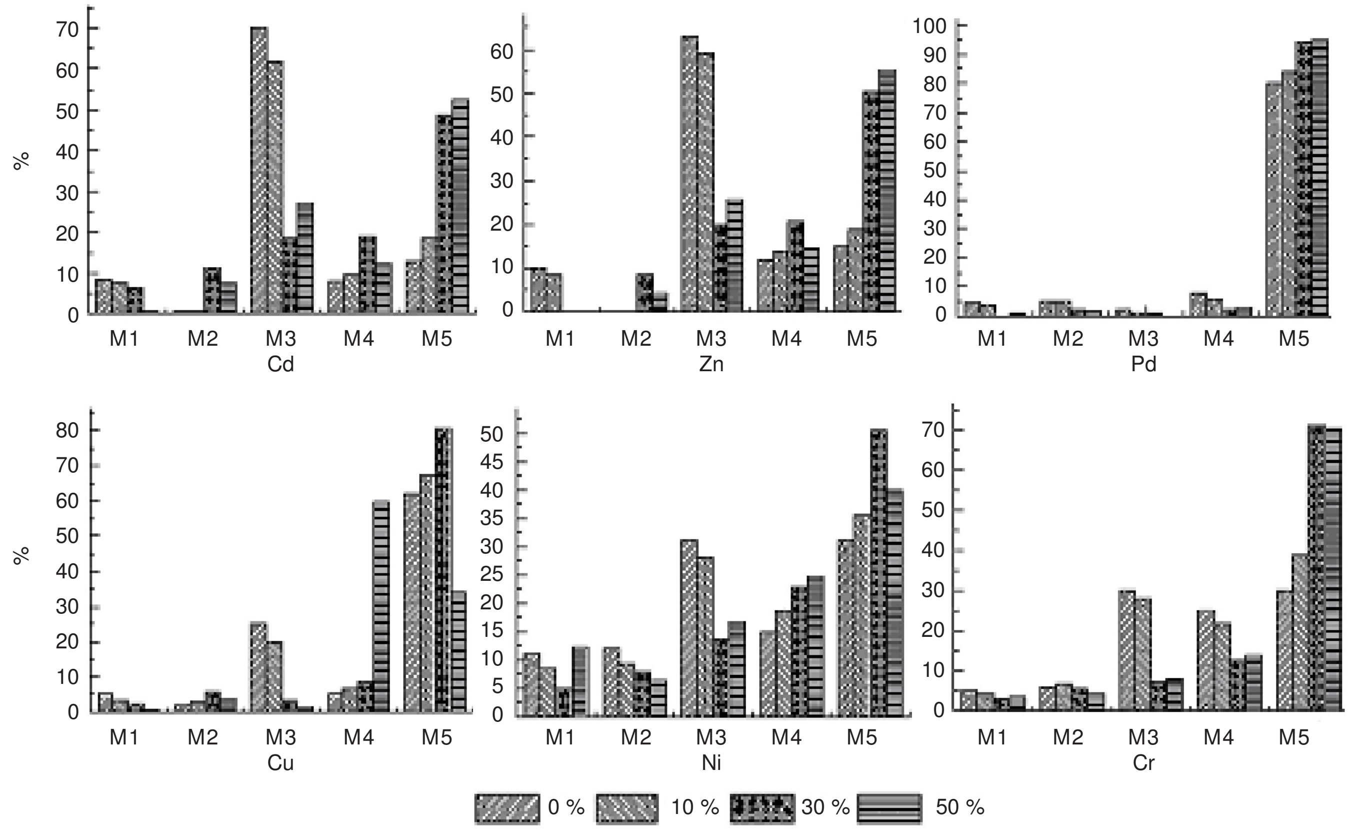

Fig. 1. Distribution of heavy metals in carbon powders in the same straw pyrolysis temperature and different proportions of the straw

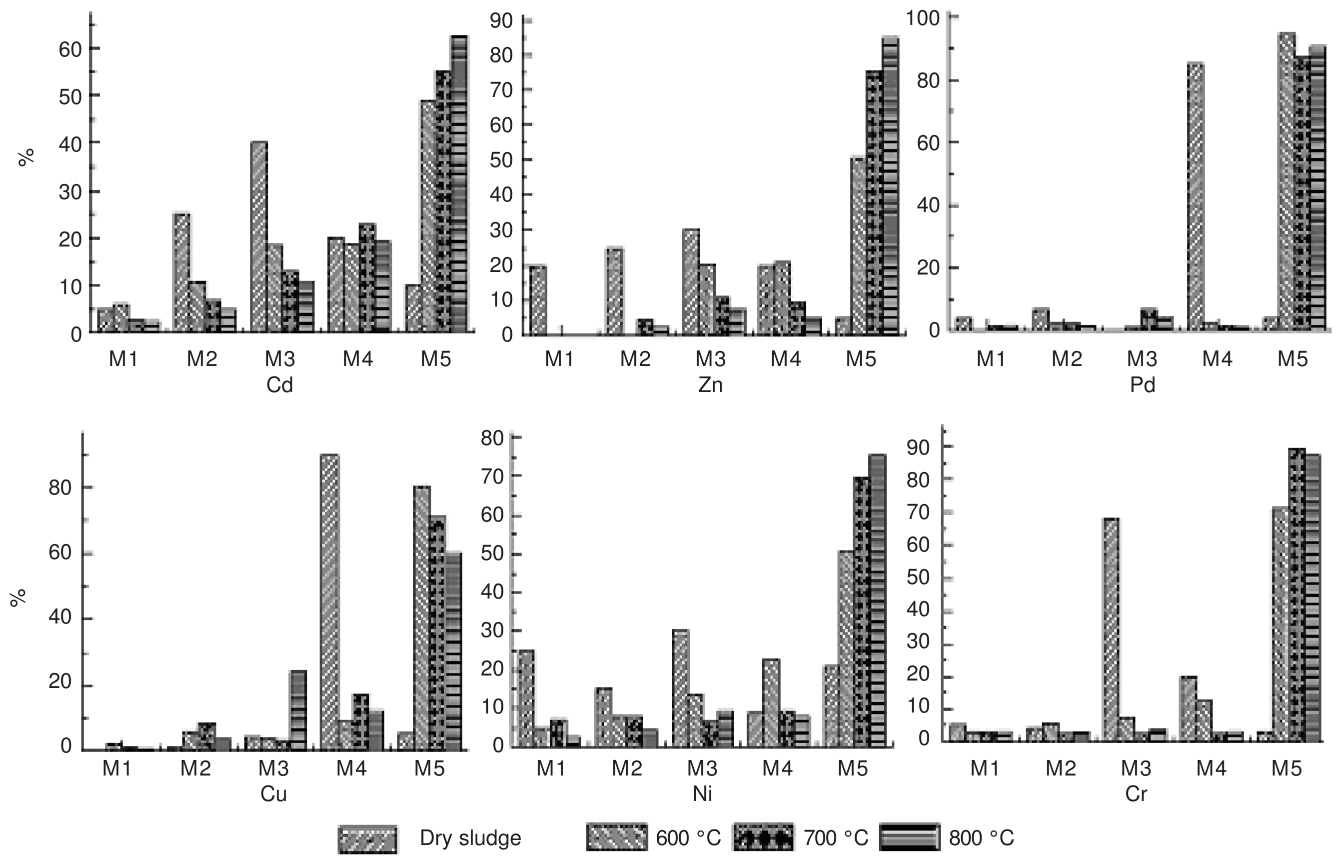

Fig. 2. Distribution of heavy metals in carbon powders in different straw pyrolysis temperature and different proportions of the straw

rule, that was in the process of the adding amount increased from 10 to 30 %. The proportion of the **M4** state and **M5** state of heavy metals increased, while the proportion of the **M3** state declined. But except that the proportion of **M5** state had few reductions, **M4** state and **M5** state among all other heavy metals and the proportion of the sum is almost constant in the process of the adding amount increased from 30 to 50 %. So, the adding amount of straws increased from 10 to 30 %. The stability of all kinds of heavy metals slightly increased, but the content of the stability was nearly the same or had few reductions when the adding amount increased from 10 % to 30 %.

Effects of the pyrolysis temperature on changes of heavy metals: The distribution of dried sludge and the same proportion of adding numbers of straws in the carbon powder under different pyrolysis temperature were shown in Fig. 2. It could be seen that the main existing state of Cd in the dried sludge was **M2**, **M3**, **M4** states, Cr after pyrolysis were mainly around **M2**, **M3** and **M4** states. When the temperature was raised, **M5** state had an obvious increase; the proportion of pyrolytic carbon powder in the steady state was more than 70 %.

Zinc in the dried sludge mainly existed in unstable state mainly because the chemical properties of the element is more active. The proportion of unstable state had an obvious reduction.

Lead mainly existed in **M4** state before pyrolysis and it in the carbon powders mainly existed as stable **M5** state, among which the content reached over 90 %. There were not very obvious changes when the temperature varied from 600 to 900 °C.

Copper mainly existed in **M4** state before pyrolysis and the content occupied 95 % in the dried sludge. Copper mainly existed in stable **M5** state after pyrolysis due to its stable chemical property, the proportion of **M4** state gradually reduced with the rise of the pyrolysis temperature. The **M5** state of Cu had no obvious changes when the temperature varied from 600 to 900 °C.

The five states of Ni in the dried sludge had the uniform distribution and the proportion was nearly the same. Nickel in the dried sludge had the distribution in various states after pyrolysis, but the proportion of **M4** and **M5** states reached 75 %.

Chromium in the dried sludge mainly existed as **M3** and **M4** states, it was around stable **M4** and **M5** states after pyrolysis and the temperature had an increase with the pyrolysis. The proportion of **M4** state had an obvious reduction and the proportion of **M5** state had an obvious increase, **M5** state increased by 3 % before being burnt to 90 %.

Conclusions

(1) The content of heavy metals in the pure sludge from high to low was Cu > Zn > Cr > Pb > Ni > Cd. The residual rate of heavy metals in the carbon powders under pyrolysis varies with elements and the temperature of pyrolysis. Cadmium had greatly affected by the temperature, its decreasing amplitude could reach 66.4 % with the temperature rising to 600 °C.

(2) All metals in the carbon powders after the mixture and pyrolysis of pure sludge and straws convert unstable states into stable states. The adding numbers of straws increased from 10 to 30 %, the stable states of heavy metals slightly increased, but the adding numbers increased from 30 to 50 %. The content of stable states was nearly the same or reduced.

(3) The temperature of pyrolysis had significant effects on the states of heavy metals. When the same ratio changed the pyrolysis, the stable states of four heavy metals *i.e.*, Cd, Cr, Ni and Zn occupy the biggest ratio. Copper and lead stable states occupy the maximum under pyrolysis of 600 °C. But the difference is slight at 700 °C.

(4) The suitable pyrolysis condition is under 700 °C and sludge: straws = 7:3. The stable heavy metals accounted for more than 90 %.

ACKNOWLEDGEMENTS

This article is financially supported by Technology opening fund project of Jiangsu Marine Resources Development Institute (JSIMR10D04) and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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