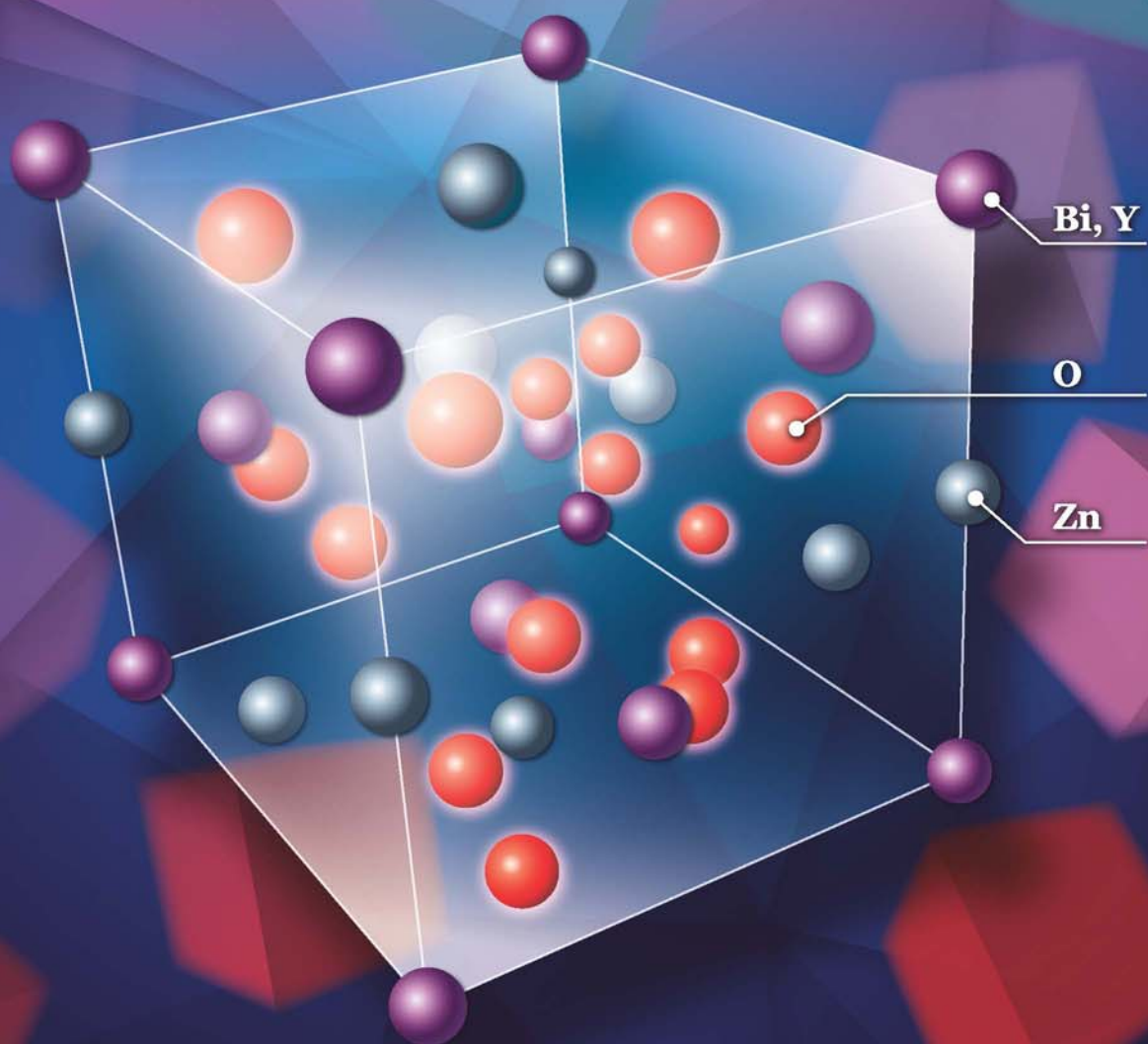


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Antimony leaching release from brake pads: Effect of pH, temperature and organic acids

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ABSTRACT

Metals from automotive brake pads pollute water, soils and the ambient air. The environmental effect on water of antimony (Sb) contained in brake pads has been largely untested. The content of Sb in one abandoned brake pad reached up to 1.62×10^4 mg/kg. Effects of initial pH, temperature and four organic acids (acetic acid, oxalic acid, citric acid and humic acid) on Sb release from brake pads were studied using batch reactors. Approximately 30% (97 mg/L) of the total Sb contained in the brake pads was released in alkaline aqueous solution and at higher temperature after 30 days of leaching. The organic acids tested restrained Sb release, especially acetic acid and oxalic acid. The pH-dependent concentration change of Sb in aqueous solution was best fitted by a logarithmic function. In addition, Sb contained in topsoil from land where brake pads were discarded (average 9×10^3 mg/kg) was 3000 times that in uncontaminated soils (2.7 ± 1 mg/kg) in the same areas. Because potentially high amounts of Sb may be released from brake pads, it is important that producers and environmental authorities take precautions.

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Introduction

Brake pads are consumable parts in cars that cannot be recycled, and deserve special attention because they are released to the environment as particulate matter, so that hazardous substances contained in them contaminate the environment (Iijima et al., 2008; von Uexküll et al., 2005). A component in brake pads that is especially problematic from a toxicological point of view is the heavy metal antimony (Sb), which is contained in a range of products, e.g., in flame retardants (Pinkerton et al., 1989) and drinking bottles made from polyethylene terephthalate (PET) (Keresztes et al., 2009; Westerhoff et al., 2008). Sb is used in the form of Sb_2S_3 , which serves as a lubricant to reduce vibrations and to improve friction stability (Iijima et al., 2008; Matějka et al., 2011; Varrica et al., 2013). It has been found that brake linings and brake abrasion particles are major sources of Sb in urban

atmospheres and soils (Bukowiecki et al., 2009; da Silva et al., 2008; Salma and Maenhaut, 2006; Wang et al., 2006), and increased concentrations of Sb in biota are also associated with road traffic (da Silva et al., 2008; Krachler et al., 1999). In addition, a large number of exhausted brake pads are replaced and discarded as ordinary waste in some countries. For example, it has been reported that 1.4 million automobile brake pads were replaced per annum in Nanjing, China, and none of these were properly disposed of (<http://finance.chinanews.com/cj/2013/04-30/4777250.shtml>). Moreover, vast amounts of unqualified brake pads or polishing powder produced in the manufacturing of brake pads are arbitrarily discarded, causing serious pollution of farmland and leading to the death of trees (<http://www.bjnews.com.cn/feature/2013/04/01/256065.html>). It has been reported that metals contained in automotive brake pads are responsible for the pollution of water, soils and the ambient air (Bukowiecki

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et al., 2009). Leaching is an important process for metals released from these products, which is responsible for the pollution of waters and soils (He et al., 2012). However, at present, many researchers have reported on particulate matter emissions from brake wear through simulated friction experiments (Garg et al., 2000; Iijima et al., 2008) but no studies have been reported on the leaching process. Therefore, this paper focuses on the leaching of Sb from brake pads under different experimental conditions (i.e., pH, temperature, and organic acids), as well as performing a preliminary evaluation of the potential environmental risks.

1. Materials and methods

1.1. Origin of samples and pretreatment

Abandoned plate brake pad samples of certain brake pad manufacturing enterprises were obtained randomly from

a discard (Fig. 1) in the suburbs of Beijing, Daxin Village in Miyun County. Coordinates of four boundary points of the sample site are: southeast (N40.3703, E116.7143), southwest (N40.3706, E116.7136), northwest (N40.3727, E116.7145), northeast (N40.3725, E116.7148).

The brake pad samples were washed with water to clean them from soil and dirt, coated with 20 layers of kraft paper to avoid direct contact and then fragmented with a hammer. Then, the particle size was homogenized to less than 0.15 mm with an agate mill and a mixed sample was made consisting of several brake pads for further analysis.

1.2. Experimental methods

Laboratory tests were conducted with ground mixed samples by means of batch leaching. To ensure the solid–liquid ratio was the same when sampling, the released concentration of Sb was measured in a series of 100 mL batch reactors, with one reactor for each sampling time. For every run, 50 mL



Fig. 1 – Disabled brake pads were discarded in the farmland.

of solution was introduced into the reactor, and a mass of 1.000 ± 0.002 g of samples was added. These reactors were put in a vapor-bath constant temperature vibrator at 120 r/min. 10-mL leaching solution samples were taken using disposable PP/PE syringes (Shanghai Zhiyu medical equipment Co., LTD, Shanghai, China) and the pH of the solution was determined using PB-10 pH probes (Sartorius (Shanghai) Trading Co., LTD, Shanghai, China) at every interval, then the solutions were filtered with CME 0.45 μm hydrophilic syringe filters.

Three factors, including pH, temperature and organic acids, were studied. The solution initial pH was adjusted to 4.0, 6.0, 7.0 and 9.0 with dilute sulfuric acid or sodium hydroxide. The four pH levels were used at two temperatures: 25°C and 40°C. Organic acids, including acetic acid, oxalic acid, citric acid, and sodium humate (Sinopharm Chemical Reagent Beijing Co. LTD, Beijing, China), represented common soil solution components. Their concentrations were 2 mmol/L, 1 mmol/L, 0.05 mmol/L and 200 mg/L, respectively, coinciding with concentration ranges in the land soil (Sposito, 2008). Before leaching, sodium humate aqueous solution was purified by a Na^+ cation exchange column (Dowex 50W-X8, Acros) (Beijing InnoChem Science & Technology Co., Ltd, Beijing, China) to eliminate interference from Sb in the original sodium humate aqueous solution. The pH values of the organic acid solutions were 3.8, 3.1, 3.5 and 7.2, respectively. In control experiments, the organic acid solutions were replaced with aqueous solutions with corresponding pH, with the same mass of sample. All solid reagents used were of analytical grade or guaranteed grade and inorganic acids were guaranteed reagents.

1.3. Analytical methods

The main metal composition of the sample was determined with a portable X-ray fluorescence detector (XRF) (Innov-X System Co., Greater-Boston, USA). In addition, analysis of a 100 mg sample was carried out by ULTIMA inductively coupled plasma atomic emission spectrometry with axial dual view (ICP-AES) (HORIBA JobinYvon S.A.S., Paris, France) according to the water and sludge analysis standard EN ISO 11885:1997, using microwave-assisted extraction and an acid mixture of 5 mL hydrochloric acid (A.R.), 1.6 mL nitric acid (A.R.) and 0.25 mL perchloric acid (A.R.). The digests and leached solutions were then analyzed for Sb and other ecologically relevant elements, barium (Ba), copper (Cu), lead (Pb), chromium (Cr) and arsenic (As), using ICP-AES.

Phase analysis of the brake pad and powder was carried out using X-ray powder diffraction (XRD) on an X'Pert PRO MPD diffractometer (PANalytical B. V., Almelo, Holland), using $\text{Cu K}\alpha$ radiation ($K = 1.5418 \text{ \AA}$). The XRD data for indexing and cell parameter calculation were collected in θ - 2θ scanning mode from 10° to 70° with a step size of 0.05°/sec.

The species of Sb that existed in the brake pad was determined by ESCALAB MK II X-ray photoelectron spectroscopy (XPS) (VG Scientific Ltd., London, UK) analysis with a monochromatic $\text{Al K}\alpha$ source and a charge neutralizer. All binding energies were referred to the C1s peak at 284.63 eV of the surface adventitious carbon and corrected.

2. Results and discussion

2.1. Analysis of main composition

The XRF and ICP-AES analysis showed the main metals in brake pads (Table 1). Clearly, Cu, Ba, Sb, Fe, Ca and Zn are the main metal elements. The total Sb (1.26×10^4 mg/kg determined by XRF) was lower than that reported by others in fresh brake pads (4.1–4.6, 3.0 and 2.1×10^4 mg/kg) (von Uexküll et al., 2005; Kukutschová et al., 2009; Figi et al., 2010).

Fig. 2 shows the XRD patterns of the brake pads. The principal peaks (marked Nos. 1–4) were well indexed to graphite or coke (Kukutschová et al., 2009), barium sulfate, Cu and ferric oxide. Although Sb (1.26×10^4 mg/kg) was detected by XRF in brake pad samples, no peak for Sb or its compounds was revealed in Fig. 2. Because of the relatively minor amounts of Sb (<5% by weight percent), its diffraction peaks were not identified by XRD.

The XPS results are reported in Fig. 3. The two strong peaks at 530.9 and 539.2 eV are assigned to $\text{Sb3d}_{5/2}$ and $\text{Sb3d}_{3/2}$, respectively. By means of the NIST X-ray photoelectron spectroscopy standard reference database 20 (Version 4.1), we concluded that the main species of Sb were composed of an admixture of Sb_2S_3 ($\text{Sb3d}_{3/2}$) and SbCl_5 ($\text{Sb3d}_{5/2}$) in the brake pads. This is consistent with the reported results on speciation of Sb in vehicle brake linings by synchrotron radiation X-ray absorption spectroscopy (Varrica et al., 2013).

2.2. General measurement of leached solution

Measurement results for all leached solutions under different conditions showed that Cr, As and Pb in the leached solutions

Table 1 – Content of main metals in brake pads (mg/kg).

Samples	Ba	Sb	Cu	As	Cr	Pb	Fe	Ca	Zn
Brake pad ^a	5.34×10^4	1.26×10^4	5.21×10^4	65	828	92	2.43×10^5	1.23×10^4	1.90×10^4
Brake pad ^b	5.29×10^4	1.62×10^4	5.63×10^4	148	982	33.4	–	–	–
Reference ^c	5.3	3×10^4	4×10^4	–	–	–	–	–	–
Reference ^d	–	$(4.1\text{--}4.6) \times 10^4$	$(1.4\text{--}2.7) \times 10^4$	83–140	740	35–67	–	–	–
Reference ^e	–	2.1×10^4	1.0×10^5	–	225–250	31.3–32.1	–	–	–

^a Refers to main metals in brake pad that were determined by X-ray fluorescence detector.

^b Refers to main metals in brake pad that were determined by inductively coupled plasma atomic emission spectrometry after wet digestion.

^c Kukutschová et al., 2009. This composition was investigated data, representing a typical semimetallic brake material available on US, European and Asian markets.

^d von Uexküll et al., 2005. Concentration of toxic metals in disc brake pads (Jurid 539-20, Textar 4700 and Iveco EuroCargo) determined with XRF.

^e Figi et al., 2010. Concentration of toxic metals in disc brake pads (VW-Bora brake pad) determined with ICP-AES using microwave-assisted extraction.

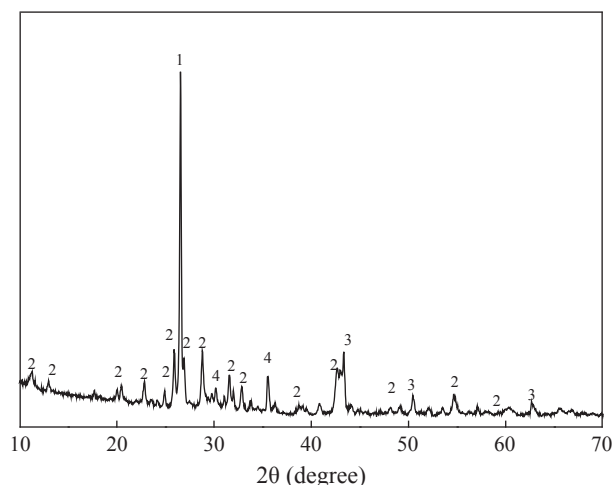


Fig. 2 – XRD pattern of brake pad. Peak 1: carbon; peak 2: BaSO₄; peak 3: Cu; peak 4: Fe₃O₄.

were all under the detection limit (0.01 mg/L). Ba was detected in extremely low concentration (0.15–0.25 mg/L) and Cu (0.038 mg/L) was detected only on the 30th day. It was only Sb that showed remarkable release (40–100 mg/L) under all experimental conditions. The results indicated that Sb is more easily released from brake pads than Ba, Cu, Pb, Cr and As, and may be the primary metal pollution source of waters.

2.3. Effect of initial pH and temperature on antimony release

Fig. 4a shows pH and pH-dependent Sb concentration changes in leached solution at 25°C. The pH values increased sharply from all initial pHs at 25°C to pH 9.0–9.8 after 1 day of leaching, even though initial pHs were different, and then stayed almost unchanged, suggesting that a released basic component contained in the brake pads increased the pH of the aqueous solutions. The Sb concentration under all experimental pH conditions increased linearly during the first day and then increased slowly, and reached a maximum concentration of 97 mg/L (at pH 9).

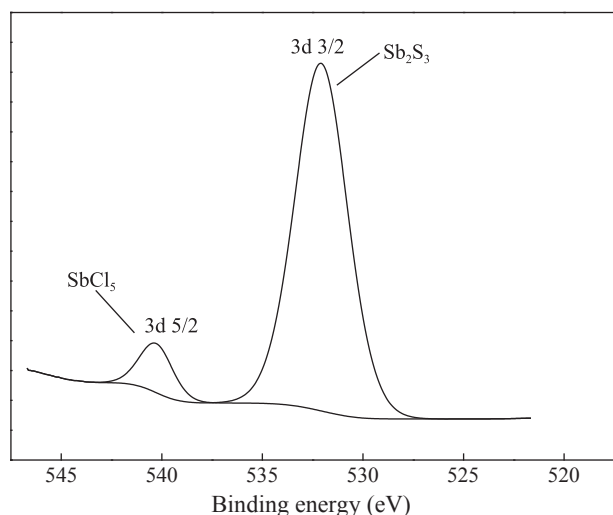
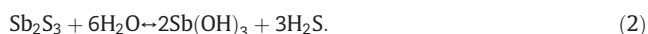


Fig. 3 – XPS pattern of Sb contained in the brake pad.

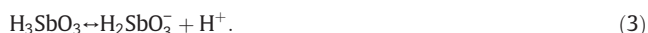
The concentration change of Sb in leached solution over time ($t \geq 1$) was best fitted by a logarithmic function. The equation to fit these data is:

$$C = k \times \ln t + C_0(t \geq 1). \quad (1)$$

where, C (mg/L) is the Sb release concentration at time t (day), and k is the rate constant and C_0 represents the Sb release concentration on the first day, and its value also refers to the release rate on the first day. Table 2 summarizes the fitted values of C_0 , k , standard error and the statistical goodness of fit (R^2) values for Sb at different pH values and temperatures. The C_0 and k in alkaline solution are larger than in acidic solution, illustrating that alkaline conditions favor the release of Sb from Sb_2S_3 in the brake pads (Biver and Shoty, 2012a). This is because Sb is in the form of Sb_2S_3 to serve as a lubricant in the brake pads, and Sb_2S_3 dissolves in water as formally represented by (Morel and Hering, 1993):



However, $Sb(OH)_3$ behaves more like an acid, so it is often written as H_3SbO_3 which is called antimonous acid. It can dissociate to form an anion (negatively charged species) according to:



Eq. (3) is sometimes also written as:



As pH is increased, more of the H_3SbO_3 is converted to the anion. As the anion $H_2SbO_3^-$ is charged, it has a very high solubility in water. This explains why more Sb released in alkaline conditions. After 30 days leaching, approximately 30% of Sb of total Sb (1.62×10^4 mg/kg) contained in the brake pads was released under alkaline conditions.

Fig. 4b shows pH and pH-dependent Sb concentration changes in leached solutions during 30 days leaching at 40°C. A higher temperature (40°C) increases the initial Sb release compared to the results at 25°C. The value of C_0 at 40°C is about 10 mg/L more than that at 25°C. About 32% of total Sb (1.62×10^4 mg/kg) contained in the brake pads was released from the brake pads after 30 days, which is slightly larger than that at 25°C. In general, the effect of temperature on Sb release was not significant.

These results suggest that abandoned brake pads would produce heavily alkaline water or soil when leached by rainwater, and then abandoned brake pads exposed to heavily alkaline waters will, in turn, release more Sb pollution, especially in the summer. Leaching of Sb may explain why the total concentration of Sb (Table 1) in the weathered brake pad was lower compared to results reported by other authors (Fig. et al., 2010; Kukutschová et al., 2009; von Uexküll et al., 2005) who used fresh brake pads. In contrast, the brake pads we used had been exposed to the environment for several years.

2.4. Effect of organic acids on antimony leaching

The effect of organic acids and corresponding controls on Sb leaching is illustrated in Fig. 5. The pH increased sharply from all initial pH values to pH 9.3–9.8 after 1 day leaching and then stayed almost unchanged, similar to the pH changes

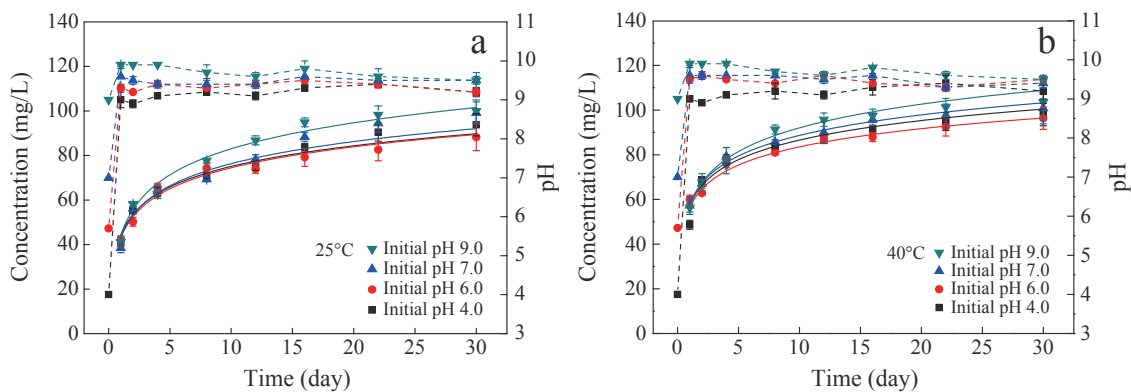


Fig. 4 – pH changes (dashed line) and fitted plots of antimony release concentration vs. time (solid line) at temperature 25°C (a) and 40°C (b).

illustrated in Fig. 4. However, the release rate of Sb was independent of pH in the presence of organic acids.

The order of Sb release for the four organic acids in decreasing order is humate, citric acid, oxalic acid, and acetic acid (Fig. 5). Acetic acid ($pK(\text{CO}_2\text{H}) = 4.76$), oxalic acid ($pK_1(\text{CO}_2\text{H}) = 1.25$, $pK_2(\text{CO}_2\text{H}) = 4.26$) and citric acid ($pK_{1-3}(\text{CO}_2\text{H}) = 3.13, 4.76, 6.40$) could form Sb(III)-ligand complexes under alkaline conditions (Biver and Shotyky, 2012b; Filella and May, 2005; Tella and Pokrovski, 2009). It is reported that the average thermodynamic stability constants ($\lg K_i$) at zero ionic strength for Sb-oxalic acid and Sb-citric acid at 20°C are 3.8 ± 0.2 and 4.6 ± 0.3 . The average $\lg K$ for Sb-acetic acid was estimated to be close to or slightly below 3.8 ± 0.2 through comparing Sb concentrations in acetic acid with those in oxalic acid (Tella and Pokrovski, 2009). In citric acid solution, more Sb was bound to citric acid, the dissolution balance of Sb_2S_3 was disturbed, and more Sb was released than in acetic acid and oxalic acid. Notably, sodium humate is more favorable than other organic acids for Sb release, because humate has natural organic components, including a mixture of organic heterogeneous structures rich in oxygen-containing functional groups (i.e., phenolic hydroxyls, alcoholic hydroxyls, carboxylic acids, ketones, quinones, etc.) (Schnitzer, 1991), it can act as a multidentate chelator and increase Sb release to a very great degree (Furrer and Stumm, 1986).

It was noted that Sb release in the presence of organic acids was less than that in controls. The inhibition of Sb release in the presence of organic acids had only a small relationship with the effect of pH because they maintained the pH at steady state

values at all experimental conditions. The other speculation is that the strong chemical affinity of other high content metals such as Ca, Cu and Fe with organic acids played a role. These metals were already bound to these organic acids, competing for reaction sites with Sb and decreasing the release of Sb. However, the cumulative stability constants ($\lg \beta_n$) at 0.5 mol/L ionic strength for Ca^{2+} , Cu^{2+} , Fe^{2+} and Fe^{3+} with citric acid are 3.5, 18.0, 15.5 and 25.0. In addition, $\lg \beta_n$ for Cu^{2+} , Fe^{2+} , Fe^{3+} and Mn(III) with oxalic acid are 4.5, 2.9, 9.4 and 9.98, and $\lg \beta_n$ for Cu^{2+} , Mn^{2+} with acetic acid are 2.16, 9.84 respectively at 18–25°C (Chen and Zhang, 2010). These data all supported the hypothesis that other high content metals in brake pad were bound to these organic acids, forming stable metal-organic complexes, competing for reaction sites with Sb and decreasing the release of Sb.

After 30 days leaching, approximately 15%–28% of total Sb contained in the brake pads was released in the presence of organic acids.

2.5. Potential environmental risks from antimony release

Through determining Sb contained in the top soils from a brake pad dumpsite in the suburbs of Daxin Village, Miyun County, we found average 9×10^3 mg/kg Sb. By contrast, Sb content in the uncontaminated soils in the suburbs of Daxin Village in Miyun County was only 2.7 ± 1 mg/kg. Clearly, a huge amount of Sb in the brake pads discarded on the land was released by means of leaching by rainwater or pore water in the soils. This may be just one case of many pollution accidents, but it should arouse the public’s attention that Sb pollution from brake pads should not be ignored anymore.

With the increase of car ownership, more brake pads are in demand. In China, since 2004, the demand for brake pads was more than 80 million, with a growth rate of 16%. The total demand for brake pads in car markets reached up to 130 million in 2010 (http://www.autoinfo.gov.cn/autoinfo_cn/channel/sjqcgy/index.html#sjzx). At present, no specific treatment method of disabled or used brake pads was found. If all of these brake pads are carelessly disposed, plus emitted dust from abrasion in braking process, a huge quantity of Sb will be released into the environment. In addition, according to data released by the OICA (The International Organization of Motor Vehicle Manufacturers) in 2011, worldwide total automobile stocks have exceeded 1 billion and increase at a rate of 30

Table 2 – Fitted parameters for a time-dependent logarithmic function (Eq. (1) at different initial pHs and temperatures.

Experimental conditions		k	C_0 (mg/L)	R^2
Initial pH 4.0	25°C	13.35±0.85	42.35±1.51	0.9724
	40°C	12.62±1.40	57.50±2.49	0.9197
Initial pH 6.0	25°C	13.61±1.17	43.13±2.05	0.9505
	40°C	11.74±0.82	56.51±1.45	0.9672
Initial pH 7.0	25°C	14.33±1.67	43.34±2.96	0.9128
	40°C	13.27±0.41	58.12±0.82	0.9933
Initial pH 9.0	25°C	16.88±1.16	44.15±2.07	0.9677
	40°C	15.28±0.72	56.86±1.41	0.9846

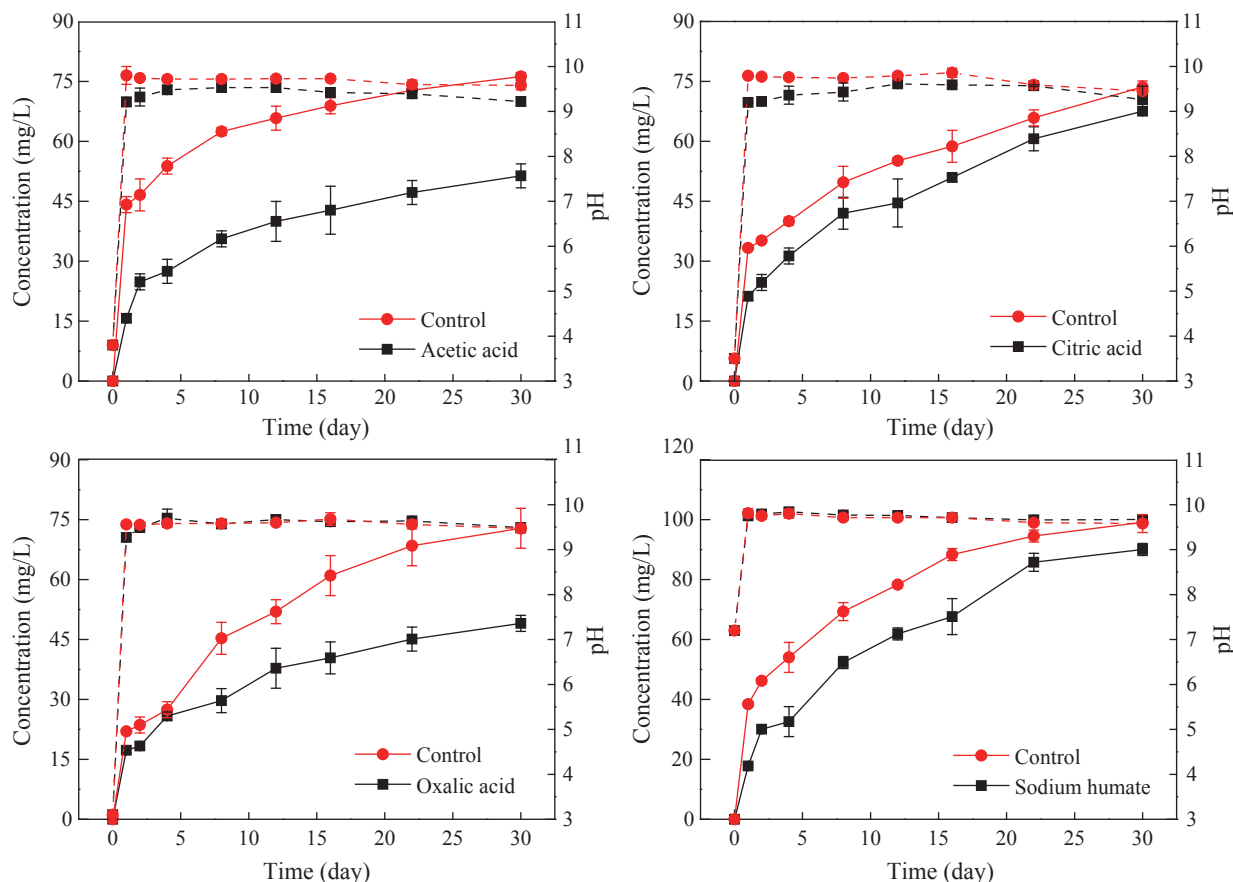


Fig. 5 – Effects of four organic acids and corresponding controls on antimony release at 25°C: pH changes (dashed line) and antimony release concentration vs. time (solid line).

million per annum, so we can predict that many more brake pads will enter the environment. Some studies indicate that metals from automobiles have adverse effects on the environment and have described the effects of metals from brake pads on water quality (Hjortenkrans et al., 2007; Napier et al., 2008; Nixon and Saphores, 2003). von Uexküll et al (2005) showed that Sb in brake dust was soluble in calf serum ($8.5 \pm 1.2\%$, 8.9 ± 1.7 mg/L at 37°C for 3 days). Hence, such a high release of Sb can cause enormous potential risks of water or soil contamination and human health risks through inhalation exposure and ingestion of Sb contained in biota.

3. Conclusions

Currently, metals released from brake pads have become a problem that cannot be ignored, especially those released through leaching. Although Cu, Ba and Sb were contained in the brake pads in high concentrations, only the release of Sb was remarkable. In alkaline aqueous solution and also at lower temperature, around 30% of total Sb contained in the brake pads was released after 30 days of leaching. Due to unsound waste disposal and management systems for brake pads in some countries, a number of unqualified or scrapped brake pads have been discarded as ordinary wastes and cause pollution of the soil and waters, thus affecting living beings

near the discard areas. However, the environmental behavior and potential risks of Sb contained in brake pads are still unknown and need to be further explored. In view of the potentially high amounts of Sb that may be released from brake pads, it is important that producers and environmental authorities take precautions.

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