Review

# Antimony contamination, consequences and removal techniques: A review

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## ABSTRACT

A significant amount of antimony (Sb) enters into the environment every year because of the wide use of Sb compounds in industry and agriculture. The exposure to Sb, either direct consumption of Sb or indirectly, may be fatal to the human health because both antimony and antimonide are toxic. Firstly, the introduction of Sb chemistry, distribution and health threats are presented in this review, which is essential to the removal techniques. Then, we provide the recent and common techniques to remove Sb, including adsorption, coagulation/flocculation, membrane separation, electrochemical methods, ion exchange and extraction. Removal techniques concentrate on the advantages, drawbacks, economical efficiency and the recent achievements of each technique. We also take an overall consideration of experimental conditions, comparison criteria, and economic aspects.

## 1. Introduction

Heavy metals pollution has been a worldwide problem, accomplishing with many industrial and environmental accidents occurred (Zhou et al., 2016). Sb pollution is a potential disaster in many countries since the use of Sb has increased worldwide (He et al., 2012). Approximately 140,000 t of Sb was mined and devoted to various industrial sectors annually (Filella et al., 2002a; Shan et al., 2014). Many research articles have paid attention to the effective techniques for Sb removal since the 1970s. Sb is a metalloid, having properties of metal and nonmetal and existing in the environment like arsenic in two oxidation states mainly, i.e., trivalent antimony (Sb(III)) and pentavalent antimony (Sb(V)) (Shan et al., 2014). Sb(V) generally exists in oxidizing environments, and Sb(III) mainly exists in reducing environments (Rakshit et al., 2011).

Sb as a heavy metal element arose people's attention because of its toxicity. Sb and its compounds easily combine with the internal sulfhydryl in animal or human body, interfering with the activity of the enzyme in the body and destroying the ion balance in the cell, leading to hypoxia (Ning and Xiao, 2007). This can lead to metabolic disorders that damage organs especially the nervous system. Sb(III) compounds are 10 times more toxic than Sb(V) compounds but the mobility and solubility of Sb(V) are greater than Sb(III) (Mitsunobu et al., 2008; Mitsunobu et al., 2010). In addition, Sb can easily enter the human body in many ways, such as skin contact, respiration, and food chain. All of antimony and antimony compounds have toxicity to the human body. Furthermore, the sources of Sb pollution are diverse. For example, natural weathering of Sb ore, mining, smelting, the burning of fossil fuels and the wide use of antimony compounds increase the concentration of Sb in the geochemical environment, causing atmosphere, water and soil pollution (Hu et al., 2017).

The increasing use of the product containing Sb inevitably leads to the release of Sb into the environment. China is the country with the richest Sb resources. Large quantities of Sb were released from mining and smelting processes in the mine or nearby areas, causing serious Sb contamination (Hu et al., 2016). The European Union has listed Sb as a priority control pollutant in 1976, and the United States Environmental Protection Agency listed it as control pollutant in 1979 (Rakshit et al., 2011). Since 1980, many countries and regions made relevant measures to control and limit the content of Sb in the living environment. The European Community (EC) stipulated the maximum allowable concentration of Sb in drinking water as 5 μg/L in 1988, and the standard in Japan was 2 μg/L (Kang et al., 2003). In 2002, Chinese standard of surface water quality standards required that the concentration of Sb in

water sources should not exceed 5 µg/L (Rakshit et al., 2011).

In this paper, the sources and distribution of Sb and health hazards to the environmental ecosystem are reviewed. Then the special emphasis is given to the removal techniques of Sb, including adsorption technologies, coagulation/flocculation, membrane separation technology, the electrochemical method, ion exchange method, and extraction. Furthermore, the future researches of Sb removal are also discussed in this article.

## 2. Sources of antimony in the environment

Sb has inorganic and organic forms in the environment (Cai et al., 2016). Although the amount of Sb in the crust is very low, belonging to the scarce mineral resources, the content of Sb in the geochemistry environment increased because of the exploiting of Sb ore and the use of Sb compounds (Ning and Xiao, 2007). Besides, the weathering of rocks, the loss of soil and the widespread use of Sb industrial products are also important causes of Sb pollution (Wu et al., 2008; He et al., 2012).

Different countries and regions, including China, Norway, Finland, Ethiopia, North Pacific, North Atlantic, Switzerland, Germany, Japan, have detected the concentrations of Sb in surface waters, groundwater, marine waters, soil and living organisms respectively, the details as below (Table 1).

### 2.1. Surface waters

Sb is everywhere because of natural processes and human activities. The dissolved Sb is mainly released into the water by land surface rivers, groundwater, dry air, wet deposition, the release of sediment and suspended particulate matter (Ungureanu et al., 2015). Sb in surface water is mainly derived from soil and atmospheric deposition, while Sb in soil and atmospheric precipitation is caused by ore mining or weathering. The concentration of Sb in surface water mainly depends

on whether they are close to the source of pollution (Filella et al., 2002a; Filella et al., 2002b; Filella et al., 2002b). And it is relevant to geographical location, physical and chemical conditions (Ulrich, 2000). Sb pollution is associated with human activity since the content of Sb in the uncontaminated water environment is not high. Surface water samples from 11 different countries and regions, including Northern European, Southern European, Germany, Austria, Alaska, Scotland, Ireland, Canada, Japan, Svalbard, and Finland, indicated that the median values of Sb ranged from 0.03 to 0.07 µg/L (Reimann et al., 2010). The content of Sb in European Union ranged from 0.002 to 2.910 µg/L, testing from 807 samples of surface water (Salminen et al., 2005). The concentration of Sb(III) and Sb(V) in the Yangtze River were in the range of 0.029–0.736 µg/L and 0.121–2.567 µg/L which mainly existed in surface water, with the median values of 0.152 µg/L and 0.592 µg/L, respectively (Wu et al., 2011b).

### 2.2. Groundwater

Groundwater is one of the most important freshwater resources to human beings. It is indispensable to daily drinking, cleaning, and irrigation. However, with the aggravation of Sb pollution, groundwater pollution is worrying problem, many countries have detected Sb in their groundwater (Sui et al., 2015). Except for some hot springs and geothermal water up to 500 µg/L (Filella et al., 2002a), the concentration of Sb in groundwater is about several µg/L (Niedzielski et al., 2001). Nevertheless, to a great extent, the enrichment of Sb in groundwater is affected by human activities, and the concentration of Sb in the contaminated zone can reach 100 µg/L (Filella et al., 2002a). Frengstad et al. investigated the concentration of Sb in 476 groundwater samples in Norway and found that the content of Sb was 0.002–8.000 µg/L, and the median value was 0.03 µg/L (Frengstad et al., 2000). The concentration of Sb of groundwater in 739 Wells in Finland was 0.02–0.82 µg/L, and the median value was 0.03 µg/L (Lahermo et al., 2002). The concentration of Sb in 138 unfiltered groundwater samples

**Table 1**
Concentrations of antimony in the environment.

| Location (Countries) | Environmental sources | Concentrations | References |
|---|---|---|---|
| 11 different countries and regions | Surface waters | 0.03–0.07 µg/L | Reimann et al. (2010) |
| Yangtze River, China | Surface waters | 0.029–0.736 µg/L (Sb(III)) 0.121–2.567 µg/L (Sb(V)) | Wu et al. (2011a, 2011b) |
| 476 groundwater samples, Norway | Groundwater | 0.002–8.000 µg/L | Gill et al. (2000) |
| 739 Wells, Finland | Groundwater | 0.02–0.82 µg/L | Lahermo et al. (2002) |
| 138 unfiltered groundwater, Ethiopia | Groundwater | 0.002–1.780 µg/L | Reimann et al. (2003) |
| Anoxic environment of groundwater | Groundwater | 0.008 µg/L (Sb(III)) 0.012 µg/L (Sb(V)) | Sun et al. (1993) |
| Bottom layer in Yangtze River, China | Groundwater | 0.023–0.116 µg/L (Sb(III)) 0.047–0.441 µg/L (Sb(V)) | Wu et al. (2011a, 2011b) |
| North Pacific | Marine waters | 0.09–0.14 µg/L | Donat and Bruland (1995) |
| North Atlantic | Marine waters | 0.21 µg/L | Donat and Bruland (1995) |
| Western Atlantic ocean | Marine waters | 0.13 µg/L | Cutter et al. (2001) |
| 300 m of new South Sales mine, Australia | Soil | 39.4 mg/kg | Tighe et al. (2005) |
| Xishan mines, China | Soil | 5949.20 mg/kg | Qi et al. (2011) |
| Shooting filed, Swiss | Soil | 13.8 g/kg | Johnson et al. (2005) |
| Buenos Aires, Argentina | Atmosphere | 0.9–15.3 ng/m$^3$ | Smichowski et al. (2004) |
| Tokyo, Japan | Atmosphere | 5.7–16 ng/m$^3$ | Furuta et al. (2005) |
| Tin mining of Dachang, China | Atmosphere | 575 mg/m$^3$ | Zhang et al. (2009) |
| Achillea in old Sb area, Italy | Organisms | 1367 mg/kg (Leaves) 1105 mg/kg (flowers) | Baroni et al. (2000) |
| Plantago in old Sb area, Italy | Organisms | 1150 mg/kg (roots) | Baroni et al. (2000) |
| Silene in old antimony area, Italy | Organisms | 1164 mg/kg (vulgaris stems) | Baroni et al. (2000) |
| Fish in contaminated river, Japan | Organisms | 0.06 µg/g (Omnivorous fish) 0.42 µg/g (Carnivore fish) | Kawamoto and Morisawa (2003) |
| 19 vegetables grown in the abandoned mining soil | Organisms | < 0.02–0.09 mg/kg (root) 0.02–2.2 mg/kg (leaves) 0.02–0.06 mg/kg (fruit) | Hammel et al. (2000) |
| Oryza sativa growing in the antimony smelter in tin, China | Organisms | 225.34 mg/kg (roots) 18.78 mg/kg (stem leaves) 5.79 mg/kg (Seeds) | Feng and Wei (2012) |

in Ethiopia was 0.002–1.780 µg/L, and the median value was 0.028 µg/L (Reimann et al., 2003). According to the surveys, Sb in hypoxia environment exists in Sb(III) and Sb(V) form (Yang et al., 2015a). Sb(V) content in the anoxic environment of groundwater was 0.012 µg/L and the Sb(III) was 0.008 µg/L (Sun et al., 1993). The research about the concentration of Sb in the Yangtze River showed that enrichment of Sb in the bottom layer was lower than the other layers. In the bottom layer, the concentrations of Sb(III) and Sb(V) respectively ranged from 0.023 µg/L to 0.116 µg/L, with the median value of 0.050 µg/L and 0.047 µg/L to 0.441 µg/L, with the median value of 0.194 µg/L (Wu et al., 2011b). Apparently, the concentrations of Sb in unexploited water did not exceed the relevant standards (except the Sb polluted area).

## 2.3. Marine waters

Due to the limitation of technical conditions and diverse ocean area, there is a diverse data of Sb concentration in different kinds of literature. Sb is inactive in chemical properties in seawater, and its concentration can reflect the geochemical characteristics of the coastal environment (Zhang et al., 2010). The average concentration of Sb in seawater in the seven seas was about 0.2 µg/L (Williams, 1996). The Donat and Bruland's survey found that the concentration of Sb in the north Pacific and north Atlantic was ranging from 0.09 to 0.21 µg/L (Donat and Bruland, 1995). The concentration of Sb in surface waters of western Atlantic ocean was 0.13 µg/L (Cutter et al., 2001). Changjiang Estuary and Hangzhou Bay were the Sb enrichment spots of Changjiang, China (Ren et al., 2016).

## 2.4. Antimony in soil

The enrichment of Sb in sediments and soils are affected by many factors, such as the geological setting, groundwater, the presence of volcanic ash, anthropogenic sources and others (He et al., 2012). Antimony and antimonide are components of crust, the concentration of Sb in the crust is about 0.3 µg/kg, and the concentration in the upper and lower crust is similar (Gómez et al., 2005). The enrichment of Sb in the soil exceed that in the parent rock, and its soil background value was 0.3–8.6 mg/kg, and the median was 1 mg/kg, but usually less than 1 mg/kg (Johnson et al., 2005). There is no international unified standard level for Sb in soils. Some countries make their own maximum permissible level. For instance, in Germany, the maximum permissible level of Sb in soils is 3.5 mg/kg, and 5 mg/kg is the maximum permissible level of Netherlands (He et al., 2002).

According to the trace metals quantitative assessment of contamination in soils, it was estimated that $(4.7–47) \times 10^6$ kg of Sb were released into the soil every year.(Li et al., 2011). Mineral exploitation and mineral use are the main causes of Sb pollution. Most of the Sb released from different sources of pollution was absorbed by aluminum, iron and manganese oxide in the soil, and the soluble antimonate in oxidizing and alkaline conditions mainly exist in Sb(V) form (Ji et al., 2017). The soil in the mining area has the most serious Sb contamination. In Australia, the concentration of Sb reached up to 39.4 mg/kg within 300 m of the new South Wales mine (Tighe et al., 2005). Sb concentrations reached up to 5956 mg/kg around an abandoned Sb ore field in Portugal (Pratas et al., 2005). The average concentration of Sb in the soil around Xishan mine in the Lengshui Jiang city of Hunan province reached 5949.20 mg/kg, accompanying with other heavy metal pollution such as arsenic, cadmium, and mercury (Qi et al., 2011). As one of the main raw materials of the bullet, the soil of the shooting filed also suffers from the serious pollution of Sb. For example, Sb concentration in the surface soil of the Swiss shooting range was 13.8 g/kg (Johnson et al., 2005). The sedimentation of polluted atmosphere and the discharge of sewage are also one of the causes of soil Sb pollution. Due to the excessive use of gasoline and Sb in tires and brake linings, the concentration of Sb in the soil near the highway also exceeds the vicinity (Zhang et al., 2011; Hu et al., 2015).

## 2.5. Antimony in atmosphere

Sb mainly exists in the particle form in the atmosphere, according to existing researches in the 2010s, the concentration of Sb was general from several ng/m$^3$ to scores of ng/m$^3$ worldwide (Smichowski, 2008; Sundar and Chakravarty, 2010). Although Sb is not the main pollutant in the atmosphere, the continuous mining, smelting, and burning fossil fuels led to a mass of Sb into the atmosphere, exceeding the capacity of the environment. For example, in Buenos Aires, Argentina, the amount of Sb in the atmosphere was between 0.9 and 15.3 ng/m$^3$ (Smichowski et al., 2004), and the concentration of Sb in the atmosphere of the Japanese city of Tokyo was between 5.7 ng/m$^3$ and 16 ng/m$^3$ (Furuta et al., 2005).

The sources of Sb in the atmosphere mainly include fossil fuels and volcanic eruptions. About 2800 t of Sb were released into the atmosphere due to mining, burning of fossil fuels and smelting of Sb (He et al., 2012). The concentration of Sb in the general mining area air is high. For example, the concentration of Sb in PM10 particles exceeds 575 mg/m$^3$ in the tin mining area of Dachang, Guangxi, China (Zhang et al., 2009).

About 700 t of Sb were released into the atmosphere by volcanic eruptions every year (Filella et al., 2002a). According to Shotvk's investigation, the amount of Sb released from the volcano was about 3% of the global release of Sb (Shotyk et al., 1996). However, the Sb pollution in the urban atmosphere mainly comes from the transportation, including the burning of gasoline and the brake wear (Smichowski, 2008). Some countries have already developed Sb environmental standards for atmosphere: the United States stipulated that the amount of Sb contained in the air should not exceed 0.5 mg/m$^3$ (Rakshit et al., 2011).

## 2.6. Antimony in organisms

Sb has been detected in plants, animals, and humans (Feng et al., 2013). Sb can enter humans' body and animals' body through breathing, eating or body surface contact, and exists in the form of organic antimony (Belzile et al., 2011; Filella et al., 2013). The proportion of antimony in the human body is 0.1 µg/g, it can be found in human's bone, hair and blood (Filella et al., 2012; Wu and Chen, 2017).

Sb in the soil has high mobility, and can easily move and accumulated in plants. It was reported that a certain amount of Sb in algae and other freshwater plants was detected, confirming that Sb could be transferred and accumulated in plants (Hammel et al., 2000; Tisarum et al., 2015). Sb is not a necessary element for plants, but plants can absorb the dissolved Sb (Baroni et al., 2000; Feng et al., 2013). Sb exists predominantly in the form of organic matter in plants, with monomethyl Sb as the main organic form (Feng et al., 2013). In the untreated terrestrial plants, the concentration of Sb was between 0.2 ng/g and 50 ng/g, but in contaminated areas, the Sb content in plants was much higher (Feng et al., 2013). Achillea ageratum, Plantago lanceolata and Silene vulgaris and other plants can be used as the soil indicator of Sb. In the old Sb miner area of Italy, the accumulation of Sb in leaves and flowers of achillea reached up to 1367 mg/kg and 1105 mg/kg, the roots of Plantago lanceolata accumulated Sb up to 1150 mg/kg, Silene vulgaris stems up to 1164 mg/kg (Baroni et al., 2000). In the mossy plants, water is the medium of Sb entering the plant body (Culioli et al., 2009).

Sb was also found in common foods, which is evolving into a potential time bomb to the human health. In the polluted river in Japan, the concentration of Sb in the omnivorous fish flesh was 0.06 µg/g, while the concentration of Sb in carnivore fish flesh was 0.42 µg/g (Kawamoto and Morisawa, 2003). The waste mining area affected by Sb contamination in Germany, Sb was detected in 19 vegetables and food crops such as carrots, onions, tomatoes, and beets. The concentration of

Sb in the root was less than 0.02–0.09 mg/kg, the concentration in the stem leaves was 0.02–2.2 mg/kg, the concentration in the fruit was 0.02–0.06 mg/kg, but the concentration of Sb in lettuce, celery, and spinach even reached up to 212 mg/kg (Hammel et al., 2000). High concentration of Sb existed in Oryza sativa which was grown nearby Sb tin smeltery in Hunan province, China, and the levels of Sb in rice roots, stem leaves, and seeds were 225.34, 18.78 and 5.79 mg/kg, respectively (Feng and Wei, 2012).

## 3. Health hazards

Sb is toxic to human and organisms and even suspected as a carcinogen. Besides, antimony and antimonide have been classified as pollutants in the U.S. and Germany (Smichowski, 2008). Different antimonides have different physicochemical properties and toxicity. Wang et al. calculated Sb's toxicity coefficient based on Hakanson's principles (Wang et al., 2017). In general, organic antimonides are less toxic than inorganic antimonides. Sb(III) is more toxic than Sb(V). Water-soluble antimonide is more toxic than poorly soluble antimonide (Ungureanu et al., 2015; Saleh et al., 2017)

Antimony and antimonide are dangerous substances with chronic toxicity and potential carcinogenicity, once it enters the supergene environment, it will cause toxic effects to the animal and plant body (He et al., 2012). Antimony and antimonide enter into human beings through the pathway of the respiratory tract, digestive tract, and skin (Fig. 1), causing Sb poisoning (Bazzi et al., 2005; Belzile, 2013). The amount of Sb absorbed by the body through food and water was estimated at 4.6 μg/day (He and Wan, 2004).

Sb poisoning can be divided into the following two categories: acute poisoning and chronic poisoning. The acute poisoning of Sb manifests as stomach, vomit, dehydration, muscle pain, cramps, haematuria. Enuresis and urine toxin and even causes liver cirrhosis, muscle necrosis, nephritis, pancreatitis (Pierart et al., 2015). The chronic poisoning manifests as lung function changes, chronic bronchitis, emphysema, early tuberculosis, pleural adhesions and even pneumoconiosis

caused by long-term working in low-concentration Sb environments (Pierart et al., 2015; Belzile et al., 2011). Antimonide is potentially toxic to the human body's immune system (e.g., nervous system, gene, and physique growth) (Miao et al., 2014). Sb has been shown to be toxic and carcinogenic to humans and organisms, leading harms to the liver, skin, lungs and even cardiovascular system. Sb poisoning has long incubation period (He and Wan, 2004). Excessive Sb can lead to acute heart diseases, which is suspected to be one of the tensions concerning about sudden infant death syndrome (McCallum, 2005).

The top limit concentration of Sb in potable water was studied in the experiment, which showed that "unobserved secondary effect concentration" of Sb in drinking water (NOA-EL) was 0.06 mg per kilogram of body weight per day (Poon et al., 1998). The international IARC group thought $Sb_2O_3$ might be carcinogenic, but there was no evidence showed that $SbCl_3$ was carcinogenic. The exposure of $SbCl_3$ in the short period of human cells can lead to cell changes, proving that $SbCl_3$ has genetic toxicity and cytotoxic properties (von Uexküll et al., 2005). Besides the toxicity mentioned above, antimonide also affects the function of some enzymes and organs in the human body. For example, trivalent antimonide $SbCl_3$ and $Sb_2O_3$ can speed up the exchange rate of human lymphocyte sister chromosome (SCE). Pentavalent antimonide $Sb_2O_5$ and $SbCl_5$ have no influence on the exchange rate of human lymphocyte sister chromosome (SCE) (He and Wan, 2004).

Sb also has acute poisoning and chronic poisoning effect on animals. Huang found that Sb infected mice appeared the acute poisoning symptoms of lying, less moving, more frequent breathing and even death in the acute toxicity experiment of $Sb_2O_3$ to rats. Rats were found to have different levels of physiological changes with the feeding of different concentrations of Sb (Ge and Wei, 2011).

The absorption of Sb by plants exists in both passive and initiative ways, which mainly depends on the form of Sb. Some studies have shown that low concentrations of Sb can stimulate the growth of certain plants, while high concentrations of Sb have toxicity to the plants (Ge and Wei, 2011). Low concentration of antimony potassium tartrate ($C_8H_{18}K_2O_{15}Sb_2$) (< 20 mg/L) played a promoting role in plant growth
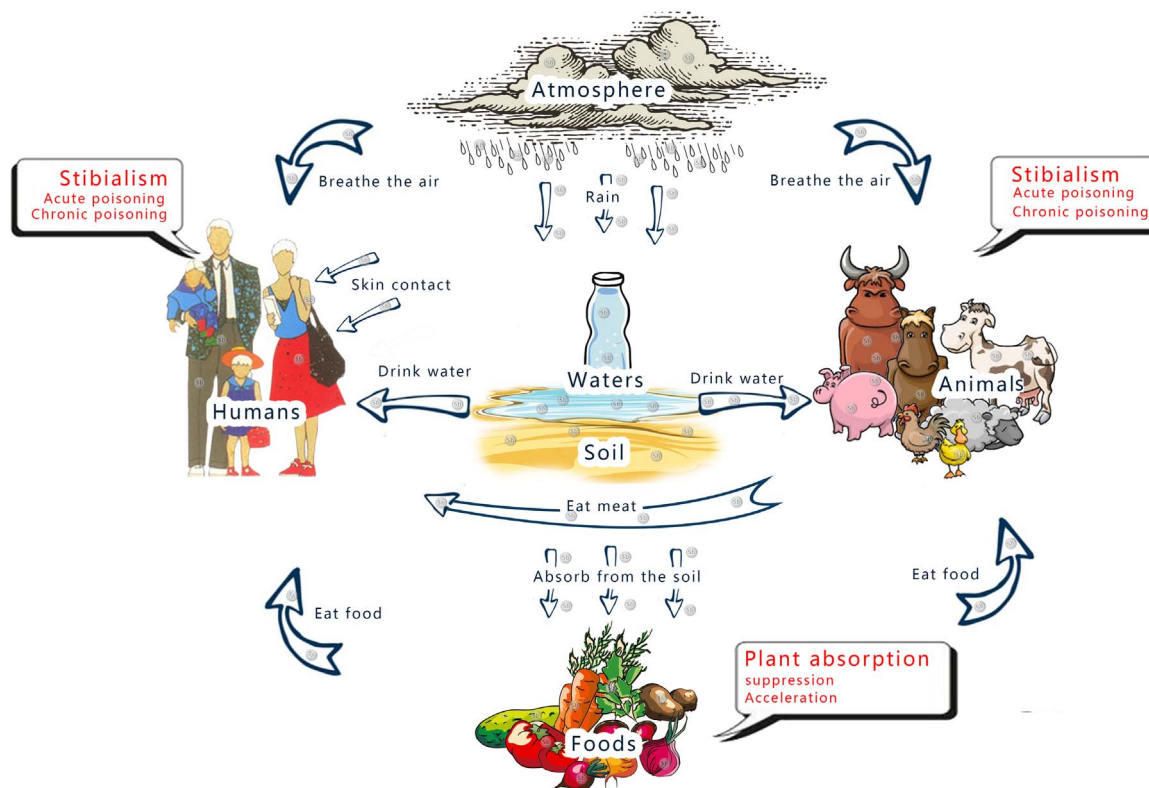


Fig. 1. Sb exposure media and pathways.

and benefiting physiological and biochemical characteristics, but a high concentration of antimony potassium tartrate (> 40 mg/L) have the inhibitory effect on these aspects (Liao and Zhao, 2008). The amount of Sb adsorbed and accumulated by plants is strongly affected by the plant species and contaminated sites. The toxicological effects of Sb in water environment microorganism are mainly concentrated in algae (Li et al., 2013).

The environmental standard for Sb has been developed for many countries. Sb has been listed as hazardous waste in the Basel Convention on the cross-border migration of hazardous wastes. Besides, the U.S. environmental protection agency and the European Union have prioritized Sb pollution and stipulated that the amount of Sb contained in the working environment should be limited to 0.5 mg/m$^3$ . In 2002, Chinese standard of surface water quality standards required that the concentration of Sb in water sources should not exceed 5 µg/L (Rakshit et al., 2011).

## 4. Different techniques to remove antimony

Not only drinking water but also daily foods such as rice, vegetables, and meat smuggle Sb into human the body (Wu et al., 2011a). But Sb is not the essential trace elements in the human body (Ren et al., 2014). Developing portable and accurate testing kits for detecting environmental Sb and avoiding unnecessary contact is necessary. Here dealing with the presently available technologies, especially adsorption, coagulation/flocculation, membrane separation, electrochemical methods, electrochemical methods, extraction will be discussed, respectively (Fig. 2).

### 4.1. Adsorption

Adsorption remains to be an efficient technique to the decontamination of Sb due to the advantage of cost-effectiveness, minimal sludge production, the simplicity of operation and regeneration capability (Gu et al., 2005; Rahaman et al., 2008). Adsorption effect mainly depends on two aspects, one is the chemical property of the adsorbents and the other is adsorbates (Zhou et al., 2017). Hydroxyl, carboxyl, and amino groups are relevant to Sb(III) adsorption mechanism (Ungureanu et al., 2015). The chemical properties of adsorbents and adsorbates are vital to the adsorption process. A variety of materials for Sb adsorption have been studied, including metalloid, bio-material and so on.

Conventional sorbents used include commercial activated carbons, activated alumina and ion exchange resins (Ungureanu et al., 2015). In addition, the scholars listed many other potential low-cost adsorbents, including clay minerals, bio-materials, sand and even some wastes (Lin and Juang, 2009). The maximum adsorption capacities (Q$_m$) reported in studies depended on different categories of adsorbents.

### 4.1.1. Metal oxides and inorganic minerals

Metal oxides and inorganic minerals have superiorities in adsorption and the experimentally confirmed absorbents of Sb including illite, montmorillonite, kaolin, bentonite, zeolite, diatomaceous earth, quartz sand, iron ore, hydroxyapatite powder, hydrated manganese oxide, hydrated alumina, hydrated iron oxide, nano titanium dioxide (Ungureanu et al., 2015). Here, we aim to find the advantages and disadvantages of each adsorbent. Bentonite, diatomite, and goethite are common adsorbents, but they are devised in adsorption capacity. Xi et al. discussed the sorption behavior of Sb(III) on kaolinite with batch experiment. By means of changing the solution properties, including



**Fig. 2.** Removal technologies of antimony.

pH, temperature, initial Sb concentration and humic acid (HA), the experiment proved that pH was the core factor affecting sorption behavior of Sb(III) on kaolinite and the sorption behavior enhanced with decreasing pH. There is no obvious effect of competitive anions on the adsorption of Sb(III) on kaolinite (Xi et al., 2016).

The laws about adsorption of Sb(III) and Sb(V) on bentonite was explored and found when temperatures between 278 and 323 K, pH 6.0, the adsorption capacities of Sb(III) and Sb(V) on bentonite were in the range of 0.37–0.56 mg/g and 0.27–0.50 mg/g (Xi et al., 2011). Low-cost diatomite to adsorb Sb(III) from aqueous solution was proved to be feasible, and the adsorption capacity of diatomite to Sb(III) reached almost 25 mg/g (Sarl et al., 2010). The adsorption of Sb(III) on goethite was studied and proved when the initial concentration was 15 mg/L, pH 7.0, the adsorption capacity of goethite to Sb(III) was in the range of 18–19 mg/g. So, in a very different equilibrium concentration range, diatomite is superior to goethite and bentonite in respect of adsorbed capacity of Sb(III). In addition, the equilibrium time is different, for bentonite and goethite, 24 h-contact time is necessary to achieve the steady state (Xi et al., 2013), but for diatomite, just half an hour is enough (Sarl et al., 2010).

Besides the adsorbents mentioned above, some other metal oxides and inorganic minerals are also used to remove Sb. Forming the inner-sphere complexation was the mechanism of iron and aluminum oxides absorbing Sb(III) (Guo et al., 2014; Shan et al., 2014). The photocatalysis of different Fe(III) species plays an important role in the geochemical cycle of Sb(III) in surface soil and aquatic environments (Kong et al., 2016). Rapid photo-oxidation of Sb(III) occurred in a Fe(III)-oxalate solution when pH ranged from 3.0 to 7.0 (Kong and He, 2016).

It was found that Sb(III) adsorption was spontaneous and exothermic in bentonite, diatomite, and goethite. In the adsorption of goethite to Sb(III), parallel oxidation of Sb(III) to Sb(V) was observed in the report (Xi et al., 2013). For bentonite, the adsorption ability of Sb(III) was superior to Sb(V), in addition, the anti-interference of Sb(III) was stronger than Sb(V) in term of anions competition (Xi et al., 2011).

Manganite has no absorption capacity on Sb(III) essentially, but manganite can absorb Sb(V). The mechanism of manganite absorbing Sb(III) is that Sb(III) is oxidized to Sb(V) and then absorbed by the manganite. The adsorption of Sb(V) onto manganite is promoted by $NaNO_3$ (Wang et al., 2012).

In addition, hematite coated magnetic nanoparticles have been proved to be an excellent adsorbent for Sb. The adsorption ability reached 36.7 mg/g, which was twice of commercial $Fe_3O_4$, receiving a good effect of reducing the concentration from 110 mg/L to 5 mg/L in the experiment. Except for the adsorption ability, hematite coated magnetic nanoparticles removing Sb doesn't inhibit by pH, ion interference, ionic strength, or natural organic matter (NOM) and the solid/liquid separation was convenient (Shan et al., 2014). 1.76 mmol/g was the peak capacity of iron-manganese binary oxide in adsorbing Sb(III) at pH 3.0, which was much higher than that $MnO_2$ (0.81 mmol/g). In the process of reaction, the manganese oxide covert the Sb(III) to Sb(V) by oxidation and the iron oxide carried on the adsorption of Sb(III) and Sb(V) (Xu et al., 2011).

Binary iron oxides, iron-zirconium bimetal oxide present good performance in absorbing Sb(V). Comparing to the single metal oxides, a number of binary iron oxides showed a better performance in Sb removal (Xu et al., 2011). Iron-zirconium bimetal oxide showed an adsorption ability of 51 mg/g, at pH 7.0, estimated with Langmuir modeling (Li et al., 2012a, 2012b). Synthesized Fe-Zr binary oxide as the adsorbent to adsorb Sb(V), with co-precipitation method, received a better performance for Sb(V) removal than amorphous ferric oxide or zirconium oxide separately (Li et al., 2012a, 2012b).

The adsorption capacities of antimonite and antimonate on MO-2 were investigated, utilizing batch experiments. The experiment showed that the adsorption process of MO-2 to Sb was spontaneous, exothermic, and pH-dependent. The adsorption capacities of MO-2 to Sb(III) and Sb

(V) were 111.70 and 89.99 mg/g, respectively (Luo et al., 2017).

Investigation of the adsorptive behaviors of fresh ferric hydroxide (in-situ FeOxHy) toward Sb(III) and Sb(V) showed that 120 min was sufficient to reach adsorption equilibrium state for Sb(III) and Sb(V), and the maximum adsorption capacity of Sb(III) and Sb(V) by fresh ferric hydroxide was 12.77 and 10.21 mmol/g, respectively (He et al., 2015). The catalysis of positively-charged Cd(II) was proved efficient in the study of the removal of Sb(V) ions by Fe-Mn binary oxide (FMBO). The results showed that Cd(II) at above 0.25 mmol/L improved Sb(V) adsorption onto FMBO and the catalytic performance of Cd(II) in Sb(V) adsorption exceeded $Ca^{2+}$ and $Mn^{2+}$, besides, Sb(V) adsorption decreased with elevated pH (Liu et al., 2015).

Magnetic $Fe_3O_4$ particles have been considered as a low-cost adsorbent for Sb contamination because of the high separation ability from solution. Adding Ce(III) into $Fe_3O_4$ increased the adsorption efficiency of Sb(III) and Sb(V) on Magnetic $Fe_3O_4$, which upgraded the restriction of limited adsorption capacity and enhanced the practical application. Comparing to un-doped $Fe_3O_4$, the adsorption capacity to Sb(III) and Sb(V) in Ce-doped $Fe_3O_4$ increased from 111.4 to 224.2 mg/g and from 37.2 to 188.1 mg/g at neutral pH values, respectively (Qi et al., 2017). Except Ce(III)-doped $Fe_3O_4$, Cu-doped $Fe_3O_4$ (magnetite) also enhanced the removal capability of aqueous Sb comparing to non-doped. The maximum adsorption quantity by non-doped $Fe_3O_4$ was 34.46 mg/g of Sb(III) and 7.07 mg/g of Sb(V) at pH 7.0. The Cu-doped $Fe_3O_4$ improved the Sb adsorption to 43.55 mg/g of Sb(III) and 30.92 mg/g of Sb(V) correspondingly (Qi et al., 2016). Weak magnetic field increased the removal capacity of Sb(III)-tartrate and Sb(III) by zerovalent iron and elaborated the mechanisms of the inhibiting effect of tartrate (Fan et al., 2017).

### 4.1.2. Carbon-based materials

Activated carbon (AC) is a common adsorbent and widely used in commercial scale. Developed porosity, large surface, the high degree of surface reactivity and variable surface chemistry endow its removal ability. However, the potential adsorption ability of AC to Sb, the mechanism, and reaction conditions are still not clear. Researches concerning AC adsorbent are common, but as an adsorbent for Sb removal are rare and lack of relevant experimental data. Those published researches related to carbon adsorbents concentrated on Sb(III), rather than Sb(V). Granular activated carbon (GAC) is an activated carbon modified by $FeCl_3$, with the adsorption capacity 2–3 mg/g of Sb(III), whose adsorption capacity was 3.5 times as much as original AC (pH = 7.0 and 25 °C) (Yu et al., 2014). Carbon nanotubes (CNT) increased the adsorption capacity from 3.01 to 6.23 mg/g after modified by Fe(III), pH 7.0 and initial Sb(III) concentration of 1.5 mg/L, the removal efficiency reaching up to 99.97% (Yu et al., 2013). Raw and modified carbon nanotubes, a new kind of carbon-based adsorbents, showed better adsorption performance of Sb(III) from the water (Salam and Mohamed, 2013; Yu et al., 2013). Multi-walled carbon nanotubes (MWCNT) can remove 80% of Sb(III) in solution, with the initial concentration of 4 mg/L, pH 7.0 (Salam and Mohamed, 2013). Compared to Sb(III), the removal of Sb(V) is hard and also less published papers concentrates on the adsorbents. Sb(V) is negative charge in almost the entire pH range, lending the difficulty of adsorbing Sb(V) (Ungureanu et al., 2015).

Graphene oxide (GO), $Fe_3O_4$/GO and a composite of quartz sand coated with $Fe_3O_4$ and graphene oxide (QFGO) had the adsorption effects in Sb(III). GO, $Fe_3O_4$/GO, and QFGO adsorbed Sb(III) rapidly and the adsorption amount increased with the increase of GO, $Fe_3O_4$/GO and QFGO. The static adsorption experiment of the three substances mentioned above showed that with the increase of additive quantity, the removal rate of Sb(III) ions in the solution increased and three kinds of materials absorption to Sb(III) in an aqueous solution was a rapid process (Yang et al., 2015b). Co-existing anions including sulfate, chloride, and nitrate have no obvious influences on the removal of Sb(V), but phosphate, carbonate and silicate present restraint effects when

the concentration is high (Zou et al., 2016).

### 4.1.3. Biosorbents

Biosorption is a potential technique for heavy metals removal from aqueous solutions (Zhou et al., 2016). The repair of heavy metal pollution by the plant was commonly adopted, and it could be divided into plant accumulation, plant volatilization, and plant curing (Bhatia and Goyal, 2014). Many crops in mining areas accumulated high levels of Sb in their edible parts, bringing potential threat to human health (Feng et al., 2013). The waste green bean husk had the adsorption capacity of 20.13 mg/g for Sb(III) (Iqbal et al., 2013). Bai Yufeng tail fern and Indian mustard could adsorb Sb(III), Sb(V), methyl antimony (TMSb) and significant enrichment effect was obtained by Pteriscretica and Brassica juncea. The order of adsorption ability is Sb(III), Sb(V), TMSb of the two plants (Wang et al., 2014). Arbuscular mycorrhizal fungi (AMF) was proved to play an important role in the biogeochemical cycle of Sb. Sb accumulation in the clover was observed after inoculating AMF to clover (Chen et al., 2015). Hydrochars and pyrochars was extracted from animal manures to remove Sb(III) from aqueous solution, which proved to be effective (Han et al., 2017). Biogenic Fe-Mn oxides (BFMO) was applied to groundwater removal. Results indicated that microbial degradation consolidated by bio-augmentation strengthened the performance of Fe-Mn oxides, indirectly benefiting the remove ability of pollutants. which presented an alternative route to treat the Sb contaminated groundwater (Bai et al., 2016).

### 4.1.4. Organic adsorbents

Natural organic adsorbents (e.g., cellulose, chitosan, starch, husk ash, chitin) have been used for Sb removal. Most organic adsorbents are modified to be used for adsorption of antimony. The adsorbent modified has the specific surface area, and also has the activated group, which can improve the adsorption capacity. A new chemically bonded adsorbent designated as ICAA-PPG, which contained 1, 2, 3-three benzene phenol, was used to adsorb Sb. ICAA-PPG had the advantages of good adsorption stability and being less affected by pH (Yu et al., 2014). Ammonia diacetate chelate porous hollow fiber membrane was proved feasible to antimony adsorption. The leakage curves of the Sb was drawn and proved the hydrochloric acid eluting showed no effect on adsorption of Sb (Nishiyama et al., 2003). Chaff ash could adsorb Sb and met the Freundlich isothermal adsorption model. The adsorption ability was improved as the temperature rising. In the experiment, 0.01 mol/L acid solutions was found as the best solution condition of the experiment and the equilibration time was 10 min (Khalid et al., 2000).

### 4.2. Coagulation/flocculation

Coagulation and flocculation are able to reduce metalloids in waters. 83% Sb was removed from solution, reducing the Sb concentration from 300 mg/L to 25 mg/L, with precipitation of Sb (Zhang et al., 2002a). 80–90% Sb in the solution was removed with FeCl$_3$ as coagulant in specific controlled pH (Nakamura and Tokunaga, 1996). It was reported that 98% of Sb(V) was removed with proper pH and the proper dose of ferric coagulants. The removal of Sb(III) needed less ferric coagulant dose and certain pH range between 4.0 and 10.0. Comparing behaviors between Sb(III) and Sb(V) during coagulation, the removal efficiency of Sb(III) was higher than Sb(V) during ferric coagulation. In addition, Sb(III) was less affected by the interfering components like phosphate and humic acids (Guo et al., 2009). However, for Sb(V) removal, sulfate, bicarbonate, humic acids and phosphate are significantly influencing factors (Wu et al., 2010). Low capital costs, the wide range of pH, large-scale application and simple operation are the advantages of coagulation/flocculation technique on Sb removal (Mondal et al., 2013). But the formation of toxic by-products are often regarded as the disadvantage of coagulation/flocculation process on Sb removal.

### 4.3. Membrane separation

Membrane separation technique is a new water treatment technology. The mechanism of membrane separation technique is the selective permeability of the membrane. The applicable condition is the pressure difference or powered electrical potential difference between the membrane sides (Skilhagen et al., 2008). Comparing with the traditional coagulation, precipitation, ion exchange, membrane separation technology has the very significant superior performances, such as more convenient, low energy consumption, high efficiency, small covers, small investment, and simple operation (Nishiyama et al., 2003). Generally, membrane filtration is classified into four types: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Membrane filtration is an effective method to remove arsenic, however, the study about the removal of Sb by membrane filtration is rare. Better effects of removal Sb(V) than Sb(III) was obtained with reverse osmosis (RO) regardless of the pH condition (Nishiyama et al., 2003). Chelating porous hollow-fiber membranes were used to treat Sb contamination, and proved effective (Saito et al., 2004). A polyol ligand, which had inner porous hollow fiber membrane, was used to remove Sb(III) from a fluid and achieved good effect (Tsuneda, 2004). Enhancement of ultrafiltration membrane was proved to be effective to Sb(V) removal and the removal of Sb(V) by the integrated ultrafiltration (UF) membrane process was simple and convenient (Ma et al., 2017). Integrating adsorbents with UF membranes is a prospective method, but facing a number of problems such as high probability of membrane surface damage, high running cost, low efficiency in-situ chemical cleaning, etc. So, many researchers have commenced to study the optimization measures to solve the problems membrane separation faced. But, it is still insufficiently documented and only little research findings has been obtained. i.e., injecting hydrolyzed flocs into the membrane tank to enhance the adsorption ability of UF membrane (Ma et al., 2017).

### 4.4. Electrochemical methods

Electrochemical methods mainly have the functions of coagulation, flocculation, flotation, oxidation and micro electrolysis. The process of electric coagulation, electric flocculation, electric floatation and electrooxidation in wastewater treatment are often carried out at the same time. Electrocoagulation is based on the electrolytic oxidation of anode materials and the generation in-situ of coagulant. Under potential deposition (UPD) of Sb was proved to be feasible with the electrochemical techniques, including potential step and potential sweep. The potential applied determined the absorption capability of UPD to Sb (Li et al., 1994). Later, Zhu et al. used electrolytic reductions to remove Sb from flotation-water in an Sb mine and studied the effects of operation parameters of electrocoagulation technique, including current density, standing time and initial pH. The wastewater treated by electrolytic reductions not only reached the emission standard system set by State Department of Environmental Protection but also State Administration of China, with Sb concentration lower than 1 mg/L (Zhu et al., 2011). Electrowinning method was used for the recovery of Sb from sulphide alkaline solutions and received the purity about 99.6% (Awe and Sandström, 2013). In addition, Awe et al. also studied Sb sedimentation from sulphide solution in a non-diaphragm electrolytic cell. Results showed that in the solution, there was no negative effect of Sb deposition from sulphite and sulfate ions (Awe et al., 2013a). Furthermore, this group reduced the concentration of Sb from 1.7% to less than 0.1% in the copper concentrate and pointed out that sodium sulphide was adverse to Sb leaching and electrolytic process, and high temperature advanced both leaching and electrolytic process. Based on this study, they put forward a flowsheet for Sb recovering in copper concentrates named hydro-/electrometallurgical process (Awe et al., 2013b). Although the efficiency of electrolytic reduction is high, reaching up to 96–100%, but the economic input is an important issue

to overcome in the practice of this technique.

### 4.5. Ion exchange

The mechanism of ion exchange is similar to that of adsorption, which both can absorb solute from the solution. Ion exchange is a process of chemical reaction, but adsorption is a physical process. It is an important method to heavy metals removal in wastewater. The XAD-8 ion-exchange resin can remove Sb because the ion exchange resin has a strong exchange capacity for Sb(III) and Sb(V) (Ozdemir et al., 2004). Luo et al. carried on batch experiments to study the adsorption isotherms and kinetics of Sb(III) and Sb(V) with zirconium oxide (ZrO₂)-carbon nanofibers (ZCN). The result showed that ZCN had Sb(III) adsorption capacity of 70.83 mg/g and Sb(V) adsorption capacity of 57.17 mg/g. The adsorption process of ZCN on Sb was exothermic and followed an ion-exchange reaction (Luo et al., 2015). On account of the common appearance of Sb in copper electrolytes, Riveros et al. carried on a study with the ion exchange method to remove Sb(III) and Sb(V) from copper electrolytes. The two species presented a different reflection in the synthetic copper electrolyte in solubility and elution. For details, the solubility of Sb(III) was more affected by temperature than Sb(V) and when extracting Sb(III) and Sb(V) with an amino phosphonic resin, Sb(III) was easily eluted by HCl than Sb(V). Sb(V) easily accumulated on the resin, weakening the ion exchange process (Riveros et al., 2008).

### 4.6. Extraction

Extraction refers to the transfer of material from one solvent to another solvent where the solubility or distribution coefficient is different. By repeated extraction, the majority of the material can be extracted (Yang et al., 2015b). Many researchers have studied extraction methods for Sb removal. But it is still not sufficiently well documented. Leaching of Sb from three representative Sb ore (Tongkeng Antimony Mine, Muli and Banxi) was proved feasible, with pH-static leaching method (Hu et al., 2016). Extraction of Sb in low temperature from stibnite concentrate, with iron oxide as sulfur-fixing agent was proved effective and showed that in the optimum conditions, the recovery rate of Sb can be achieved by 91.48% and achieved crude Sb with a purity of 96.00% (Li et al., 2017). The possibility of extraction Sb(V) from fluoride solutions was proved and the hydrate-solvate mechanism make the extraction occurred. The extraction efficiency was enhanced at a transition from Tri-Butyl-Phosphate (TBP) to n-octanol (Kirichenko et al., 2013). Extracting hazardous Sb from Sb minerals was proved to be feasible. 12 samples of antimony-bearing ores from eight large mines from China in Hunan, Yunnan, Guizhou and Guangxi provinces were taken as samples. The study showed that Sb extracting results were related to type of ores, species of Sb and pH value (Hu et al., 2016).

## 5. Concluding remarks and future research needs

Potential risks of Sb have attracted high attention as a kind of potential toxicity and carcinogenicity element, though a lot of methods have been developed to curb Sb pollution over the last few years, however, compared to arsenic, removal of antimony is not sufficiently documented. There is a lack of systematic understanding of the environmental pollution process and bio-geochemical cycle of Sb. Fewer studies report the adsorption of Sb in soil and water, therefore, to understand the influence of the use of Sb on the environment, a systematic analysis on environmental sources, hazard and removal of Sb is necessary. Nowadays, adsorption technologies, coagulation/flocculation, membrane separation method, electrochemical method, ion exchange and extraction are used in varying degrees. However, these adopted techniques have some weak points and their by-products hide threaten of secondary Sb pollution. For examples, for adsorption technique, the difficulties of adsorbents regeneration, recycling and reuse are the

disadvantages of Sb removal. For coagulation/flocculation, the toxic by-products and large amount of coagulant demand are regarded as the disadvantages of Sb removal. For membrane separation technique, membrane contaminated, clogged and decay of membrane flux are the disadvantages of Sb removal. For electrochemical methods, the economic input is an important issue to overcome in the practice. Therefore, for the sustainability of the environment, new technologies and integrated technologies are urgently needed to develop. In addition, for better investigation and application of Sb, it is also necessary to carry out these tasks: (I) Assessing diet characterizing toxicokinetics and bioavailability for more Sb species, (II) Developing portable and accurate testing kits for detecting environmental Sb, (III) Finding out suitable methods for Sb removal in commercial scale, (IV) Developing evaluation methods to multiple medium exposure and different approaches exposure, (V) Finding effective means to reduce the exposure risk of dietary, particularly in the necessities of rice and vegetables.

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