

Mercury Contamination of Water and the Removal of Mercury from Water

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Abstract. Mercury is a common element in nature. Mercury that is in compound form does not severely harm the environment and human being. However, when the mercury element is by itself, that is when its oxidation state is zero, it easily gets into the air or the water. And because the mercury is not in any compound form, nothing restricts its toxicity, it affects the environment and people's health. Both anthropogenic reasons and natural factors lead to the mercury contamination in water. Coal combustion, zinc smelting, gold rushing, and mercury mining are the major anthropogenic reasons. And since mercury naturally exists in the nature, natural soil would release mercury, which then goes into water as rainwater or flows pass by. Removing mercury from water has been a focus in many places like Guizhou, China and Peru. Ion exchange resins adsorption and multifunctional chitosan non-woven fabrics modified with carbon dots (CDs) can be used. Ion exchange resins adsorption includes a wide variety of substrate. And with these binding agents, mercury, along with many other heavy metal ions, can be easily adsorbed. CDs are carbon nanoparticles that exhibit high sensitivity and good ability to fluoresce, With the modification with CDs, fabrics can change into a cheap and easy tool to remove mercury from water. Studying the removal of mercury contamination from water helps reduce gradual damage to the environment and to human bodies.

Keywords: Mercury Contamination, Water, Carbon Dots, Causes, Methods.

1. Introduction

Mercury (Hg) is an element that has the atomic number of 80 and atomic mass of 200.59. It is commonly used in daily life, such as in the thermometers and barometers. Mercury can either exist in inorganic form, like in its element form or in inorganic salt form, or participate in any organic molecules. No matter if the mercury is in inorganic form or organic form, it can be toxic and cause damage to humans and the environment. Corrosion to eyes and skin can happen if humans get contacted with inorganic mercury salts. If ingested, gastrointestinal tract and kidney would be seriously affected [1].

Mercury contamination did not start until recently. In fact, back in 1865, not long after the concept of organic mercury compounds arose, fatal cases with methylmercury were reported [2]. Around that time, gold mining became popular in the west coast. Many people moved to California for gold mining. Mercury, used as a facilitator in the gold recovery process to help separate gold from gravels and sands, then became a major pollutant to the environment [3].

Anthropogenic reasons are the major factors that lead to the level of mercury contamination nowadays. In the past, coal combustion was the major method to obtain energy and generate electricity—in some places, electricity is still obtained from burning coals. The combustion of coal resulted in the release of mercury into the air. Even though the mercury does not directly go into water from the combustion of coal, fish in the water would get mercury poison and die. Zinc smelting also releases mercury in the process. Mercury is often in its compound form before zinc smelting. However, the extremely high temperature in the process of zinc smelting results in the change of oxidation state of mercury. After the process, mercury changes from compound form to single element, which has the oxidation state of zero. Then, it is easy for mercury to get into air, soil, and water, which causes extreme harm to the environment and human health. Not strictly following the environmental guidelines can also emit mercury into the environment.

Natural emission of mercury also causes some degree of mercury contamination in water. Not only natural soil emits mercury, which gets into the water when rain water flows through the soil, but also natural water, which gets mercury from the natural exchange with air.

Mercury contamination severely affects peoples' health as well as the environmental conditions, so removing mercury from the environment is urgent. This review article first studies the causes of mercury contamination in water, which are human activities and emission from natural sources. Then, methods of mercury removal from water are discussed. Traditional methods and novel techniques are applied to aiming for effective removal of mercury from water.

2. Causes of mercury contamination in water

2.1. Human activities

The anthropogenic emission of mercury has been increasing these years. Guizhou, China is one of the places that has the most mercury emissions. Around year of 2000, Guizhou province contributed around 22.6 to 55.5 tons per year, which was roughly 6.3% to 10.3% of the total anthropogenic mercury emissions at that time in China [4].

2.1.1 Coal combustion

Coal combustion is an anthropogenic source of mercury emission into the atmosphere. Even though mercury does not dissolve in water, mercury resulted from the combustion of coal cannot directly dissolve in rivers or water bodies nearby, and the deposition of mercury from the atmosphere leads to the elevated levels of mercury in fish [5].

The combustion and pollution control affect the emission rates of mercury. Feng et al. (2008) got the statistical data for coal consumption which suggested that domestic users, large-scale coal-fired power plants, and industrial sectors consumed about 22%, 30%, and 48% of the total coal consumptions in Guizhou respectively. Another group of scientists, Tang et al. (2007) used a mass balance technique to estimate the mercury emission factors. The Hg emission factors of a small industrial coal-fired boiler with flue gas desulphurization (FGD) systems and without FGD systems were 26% and 66% of total Hg presented in coal. With electrostatic precipitators (ESPs) systems, the Hg emission factors of a large coal-fired power plant could go up to 85% of total Hg presented in coal. If employed with FGD systems, the large coal-fired power plant would decrease its emission factors to 43%. Streets et al. suggested that Guizhou released 56% of Hg from coal combustion as Hg^0 , 33% as Hg^{2+} , and 13% as Hg^P .

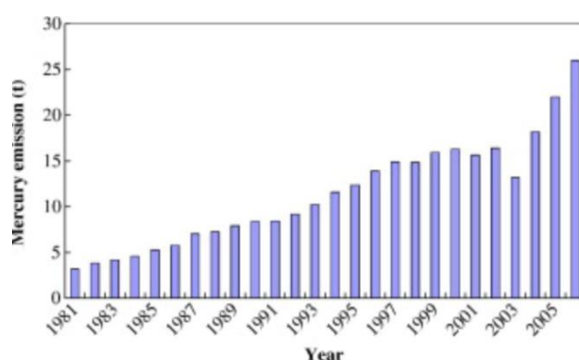


Figure 1. Mercury emission from coal combustion in Guizhou, China from 1981 to 2006 [6]

Using the Hg combustion emission factors, the annual emission of total Hg into the atmosphere can be estimated in Guizhou. Figure 1 shows the trend from 1981 to 2006. The mercury emission was less than 5 tons in Guizhou in 1981, but until 2006 it reached around 26 tons (Fig. 1). The emission of mercury into the atmosphere from coal combustion would keep increasing following this trend.

2.1.2 Emission from smelting of zinc

Zinc smelting is the process of converting impure solids into pure zinc by industrial methods. In the process of zinc smelting, many pollutants are released. Cadmium is a major pollutant that can be

released due to mineral processing activities, and it impacts soil, vegetables, water, and in some cases, even human health [9]. Like cadmium, mercury is another pollutant released in the process of refining. Mercury usually exists in compound forms. However, at the temperature of 700-800 degree Celsius, most mercury compounds would automatically decompose [10]. When the mercury is not in a compound, its oxidation state becomes zero. Therefore, when the smelting of zinc is occurring, the temperature reaches at least 700 degrees Celsius, then all the mercury that's originally from the impure solids are turned into mercury that has oxidation state of zero. If mercury is in its compound form, the toxicity is not easy to be released, because mercury is coupled with other elements. However, when the mercury is by itself, which is when it has the oxidation state of zero, it is easy for the mercury to get emitted into the environment, and thus creating severe harm to not only the environment, but also human health [11].

2.1.3 Emission from gold mining

In the past centuries, gold mining was a trend in the United States. When gold mining was in progress, hydraulic method was one of the most effective ways because of its high recovery rate, hence the most popular methods [3]. And back then, placer ores that could possibly produce gold were broken down by monitors or water cannons so that gold can be extracted from inside [3]. Some ores contained mercury, so as the process went on, mercury was emitted into the environment.

In California and during the gold rushing times, a lot of mercury was used for gold recovery since the application of liquid mercury could enhance gold recovery [3]. In the mining process, the amalgam of gold and mercury along with gold would sink to the bottom as a result of high density of mercury, while sand and gravels tend to stay at the top. Then, large amount of water would run through the mercury and gold in order to wash away unwanted gravels and sands [3]. A portion of mercury then gets the chance to mix with water and finally get to rivers, which pollutes large area of water body. The reported mercury production of mercury from 1850 to 1981 was 220 million pounds solely in California [12]. Therefore, the large amount of mercury production could cause severe pollution to the environment.

2.1.4 Emission from artisanal mercury mining

Starting from the beginning of the 21st century, mercury mining activities were ceased because of low profit in Guizhou, China. However, the demand of mercury increased afterwards because China started to restrict the import of mercury from Europe. Artisanal mercury mining activities then revived [13]. Because of the use of indigenous methods, the artisanal mercury mining activities would not strictly follow the environmental guidelines. Hence, much mercury of oxidation state of zero was produced. And the pollution became more severe.

2.2. Emission from natural sources

2.2.1 Emission from natural soil

Many places that are at high altitudes in the world have high-Hg level of geological baseline, like Guizhou, China. In situ total gaseous Hg (TGM) exchange fluxes between air and soil surface were intensively measured in Guiyang and Hongfeng reservoir area [13]. And results from practical determinations have shown that the emission of mercury fluxes from natural soil reached $9.64\mu\text{g}/\text{m}^2$ per year, which was much higher than the accepted values in the global mercuriferous belts.

2.2.2 Emission from natural water

Mercury contamination can also happen from emission from natural water, even though the amount is relatively lower compared to anthropogenic factors of emission, it can't be ignored. Because of the presence of mercury in the air—for instance, from combustion of coal or zinc smelting, or even mercury that's naturally in the air—when the exchange happens between surface water and the air, mercury that's present in the air would get into the water. The exchange between water at the surface and the air is significant in the global biogeochemical cycling of mercury [14]. As shown in Fig. 2, mercury gets into the surface of water through deposition. And then Hg (0), which is the mercury that has an oxidation state of zero, gets re-emitted into the atmosphere. Because of this cycle,

mercury is always present in the water, so when considering mercury contamination, this natural factor cannot be ignored.

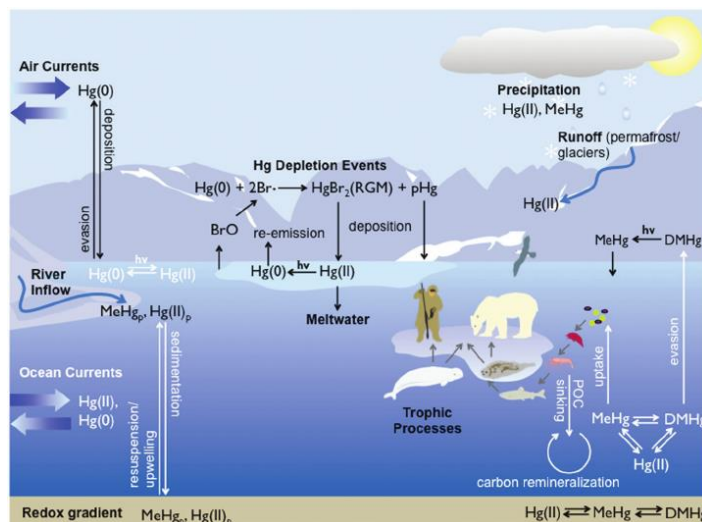


Figure 2. The global biogeochemical cycle of mercury [15]

3. Methods of mercury removal from water

3.1. Ion exchange resins adsorption

Ion exchange is a process not only used in environmental studies, but also other science fields like biochemistry. Cations or anions are chosen based on the characteristics of the desired products, and when the fluid flows through the sample, the ions deposit in the solid, and other ions from the solid are displaced in equal amount [16]. Like ion exchange, adsorption is the process of absorbing ions, atoms, or molecules from a certain liquid, gas or solid. Adsorption processes can be used, and it is the most used method of removing mercury from water compared to conventional coagulation, chemical precipitation, and reverse osmosis [17], hence it is the most studied method among these. The history traces back to 1974, when Schoor and Humenick utilized activated carbons to remove mercury from water through physical and chemical adsorption. And Logsdon and Symons found out that mercury could be absorbed on clay particles in 1975. After that, industrial methods were discovered, for instance, the industrial solid by-products. Even barks of trees can be used to absorb may heavy metal ions in industrial wastewater.

However, despite good ability of absorbing many heavy metal ions, the materials mentioned above cannot remove mercury contamination from water effectively. Discharge limits of mercury are used to measure the amount of mercury that can be left in the water, and they are set to be 10 parts per billion (ppb) in the United States in environmental legislation [18].

3.2. Multifunctional chitosan non-woven fabrics modified with carbon dots

Carbon nanoparticles, or carbon dots (CDs) are small particles that have the diameter of around 10 nanometers or smaller. They are cheap to manufactured, sensitive to be detected and can be used to bind to heavy metal ions. And CDs can be doped or combined with many other chemicals or even like fabrics in this case, then the CDs can be used to detect or remove target cooperating with the chemicals or fabrics. In this case, CDs are incorporated with a type of fabric called terylene, which is mainly composed of polyethylene terephthalate [19]. The Terylene Carbon Dots (TCDs) TCDs can be synthesized from a one-step hydrothermal method. Terylene dyed with red 167 was dissolved in ethylene glycol solution. After stirring the mixture for 15 minutes, urea was poured into the mixture and then got dissolved. The whole mixture was then transferred to a Teflon-lined autoclave and got heated for 12h at 200°C. After heating, the product was naturally cooled to room temperature, following by centrifugation and filtration. The solid TCDs were then obtained by solution drying in

the vacuum, and the product was re-dispersed into deionized water to make a solution. After that, the CDs can be modified on a wet-spun non-woven chitosan fabric by a series of different concentrations of the TCD-solution, and the fabrics were further washed with deionized water to remove the extra TCD-solution [19]. When removing the mercury ion from the water, let the water run through the doped chitosan fabric, then most of the mercury ions would attach on the chitosan fabric. A piece of fabric can be cleaned and reused five times. As it is shown in Fig. 3, the fabric keeps effective until fifth cycle. After five cycles, the fabric gets ineffective [19].

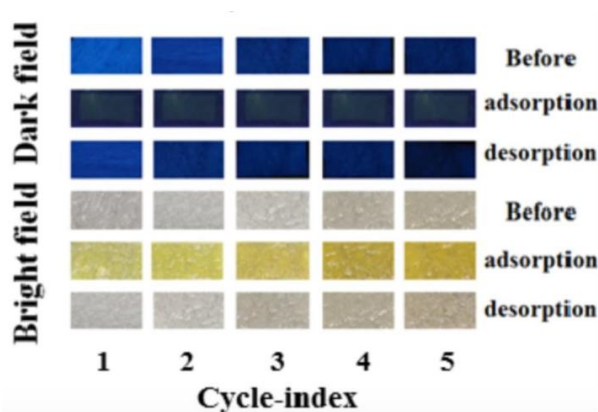


Figure 3. The before, adsorption, and desorption of five cycles in bright field and dark field [19]

4. Conclusion

Mercury contamination severely affects humans' health and the environment. Anthropogenic reasons like the recovery of gold in California, and natural sources such as mercury in the soil, both led to the level of mercury contamination in water today. From this century, researchers and scientists have been working on removing mercury contamination in water and get below the discharge limits. Traditional and popular approaches like adsorptions can be used. Additionally, novel methods like utilizing CD-modified non-woven chitosan fabrics are also feasible. Developing more environmentally friendly purifying techniques and designing more plans to prevent mercury from getting into the water is necessary. More focus will be put into this topic, and it will be beneficial all human beings, animals and plants, and the environment.

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