

ORIGINAL RESEARCH ARTICLE

Sodium dimethyl dithiocarbamate, as a capable heavy metal chelating agent: Production and applications

Yu Ying^{1,2}, Shichen Lin^{1,2,3}, Yuan Fang^{1,2}, Jiahui Gu⁴, Fenglong Gu^{1,5,*}

¹ Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, Guangzhou 510006, China

² School of Chemistry, South China Normal University, Guangzhou 510006, China

³ Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Park, Fukuoka 816-8580, Japan

⁴ Zhejiang Zuhui Environmental Technology Co., Ltd., Hangzhou 311199, China

⁵ School of Environment, South China Normal University, Guangzhou 510006, China

* Corresponding author: Fenglong Gu, gu@scnu.edu.cn

ABSTRACT

Sodium dimethyl dithiocarbamate (SDDC) is a universal heavy metal precipitant/chelating agent, which is widely used in the treatment of heavy metals in industrial wastewater and fly ash from waste incineration. It can be utilized as a heavy metal precipitant, fungicide, agricultural insecticide, rubber vulcanization accelerator, styrene-butadiene rubber polymerization terminator, polymerization inhibitor, mineral processing reagent, etc. This review article focuses on the research of the production and application of SDDC in heavy metal chelation. The following three benefits of using SDDC as a heavy metal chelating agent are: (1) it can chelate with various heavy metal ions at room temperature to generate insoluble chelate salts and precipitates, which can be easily removed; (2) SDDC can perform chelation reaction with various heavy metal ions at the same time; (3) as a heavy metal chelating agent, SDDC is simple to use and low costs, which is significantly better than other heavy metal chelating agents and precipitants. This review paper presents novel ideas for the performance enhancement based on SDDC in removing heavy metals and is a prospect for the research, development, production, and applications of SDDC.

Keywords: sodium dimethyl dithiocarbamate; heavy metal; chelating agents

ARTICLE INFO

Received: 28 July 2023

Accepted: 1 September 2023

Available online: 18 October 2023

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1. Introduction

The heavy metal pollution in China is shocking. The polluted soil of China exceeds the standard rate of more than 16%^[1]. The heavy metal pollution in the national surface water is also very serious^[2]. China has a long way to go to prevent and control heavy metal pollution. As a result, in March 2022, the Ministry of Ecology and Environment of China issued the 2022 No. 17 document “Opinions on further strengthening the prevention and control of heavy metal pollution” to control the amount of the five heavy metals: lead, mercury, cadmium, chromium, and arsenic. The total amount of pollutant discharge shall be controlled. Key industries, including heavy non-ferrous metal mining and dressing, heavy non-ferrous metal smelting, lead battery manufacturing, electroplating, chemical raw materials and chemical product manufacturing such as chromium salt manufacturing, leather tanning and processing industries, will implement key prevention and control. The goal is to curb the further deterioration of heavy metal pollution, and strive to reduce the

discharge of key heavy metal pollutants in key industries nationwide by 5% compared with 2020 by 2025^[3].

It can be seen that the treatment of heavy metals is particularly important. At present, there are five main methods for the treatment of heavy metals, including chemical reduction method, solvent extraction separation method, adsorption method, ion exchange method, and chemical agent treatment method. The advantages and disadvantages of these methods will be further compared in **Table 1**. Using chemical reactions such as neutralization reaction, ion exchange, and oxidation-reduction, the heavy metal ions in the wastewater are transformed into precipitated heavy metal compounds insoluble in water, and then the precipitates (heavy metal ions) can be removed from the solution by filtration and separation.

Table 1. The pros and cons of different methods to treat heavy metals.

Methods	Pros	Cons
Chemical reduction	Simple principle, easy to operate, applicable to large amount and high-concentration wastewater	Generation of toxic sludge
Solvent extraction	Highly selective	Unnecessary energy consumption
Adsorption	Applicable to pretreat electroplating wastewater	Low regeneration efficiency
Ion exchange	High selectivity	Large dosage consumption
Chemical agent treatment	Low cost, good effect, easy operation, no secondary pollution	Potential for chemical overuse

The chemical reduction method refers to the use of reducing agents (such as FeSO₄, NaHSO₃, iron filings, SO₂, etc.) to precipitate heavy metal ions. Its principle is simple, easy to operate, and applicable to large amounts of water and high-concentration wastewater^[4]. However, a significant drawback of this approach is the generation of toxic sludge^[5]. Solvent extraction separation method can separate heavy metal ions, but must have a highly selective extractant, the loss in the extraction process will inevitably require multiple regeneration processes, resulting in unnecessary energy consumption. These drawbacks limit the practical application of this method^[6-8]. The adsorption method is to use the unique structure of the adsorbent (such as activated carbon) to absorb heavy metal ions. This method has been widely used in wastewater treatment^[9,10], but the regeneration efficiency of activated carbon is low^[11], and the treated water quality is difficult to achieve recovery^[12]. Generally, this method is only used for the pretreatment of electroplating wastewater. The ion exchange method is to use high-efficiency ion exchangers (such as ion exchange resins, etc.)^[13]. The dosage consumption is large, so the application is greatly limited^[14]. The chemical agent treatment method, that is, the use of heavy metal chelating agents to treat heavy metals, is the most widely used method at present. Despite the potential for chemical overuse^[15], the use of chelating agents to treat heavy metals has low cost, good effect, easy operation and no secondary pollution^[16,17]. Chemical agent treatment is the method that this paper focuses on.

The chemical agent treatment method is to use the chelating group in the chelating agent to carry out the chelating reaction with the heavy metal ions to produce a chelate with a hydrophobic structure to precipitate the heavy metal ions. This method can complete the reaction process at room temperature and within a wide pH range, and is not affected by the concentration of heavy metal ions. It can better precipitate various heavy metal ions in pollutants and wastewater, even if the treated pollutants and wastewater contain complex components. This method can also handle heavy metals to meet emission standards. The chemical treatment method has obvious advantages in the removal of heavy metal ions, such as the reduction of sludge and the great flocculation effect.

At present, the most commonly used heavy metal chelating agent on the market is sodium thiocarbamate, its chemical name is sodium dimethyl dithiocarbamate (abbreviated as SDDC), also known as N,N-dimethyl N, N-dimethyldithiocarbamate sodium salt, containing two crystal waters, the molecular formula is C₃H₆NS₂Na·2H₂O. It is the sodium salt of carbamic acid, so it has the general characteristics of salt, especially

the chelating clamp (S-C-S) in SDDC molecule is very easy to chelate with metal ions to form a series of metal salts.

The pure product of SDDC is a scaly white crystal with a slight ammonia smell and is easily soluble in water. The crystal obtained by crystallization contains 2.5 molecules of crystal water (commercially available solid SDDC powder generally only contains 2 crystal water molecules), when heated to 115 °C, 2 molecules of crystallization water will be lost, and when heated to 130 °C, all crystallization water will be completely lost. The commercially available product as a heavy metal chelating agent is 40% aqueous solution of SDDC, which is a light yellow or grass green transparent liquid^[18].

SDDC is an important dimethyl dithiocarbamate, which has a wide range of applications. Because SDDC contains chelating pliers (see **Figure 1**), one of its important uses is as a heavy metal chelating agent, or heavy metal precipitating agent, which can be used for chelating reactions with heavy metal ions, resulting in high stability and difficult precipitation of heavy metal chelate salts soluble in water, efficient removal of heavy metals in pollutants or wastewater. As a heavy metal chelating agent (usually also called heavy metal ion eluting agent, heavy metal trapping agent, etc.), SDDC can interact with various heavy metal ions at room temperature and in a wide range of pH conditions, such as: copper, cadmium, chromium, mercury, lead, manganese, nickel, zinc, etc., undergo chelation reactions, and quickly generate insoluble and easy-to-remove flocculent precipitates in a short period of time, thereby achieving the purpose of removing heavy metal ions. SDDC can also be widely used in electroplating industry, electronics industry, non-ferrous metals, iron and steel smelting industry, photographic laboratory and film processing factory, chemical industry, waste incineration plant, battery factory^[19-21].

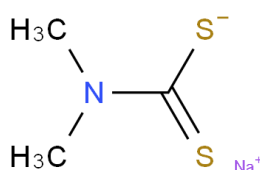


Figure 1. Molecular structural of SDDC.

The main advantages of SDDC as a heavy metal chelating agent to remove heavy metals in water are (1) low cost according to the company's report^[22]: the purified water quality is better than traditional precipitants, and its agent cost can generally be reduced by 15% to 30% compared with other heavy metal chelating agents; (2) wide range of application: the coagulation effect can be achieved when the pH is above 2.5, and it can be used to treat acidic wastewater and alkaline wastewater. Even with excessive dosage will not cause the adverse effect of water turbidity; (3) even when multiple metal ions coexist and the concentration is high, they can be removed at the same time; (4) the chelated precipitate is stable: the formed precipitate can be removed even at a high temperature of 200–250 °C or in a dilute acid solution; (5) large processing capacity: good solubility, fast formation of flocs, large processing capacity; (6) small corrosion: its alkalinity is higher than that of other aluminum salts and iron salts. SDDC solution has less erosive effect on the equipment, and the pH and alkalinity of the treated water are less changed.

In addition, SDDC has many other uses, such as terminators and vulcanization accelerators in the rubber industry, mineral processing agents in the mining industry, etc.^[23-26]. SDDC is also an intermediate of various fungicides. As early as the 1970s, Tianjin Pesticide Experimental Plant began to produce and use SDDC and its related products^[27]. It is used industrially as an accelerator and vulcanizing agent for natural rubber, synthetic rubber and latex, and as an additive for lubricating oil in oil processing. It is also used as an antifungal agent for linoleum, which can replace the highly toxic antifungal agent high mercuric chloride. In agriculture, SDDC is a protective fungicide, which is used for foliar spraying, seed treatment, soil treatment, and has a control effect on cereal smut and seedling blight of various crops, fruit trees, vegetables, wheat and other

diseases. Also applicable to fruit tree nurseries. It has a repellent effect on beetles, rats, rabbits, deer, etc., so it can also be used as a repellent.

SDDC, however, has certain toxicity and has a negative impact on the environment. Harmful to the body and irritating to the eyes if taken orally, therefore, direct contact should be avoided. Solid SDDC is wrapped tightly with black polyethylene tape inside and outside with an inner film polypropylene woven bag, and stored in a cool and dry place to prevent moisture and heat. It is noted that SDDC should not be stored in ironware. SDDC is stable in an alkaline medium, it will decompose when encountering acidic substances and high temperatures, it will easily form dimers when it contacts with oxygen, and the quality of chelation will decrease, so it should be sealed and stored^[28]. Characteristics of SDDC are summarized in **Table 2**.

Table 2. Characteristics of sodium dimethyl dithiocarbamate (SDDC).

Characteristics	Description/details
Chemical name	Sodium dimethyl dithiocarbamate (abbreviated as SDDC, also known as N,N-dimethyl N, N-Dimethyldithiocarbonate sodium salt)
Molecular formula	$C_3H_6NS_2Na \cdot 2H_2O$
Physical appearance	Scaly white crystal with a slight ammonia smell; easily soluble in water.
Characteristics of the commercial product	Contains 2.5 molecules of crystal water (commercially available solid SDDC powder generally only contains 2); 40% aqueous solution appears light yellow or green.
Temperature sensitivity	Loses 2 molecules of crystal water at 115 °C and all crystallization water at 130 °C.
Applications	Heavy metal chelating agent; electroplating, electronics, smelting industries; photographic labs and film processing; waste incineration; battery manufacturing
Storage and handling	Sealed in black polyethylene tape and inner film polypropylene woven bag; store in a cool, dry place away from moisture and heat; avoid ironware; avoid acidic substances and high temperatures.
Environmental and safety considerations	Toxic and may harm the environment; avoid ingestion or direct eye contact
Main benefits	Low cost; wide applications; chelates multiple metal ions simultaneously; forms stable chelated precipitates; large processing capacity; less corrosive.
Other uses	In the rubber industry (as terminators and vulcanization accelerators); in mining (as mineral processing agents); as fungicide intermediate, etc.

At present, most users adopt the method of purchasing products of SDDC to meet the needs of enterprises. Due to the storage and use of carbon disulfide required in the production of SDDC, special safety measures are required. Recently, the research work of Zhang and Yuan^[29], systematically introduced the various storage methods of carbon disulfide in the production of SDDC, pointed out the problems that should be paid attention to in the design of carbon disulfide storage tanks and the safety measures that should be taken for carbon disulfide in the production process of SDDC, and provided a strong reference for the industrial production of SDDC. Aiming at the current domestic SDDC automatic production technology is not mature enough, Zhang^[30] has made many attempts in the research and development of SDDC automatic control system. In recent years, with the large-scale construction of urban waste incineration power plants and the rise of global manganese prices, SDDC can be used as a metal precipitant for manganese production. The demand for SDDC has increased sharply, which has greatly improved the benefits of SDDC industry. Therefore, SDDC has also been listed as a key development industry by many cities of China.

The objectives of the paper are to survey the heavy metal pollution and its solutions, especially with the focus on the production of SDDC and its applications to remove the heavy metal pollution. The paper is organized as following. In section 2, three different methods for production of SDDC, pot reaction method, improved pot reaction method, and the microchannel continuous reaction method, are presented. In section 3, standards and methods for testing chelation performance and the environmental conditions affected on the chelation of heavy metals by SDDC are discussed. Section 4 is the applications of SDDC as heavy metal

chelating agent for wastewater and fly ash, as well as an ore dressing agent. Finally, section 5 presents the outlook of the production and applications of SDDC.

2. The production process of SDDC

In this section, three different methods for production of SDDC, pot reaction method, improved pot reaction method, and the microchannel continuous reaction method, are presented and reviewed.

2.1. Pot reaction method

Figure 2 is a schematic diagram of the pot reaction of SDDC. It consists of three main parts, an electrical machinery, a kettle, and an agitator paddle. The preparation method for the pot reaction is to add water to the pot reaction tank, put in lye and 40% dimethylamine solution under stirring, cool to about 10–15 °C and dropwise add carbon disulfide, the reaction at this time is an exothermic reaction, the temperature of the dropping reaction needs to be controlled not to exceed 30 °C. After the carbon disulfide is added drop wisely, continue to react for 1 h to 2 h, then stand still, filter out the insoluble residue, and obtain an aqueous solution of SDDC. In order to speed up the formation and precipitation of SDDC crystals, it is necessary to let the SDDC aqueous solution stand still and cool to a certain temperature, and then undergo centrifugation to obtain SDDC crystals containing crystal water, as shown in **Figure 3a**; SDDC aqueous solution is concentrated and crystallized under pressure to obtain solid SDDC. The liquid left behind after the solid-liquid separation still contains a certain amount of SDDC, which can be used as the mother liquor, and the reactants (lye, dimethylamine, carbon disulfide) are added in a continuous cycle to synthesize a high-concentration SDDC solution, as shown in **Figure 3b**. In industrial applications, SDDC solution is often shipped in tons of barrels, as shown in **Figure 3c**.

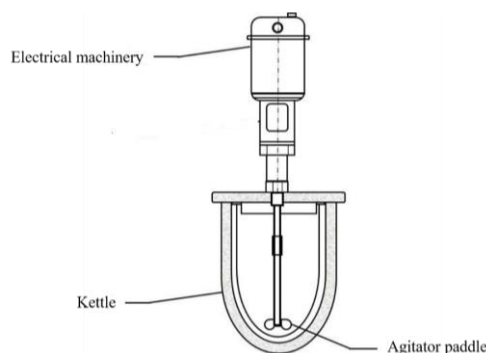


Figure 2. Schematic diagram of the pot reaction of SDDC.

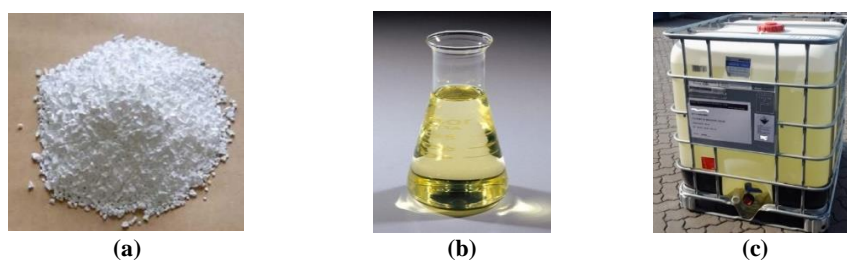


Figure 3. SDDC products. (a) crystal; (b) solution; and (c) industrial barrel.

In the industrial production of SDDC, dimethylaminodithioformic acid can also be obtained by the reaction of dimethylamine and carbon disulfide, and then sodium hydroxide solution is added to react with it to form SDDC aqueous solution. Tian^[31] elaborated on the synthesis technology, factors affecting the yield, and process flow of SDDC, combined with practical production, especially studied the influence of reaction temperature on the income of SDDC, pointed out the importance of temperature control on the production of

SDDC, and some suggestions were put forward on the application of production process technology, which provided a good reference for the technical improvement of SDDC production enterprises.

The pot type one-step reaction is given as follows:



In the process of producing SDDC by pot reaction, through a one-step reaction, as shown in Equation (1), while SDDC is produced, a side reaction between CS_2 and NaOH will inevitably occur,



The by-product $\text{Na}_2\text{CS}_2\text{O}$ is very easy to decompose, and its decomposition products are not only difficult to separate from SDDC, but will also be further mixed into the final product of SDDC, resulting in a decrease in product purity and a serious impact on product quality. In addition, the pot reaction method to produce SDDC has the following disadvantages: long production cycle and high cost; the use of normal pressure operation, the loss of raw material carbon disulfide is large, and carbon disulfide is easy to discharge from the reactor during reaction; if the temperature control is not good, it is very easy to have side reactions and affect the product quality; after a period of production, due to the emptying of the material to bring out solids, it is easy to block the emptying pipeline and cause production accidents. For this reason, it is of great significance to develop a method for synthesizing SDDC that is safe in production, low in cost, easy to operate and short in reaction time.

2.2. Improvements to the pot reaction method

The easiest way to improve the pot reaction method is to divide the one-step reaction, as shown in Equation (1), into the following two-step reactions:



From Equations (3) and (4), one can see that the one pot reaction is divided into two pot reactions. First, dimethylamine and CS_2 react in one tank, Equation (3), and then the product is reached by adding sodium hydroxide in another tank to form SDDC, Equation (4). The resulting SDDC aqueous solution thus can effectively reduce the occurrence of side reactions between CS_2 and sodium hydroxide (Equation (2)), thereby improving product quality and reducing reaction loss. Li^[32] proposed “a production device and production method of SDDC”, in which dimethylamine and CS_2 were pre-reacted in the first pipeline reactor to form an intermediate material, and then the intermediate material was injected into the reactor. It is mixed with NaOH for the second step reaction. The production device and method invented by this patent is to divide the one-step reaction of producing SDDC into two steps, which can effectively avoid the side reaction between CS_2 and NaOH , thereby improving the purity and output of SDDC. However, the two pot reactions undoubtedly increase the production costs and time, and now few manufacturers use two pot reactions to produce SDDC.

In order to overcome the various defects in the production process of SDDC, Guo et al.^[33] invented a patent “A production device for liquid SDDC and its production method”, which provides a method that can shorten the reaction time and reduce the loss of carbon disulfide. This improved method can reduce production costs, improve product economic benefit, it is easy and simple to operate to safely produce SDDC aqueous solution.

To the improvement of the method for producing SDDC aqueous solution, the production process is designed in the five main steps: (1) pour carbon disulfide and dimethylamine into their corresponding high-level tanks according to the appropriate mass ratio; (2) first pump the aqueous solution of dimethylamine into the reaction kettle, start stirring, and at the same time clamp it to the reaction cover; (3) when the temperature of the cover drops to 10–20 °C, press carbon disulfide into the synthetic cover, and keep the temperature inside the cover at 20–30 °C during the process; (4) add carbon disulfide till completion, continue to react for 20–30 min. At this time, the pressure inside the cover is 0.05–0.09 MPa, and the temperature inside the cover is

maintained at 20–35 °C; (5) NaOH aqueous solution is injected into the synthesis cover, and the pressure inside the cover is maintained at 0.08–0.15 MPa. The reaction temperature is 20–35 °C, and the reaction is continued for 25–40 min until the reaction is complete, and the aqueous solution of SDDC is obtained.

An important task in the production of SDDC is the temperature control. Zhang^[30] developed an automatic control system for the production of SDDC. According to the characteristics of the temperature change of the reactor, the temperature of the reactor is controlled by software, and the temperature of the entire production process is considered. Various exhaust gases that may be produced, the process is to collect the exhaust gases into different exhaust towers for treatment according to different types, which can reduce exhaust pollution. An appropriate amount of nitrogen is introduced in the production process to maintain the pressure balance of the container and prevent the feed port from being blocked.

2.3. Microchannel continuous reaction method

We have developed a microchannel continuous reaction preparation device for the production of SDDC (**Figure 4**), which mainly includes a mixing module and two reaction modules. The dimethylamine and NaOH aqueous solution are sent to the mixing module first, and after being fully mixed, the resulting mixture is sent to the first reaction module, and the carbon disulfide sent from different pipelines is reacted in the first reaction module to generate part of the SDDC solution. And the mixed solution that has not reacted completely is sent to the second reaction module to continue the reaction until the reaction is complete to produce the target product. Finally, the product is sent to the finished product collection tank. The advantages of the microchannel continuous reaction method are at least two main points. On the one hand, the use of this mixing method and device can effectively control the heat of reaction during the mixing process, which facilitates the rapid removal of the heat of reaction; on the other hand, it can make the amines mix uniformly, better for the production of SDDC. At the same time, the process route of the above-mentioned continuous production is simple. The whole synthesis process can realize continuous input of materials and continuous output of products, which greatly improves product quality and production efficiency. It is a very efficient reaction device. The device has been installed by Jiujiang Tianci High-tech Materials Co., Ltd. and can produce about 10 tons of 40% SDDC aqueous solution per day.

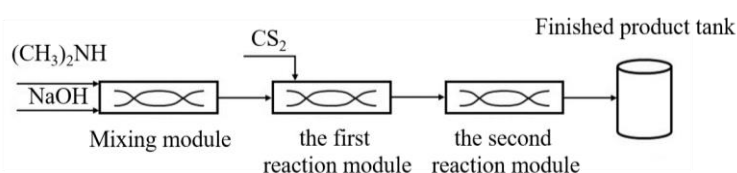


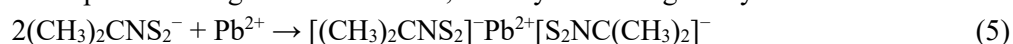
Figure 4. Schematic diagram of the preparation device and process for the production of SDDC aqueous solution by the microchannel continuous reaction method.

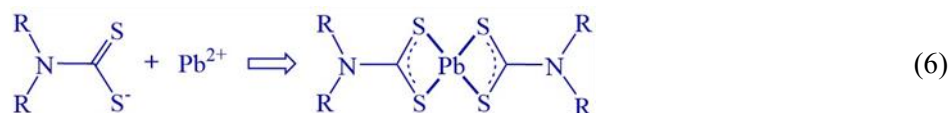
3. Performance of SDDC to chelate heavy metals

In this section, the test standards and methods for chelation performance and the environmental conditions affected on the chelation of heavy metals by SDDC are presented and discussed.

3.1. Standards and methods for testing chelation performance

The chelation reaction between SDDC and heavy metal ions (Pb^{2+} as an example), as shown in Equations (5) and (6), heavy metal ions coordinate with the chelating clamp (S-C-S) in the SDDC molecule through coordination bonds. The atoms are connected to form a chelate containing metal ions, which is similar to the chelation of crab claws, so SDDC has the ability to chelate heavy metals. SDDC and heavy metals chelate to form more stable chelate complexes through chelation effect, thereby stabilizing heavy metals.





How effective is the chelating effect of SDDC to chelate heavy metals? It needs to be verified by leaching experiments. With reference to the regulations in “Solid waste extraction procedure for leaching toxicity-acetic acid buffer solution method” (HJ/T 300-2007)^[34], the products generated by the chelating reaction of SDDC and heavy metals, soak in an extraction bottle of glacial acetic acid to control its pH to around 2.65. Then the extraction bottle containing the product was fixed on an overturning shaking device with a rotation speed of 30 cycles per minute and oscillated for 18 h. After shaking, remove the extraction bottle and let it stand for about 30 min. After the remaining solid precipitates, use a pH meter to measure the pH of the supernatant, and then vacuum filter the leaching solution with a microporous membrane with a pore size of 0.45 μm, and rinse it with dilute nitric acid. Washed, acidified to pH < 2 and stored at 4 °C, the obtained leachate can be tested for heavy metal content. If the heavy metal content in the measured leach solution reaches the national standard “GB16889-2008”^[35], it is considered qualified, otherwise it is considered unqualified.

Currently, there are many detection and analysis methods for heavy metal content, including atomic absorption spectrometry (atomic absorption spectroscopy, AAS), ultraviolet-visible spectrophotometry (ultraviolet-visible spectroscopy, UV-Vis), atomic fluorescence (atomic fluorescence spectrometry, AFS), electrochemical method, X-ray fluorescence spectrometer (XRF), inductively coupled plasma-mass spectrometry (ICP-MS), etc. One can choose any detection method to test various heavy metal contents.

3.2. Effect of environmental conditions on the chelation of heavy metals by SDDC

The research on SDDC as a heavy metal chelating agent has attracted widespread attention. The purpose of the research is to explore the best process conditions and how to use SDDC to remove heavy metal pollution more efficiently. He et al.^[36] conducted a systematic analysis and research on the removal effect of chromium ions in cadmium-containing wastewater. They used SDDC as a cadmium-removing chelating agent and polyaluminum chloride as a flocculant. The influence of various factors such as the addition amount of aluminum and SDDC, stirring time, and precipitation time on the removal effect of Cd²⁺ in cadmium-containing wastewater, the order of the strength of the influence of different factors on the mass concentration of residual Cd²⁺ is: the amount of SDDC added, stirring time, precipitation time, polyaluminum chloride addition amount. Under the best conditions, add 1.0 g/L SDDC stir for 20 min, and then precipitate for 5 h, then add 0.2 g/L polyaluminum chloride, so that 99.99% of Cd²⁺ from the cadmium-containing wastewater can be removed, the treated wastewater can be discharged up to GB8978-1996 “Standard for Pollution control on the landfill site of municipal solid waste”^[35].

Ma^[37] studied the influence of SDDC on the purification of various metal impurities produced by electrolytic manganese smelting. The main factors are the amount of SDDC, initial pH, purification temperature and time, stirring speed, and the way of adding SDDC, etc. It is found that these factors have different effects on the purification of various metal impurities. (1) The effect of acidity and alkalinity, that is, pH: for impurities such as aluminum, silicon, and phosphorus, the initial pH increase is conducive to the removal of these impurities, but when the pH exceeds a certain value, the removal effect of silicon and phosphorus becomes worse; for nickel, silicon, phosphorus, etc. For cobalt, copper, zinc, and cadmium heavy metal impurities, too high or too low pH is not conducive to the removal of impurities. Usually, it is more appropriate to control the pH at 5~6; (2) the influence of purification time: the purification time has almost no influence on the purification of impurities. Only has a certain weak effect on the removal of bismuth, nickel, lead, and copper; (3) the influence of purification temperature: temperature rise is generally not conducive to the removal of impurities; (4) the influence of stirring speed: the stirring speed has little effect on the removal of impurities by SDDC, but under the condition of high speed (400 r/min), heavy metal ions such as bismuth,

cadmium, copper, lead and other impurities have a slight re-dissolution phenomenon. This may be due to the high-speed stirring strengthens the mixing of air and the solution, resulting in higher dissolved oxygen content in the solution, which increases the possibility of SDDC being oxidized, resulting in the re-dissolution of impurities; for the removal effect of aluminum, bismuth, and zinc impurities, no matter SDDC is added in the form of solid or liquid, except for copper and lead, the difference is very small. For the removal of copper, lead, cobalt, cadmium, and nickel, it is recommended to add SDDC in liquid form; for the removal of silicon, it is better to add SDDC in solid form, which may be because the surface of solid SDDC is relatively alkaline. This makes the local pH of the solution higher, which is conducive to the hydrolysis of silicon; and when it is added in liquid form, the pH of the entire solution system is relatively uniform, and adding SDDC has little effect on the pH change of the solution, but better for silicon hydrolysis.

4. Application of SDDC as a heavy metal chelating agent

Heavy metal pollution is one of the most serious threats to the water environment^[38]. The main source of heavy metal pollution is the rapid development of industrialization and urbanization. Human activities continuously discharge a large amount of heavy metal pollutants into the water environment or the ocean. It has caused great harm to the environment and humans^[39]. Yang et al.^[40] took the seawater of China's Daya Bay as the research object, analyzed the changes in the mass concentration of copper, lead, and zinc in the seawater, and evaluated the pollution of heavy metals in the seawater, providing a basis and powerful guidance for the management of the marine ecological environment. In order to protect marine ecology from heavy metal pollution and protect our human ecological homeland, heavy metal pollutants in various water environments and industrial wastewater need to be treated to meet the discharge standards before they can be discharged.

4.1. Treatment of heavy metals in wastewater by SDDC

As a heavy metal chelating agent, SDDC has been widely used in the treatment of heavy metals in wastewater, such as the removal of copper in copper plating wastewater^[41], the removal of cadmium in cadmium-containing wastewater from zinc smelting^[36], and the removal of manganese^[37], zinc^[42], nickel^[43], and the removal of other first transition metal ions^[44]. When SDDC is used to treat heavy metals in wastewater, and the dosage required should be estimated simply. According to the content of heavy metals, the dosage of SDDC can be estimated. Generally speaking, for copper, the amount of heavy metal chelating agent SDDC is about 3–6 times of copper weight ratio, while for nickel, the amount of SDDC needs to be about 7.5 times of nickel. The actual amount of SDDC depends on the specific situation. As a heavy metal chelating agent, SDDC should first be dissolved into an aqueous solution of about 2%. Since the pH of industrial wastewater fluctuates greatly, it is necessary to use a regulator to adjust the pH of the wastewater. Common conditioners include caustic soda (sodium hydroxide), lime (calcium hydroxide), and alkali compound. Caustic soda has good solubility and will produce a certain amount of sludge after neutralization; lime is cheap, but it will produce a large amount of sludge, which is suitable for wastewater treatment enterprises with strict cost control; alkali compound is a new type of regulator, and its main component contains lime, activated white mud, diatomaceous earth, activated carbon, saturated alkali solution, etc., with the advantages of low price and less sediment. Adjusting the pH of the wastewater to the range of 2–14, pH = 8–9 is the best, and the specific initial pH depends on the water quality. Under rapid stirring (>150 rpm), add an appropriate amount of SDDC solution and react for 2–5 min. If the wastewater has a strong complexing agent (such as EDTA), the reaction time should be appropriately extended to 10–15 min. The removal of heavy metals in wastewater can be qualitatively detected. Add the heavy metal chelating agent solution to the wastewater. If the color changes or new precipitation still occurs, it means that the heavy metal ions have not been completely removed, and it is necessary to continue to add the heavy metal chelating agent solution to the wastewater; if the wastewater does not change color or no new precipitation occurs, it proves that heavy metals have been completely removed. In the same way, it is also possible to qualitatively detect whether the heavy metal chelating agent is excessive.

When the original wastewater is added, discoloration or precipitation occurs, indicating that the heavy metal chelating agent is excessive; if the color does not change or no precipitation occurs, it proves that the amount of heavy metal chelating agent is just right. If it needs determine the content of SDDC in water, one can refer to the literature^[45] for one of the precise determination methods.

In order to further improve the efficiency of wastewater treatment, 2% polyaluminum chloride (PAC) solution can be added to the wastewater already treated with SDDC, and the dosage is 0.7~1.2 times that of SDDC. PAC is a new water purification material, an inorganic polymer coagulant. It is a water-soluble inorganic polymer between AlCl_3 and $\text{Al}(\text{OH})_3$, the general chemical formula is $[\text{Al}_2(\text{OH})_n\text{Cl}_{6-n}]_m$, where m represents the degree of polymerization, and n represents the PAC product neutral level. PAC has a high degree of neutralization and bridging effect on colloids and particles in water, and can strongly remove weakly toxic substances and heavy metal ions. After adding PAC, stirring at high speed and reacting for 3~8 min, the alum flowers in the subsequent process will be thicker and the sedimentation speed will be faster. On this basis, then add 0.05% polyacrylamide (PAM) anion solution, the dosage is 5×10^{-6} of the wastewater, stirring at a slow speed (<10 r/min), flocculating for 3~5 min, and then let it settle for 30~60 min, extract the supernatant, and measure the content of heavy metal ions by using a test method introduced in section 3.1. Adding PAC and PAM after treating heavy metals in waste water with SDDC can form flocs with high strength and better sedimentation performance, which provides convenience for later solid-liquid separation. Such treatment of heavy metal pollution in waste water can greatly improve its efficiency.

4.2. Treatment of heavy metals in fly ash by SDDC

Nowadays, the amount of urban garbage in various countries around the world has increased sharply, and it has caused great pressure on urban management and environmental quality. A traditional and ancient garbage disposal method is to incinerate garbage. After the garbage is processed by incineration, the amount of garbage is significantly reduced and greatly saving land. The high-temperature incineration of garbage can also eliminate various pathogens and remove toxic and harmful substances. Therefore, the waste incineration method has become one of the main methods of modern urban waste disposal. The garbage incinerators built nowadays are all equipped with good smoke and dust purification devices, which can greatly reduce the pollution of the smoke generated by garbage incineration to the atmosphere. All large, medium and small cities in China have started to build waste incineration power plants, which have become the main way to reduce and dispose of urban waste. However, waste incineration plants inevitably discharge pollutants to the surrounding environment, such as heavy metals^[46] and dioxin-like compounds^[47], so there are certain environmental risks. Researchers^[48-51] have investigated the environmental health risk around the waste incineration plant, with a particular focus on the persistence of dioxin-like compounds in the environment and their harm to human health. Wang et al.^[51] analyzed the distribution of dioxins in the environment (air and fly ash) and the environment (air and soil) of a waste incineration plant in the Pearl River Delta, and used the risk assessment system of the US Environmental Protection Agency and applying Monte Carlo simulation method to assess the health risks of workers in the waste incineration plant and villagers around sensitive points, and provide data support for the possible health risks of waste incineration plants in China. Another work by Wang et al.^[52] is to study the risk of heavy metals in the soil around the waste incineration plant, and systematically evaluate the changes and possible risks of heavy metal concentrations in the soil around the waste incineration plant.

In China, starting from 1 January 2020, the “Regulations on the application and management of automatic monitoring data of domestic waste incineration power plants” have been officially implemented^[53], which has further promoted the construction of waste incineration power plants in major cities. Waste incineration is to reduce the volume of waste through oxidation at high temperatures through appropriate thermal decomposition, combustion, melting and other reactions. The main byproducts after waste incineration are residue or molten

solid matter and fly ash.

The fly ash produced by waste incineration is not completely composed of chemically inert substances, but contains some cadmium, lead, zinc, chromium and other toxic and harmful heavy metal substances and salts that can be leached by water. Improper handling will cause the migration of heavy metals and pollute groundwater, soil and air. How to safely and effectively dispose of waste incineration fly ash and deal with the heavy metal pollutants has become an urgent environmental and social problem.

Due to the high boiling point of heavy metals, they are easy to uniformly condense in the process of waste incineration, thus forming the core of fly ash, and the heavy metals that are volatile at high temperatures will condense on the surface of fly ash as it cools down. The leaching toxicity of heavy metals in fly ash is related to the size, surface area and pH of fly ash, and mainly depends on the form of heavy metals in fly ash. According to the different components of waste, there are currently three main treatment methods for waste incineration fly ash^[54]: (1) one way is to landfill as hazardous waste after proper treatment; (2) the other way is to use cement, asphalt, melting, chemical agents, etc. to solidify fly ash to make the heavy metals and their polluting components in the fly ash chemically inert or contain them for transportation and treatment. It reduces the toxicity of the pollutants and their migration rate to the ecosphere; (3) the third way is to separate the heavy metals from the fly ash. Recycling treatment, such as acid extraction, alkali extraction, biological extraction, etc., is carried out separately, but the cost of the separation is too high and it is difficult to apply in industry.

SDDC can be used as a chelating agent to deal with heavy metals in fly ash. At present, it has been widely used in the stabilization of fly ash in waste incineration. Japan has used SDDC as the first choice for the treatment of heavy metals in fly ash. Compared with other methods, SDDC treatment has the advantages of simple process, good stabilizing effect, low cost and etc. It has been showed by our studies that SDDC as a fly ash chelating agent could capture more than 98% of the heavy metals in the fly ash, and the stability of the products by the heavy metal chelating agent was not affected by microbial activities in the environment of the landfill plant.

According to the composition and morphological characteristics of fly ash and the characteristics of heavy metals in fly ash, adjusting the concentration of SDDC can achieve the purpose of removing heavy metals in fly ash. This method is suitable for the characteristics of China's waste incineration process. In view of the current situation that the domestic waste sorting is not strict and the content is complex, which leads to the high content of heavy metals in fly ash, the use of SDDC to treat the heavy metals in the waste incineration fly ash is the most common way because SDDC is easy to use and low in cost. It can complete the reaction of chelating heavy metals at one time under the coexistence of multiple heavy metal ions. The fly ash after treatment can meet the national standard "GB16889-2008"^[35] for the landfill requirements.

It should be mentioned that the treatment of heavy metals in fly ash requires sufficient stirring to make the chelation reaction between the chelating agent and the heavy metal ions complete.

The general process of on-site processing is as follows:

- (1) The fly ash collected from the flue gas purification system is sent to the fly ash storage bin;
- (2) Conveying the fly ash to the mixer;
- (3) Input 25%–30% of process water, and at the same time add about 1%–3% SDDC, inject into the mixer and mix thoroughly;
- (4) Stay 24 h for completely reacted, then it is transported to the waste landfill.

It should be pointed out that in the process of fly ash treatment, it is found that under acidic conditions, more heavy metal ions will be leached out, and acidic conditions affect the chelating effect of organic chelating agents on metals, which is conducive to the chelating agent to form an ion state, resulting in a better chelating effect, and the hydroxide and heavy metal ions form a precipitate, reducing the concentration of free heavy metal ions. But under the condition of too high pH, such as Pb^{2+} will form a small amount of $[\text{Pb}(\text{OH})_4]^{2-}$,

which increases the leaching concentration of Pb^{2+} . Therefore, to deal with heavy metals in fly ash, it is necessary to adjust the appropriate pH^[37].

Lv et al.^[55] tried to establish a reliable and effective method for extracting heavy metal organosulfur chelates in stabilized fly ash, and determined the optimal extraction solvent and extraction times, as well as the heavy metal chelates under optimal conditions. They found that choosing a suitable solvent can fully extract the copper chelate in the chelated fly ash of the incineration plant, followed by lead, zinc, and cadmium. Considering the nature and cost of the extractant, ethyl acetate is recommended as the best extractant, and the recovery rate of copper dimethyl dithiocarbamate can reach more than 90% under the optimal experimental conditions. Their work provides a possibility for the recycling of heavy metals in waste incineration fly ash.

4.3. Application of SDDC as an ore dressing agent

In China's gold production, cyanidation has always been the most widely used process. However, since cyanide is a highly toxic and dangerous chemical, accidents in any step such as transportation, storage, and it will cause serious environmental pollution incidents and malignant poisoning incidents. Many countries and regions have legislated to prohibit or restrict the use of cyanide to extract gold. Environmentally friendly gold selection agents are in high demand. Xiao et al.^[56] obtained the lead concentrate containing 54.32% lead and 4.66% zinc from the mixed concentrate containing 12.77% lead and 32.91% zinc by using the mixed reagent of SDDC, sodium bisulfite and zinc sulfate, and also the zinc concentrate containing 1.72% lead and 52.51% zinc. The work of Jiao^[57] found that SDDC had a strong imitation effect on iron/sphalerite, and proposed a theoretical mechanism. Other researchers^[43,58-60] have proposed a variety of precipitation methods using SDDC to separate copper from cyanide solutions, and have studied the effects of various parameters, including reaction time, concentration of SDDC, pH and temperature, on the precipitation of copper. Studies have shown that SDDC can selectively precipitate copper (as well as zinc and silver), which provides a good solution for efficient gold selection. Copper can be extracted from cyanide leaching solutions, and SDDC has also been widely used in many industries.

5. Outlook

Although SDDC has been widely used in the removal of heavy metals and ore dressing, in order to improve the performance of chelating agents, many researchers have developed new heavy metal chelating agents based on the framework of SDDC. Designing at the molecular level, chelating agents with more advantages in performance can be expected. On the one hand, by increasing the polarity of molecules, the interaction force between chelating agents and heavy metal ions can be increased, thus having a stronger ability to chelate heavy metals; on the other hand, it can make the molecular charge layout more scientific and self-assemble into more complex bridges structure, so the flocculation effect is significantly improved. Taking copper as an example, the heavy metal chelating agent can reduce the mass fraction of copper ions in copper-containing wastewater to below 10^{-7} , but the dosage is only 1/2~1/5 of similar products in the market.

As a heavy metal chelating agent, SDDC itself is not so toxic. It will not produce toxic and harmful substances such as hydrogen sulfide during processing, and even increasing the amount of SDDC will not increase the COD of wastewater. The heavy metal chelate will not decompose under high temperatures (not higher than 250 °C) and strong acid and strong alkali conditions, so no secondary pollution will occur after stabilization treatment by a heavy metal chelating agent.

The N-CS₂ chelating group of SDDC has a very strong coordination ability, which can form chelates with almost all transition metals and quickly generate insoluble, low water content, easy to filter out flocculent precipitates, so as to achieve the purpose of removing heavy metal ions. How to better apply SDDC to deal with heavy metal pollution is a great challenge. Quantum chemical calculations can provide a deeper understanding of the mechanism of action of SDDC chelating heavy metal ions. Wang et al.^[61] applied B3LYP

in density functional theory at the level of 6-31++G(d,p) and LanL2DZ mixed basis sets to carry out the analysis of SDDC and chromium, copper, cobalt, zinc, iron, cadmium, etc. Structural optimization and property calculation of mononuclear complexes formed by six heavy metal ions. The calculation shows that in the process of forming complexes between the sulfur atom in SDDC and these six heavy metal ions, electrons flow from the ligand to the heavy metal ions, the more charge transfer, the greater the absolute value of the coordination energy of the complex. The stability of the complex is directly proportional to the energy level difference of the frontier molecular orbitals and the absolute value of the coordination energy. The order of stability of the complexes and the absolute value of coordination energy is consistent, all of which are Cr^{3+} , Cu^{2+} , Co^{2+} , Zn^{2+} , Fe^{2+} , and Cd^{2+} .

With the help of the single-nanoparticle analysis method of dark-field microscopic imaging technology, Lei et al.^[25] monitored the decomposition kinetics of the chelate formed by SDDC and zinc and copper ions in real time, and found that the formation of copper ions is the most stable. Its toxicity of the chelate is greatly reduced. The recently developed new functional materials based on SDDC can be applied to the research of biological activity and molecular docking, opening up a new broad field for the application of SDDC^[62].

Although the current theoretical chemical calculation method can reasonably explain the reaction mechanism of SDDC as a chelating agent to deal with heavy metals, further in-depth discussion and preparation of new chelating agents with better chelating effect, better stability and stronger selectivity is highly required. This will need to combine machine learning and artificial intelligence technology. Work in this direction has been gradually carried out. It is expected that in the near future, the ability to deal with the pollution from heavy metals will be smarter and stronger.

Author contributions

Conceptualization, YY and FG; methodology, YY; software, SL; validation, YY and JG; formal analysis, YY and YF; investigation, YY and JG; resources, JG; data curation, YY; writing—original draft preparation, YY; writing—review and editing, FG; visualization, SL; supervision, FG; project administration, FG; funding acquisition, FG. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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